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BIOINORGANIC CHEMISTRY FOR PHARMACISTS

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МИНИСТЕРСТВО ЗДРАВООХРАНЕНИЯ РЕСПУБЛИКИ БЕЛАРУСЬ
БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ МЕДИЦИНСКИЙ УНИВЕРСИТЕТ
КАФЕДРА ОБЩЕЙ ХИМИИ

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БИОНЕОРГАНИЧЕСКАЯ ХИМИЯ ДЛЯ ПРОВИЗОРОВ

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PREFACE

This book contains exercises for 17 lessons from the course of general and inorganic chemistry. The exact topic of those lessons is known under the name “bioinorganic chemistry”, or the discipline that studies biogenic chemical elements and their compounds. Multiple choice questions, chains of chemical reactions and problems must be solved directly in this book as a part of a homework or during corresponding lessons. Protocols for experimental works must be fulfilled during the lessons. The main purpose of this book is to supply foreign students from pharmaceutical department with a relevant source of knowledge in the succinct form that is necessary to pass the exam. The authors are looking forward to receive any feedback regarding this book from both students and colleagues.

LESSON 1
INTRODUCTION TO THE CHEMISTRY OF ELEMENTS. HYDROGEN AND WATER

Main topics of the lesson:

1. *Distribution of chemical elements in Nature: comparison between lithosphere and biosphere.*
2. *Classification of biogenic elements.*
3. *Distribution of biogenic elements in the Periodic table.*
4. *Chemical properties of hydrogen and its main compounds.*
5. *Chemical properties of water.*

There are three geological spheres of the Earth: lithosphere (known as the Earth crust); atmosphere (known as the air); hydrosphere (known as the liquid water of oceans, seas, lakes and rivers). There is also a fourth sphere of the Earth known as biosphere (the term has been suggested by V. I. Vernadsky). Biosphere is the area in which the life is possible. Living organisms usually prefer to colonize areas near the boarders of geological spheres.

Actually, life is possible in the atmosphere up to the height of 15–20 km (protective ozone layer is situated there), while living organisms usually occupy the area of 15–20 meters upon the ground or water. In hydrosphere life is possible everywhere, while living organisms usually occupy the area of several meters below the border between hydrosphere and atmosphere (where the light of the Sun is used by plankton to grow a biomass) and on the border between hydrosphere and lithosphere (on the depth up to 10 km seabed bacteria and archaea use chemical sources of energy like sulfide or iron oxidation to grow a biomass). In the lithosphere living organisms can survive on the depth up to 3.5–7.5 km (on this depth the temperature is rising due to the proximity to magma), while they usually occupy several meters of lithosphere known as soil.

Some microorganisms known as extremophiles can survive in extreme conditions (at temperature near 100 °C or under the strong ionizing radiation). So, the borders of biosphere are wider than we think.

Table 1

Abundance of chemical elements in litho- and biosphere

Element	**O**	**Si**	**Al**	**Fe**	**Ca**	**Mg**	**Na**
Earth crust	49	26	7.5	4.2	3.2	2.4	2.4
Living organisms	65	< 0.01	< 0.001	< 0.1	1.4	< 0.1	0.26
Element	**K**	**H**	**P**	**C**	**Cl**	**S**	**N**
Earth crust	2.4	1.0	0.7	0.35	0.20	0.10	0.04
Living organisms	0.27	10	0.9	18.5	0.25	0.21	2.65

As one can see in table 1, some chemical elements demonstrate higher abundance in biosphere than in lithosphere (oxygen, hydrogen, phosphorus, carbon, chlorine, sulfur, nitrogen), others are not accumulated in living organisms (silicon, aluminum, iron, calcium, magnesium, sodium, potassium). However, it doesn't mean that elements with higher abundance in lithosphere are not essential for living organisms.

Biogenic elements are always present in the organism and take part in certain biochemical and physiological processes. Criterions to approve that a given chemical element is biogenic are: 1) the same content of the element in bodies of all the organisms of a given species; 2) existence of specific organs or tissues accumulating a given element; 3) the lack of the element in the diet causes certain biochemical and physiological changes which can disappear completely after the return of a given element in the diet. The chemistry of biogenic elements now goes under the name "bioelementomics". The major field of that science is "metallomics" focusing on the role of metal cations in the functioning of enzymes.

Taking into account their functional roles, biogenic elements can be classified into organogenic (carbon, hydrogen, oxygen, nitrogen, sulfur and phosphorus), the elements forming major electrolytes of the body (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-), and microelements (all other elements including Fe, Zn, Mn, Cu, etc.). According to their abundance into human body elements can be classified into: macroelements (C, H, O, N, S, P, Na, K, Mg, Ca, Cl and Fe — their abundance is higher than 0.01 % by mass), microelements (Zn, Mn, Mo, Cu, I, F, Br, etc. — their abundance is from 10^{-3} to 10^{-5} % by mass) and ultramicroelements (Al, Cr, Se, etc. — their abundance is lower than 10^{-5} % by mass).

Endemic diseases occur in areas with extremely low or high abundance of the certain chemical element(s) in soil. Those areas are called biogeochemical provinces. For example, the lack of fluorine leads to caries, the lack of iodine leads to hypothyroidism. In figure 1 one can see the distribution of biogeochemical provinces with low content of iodine in soil.

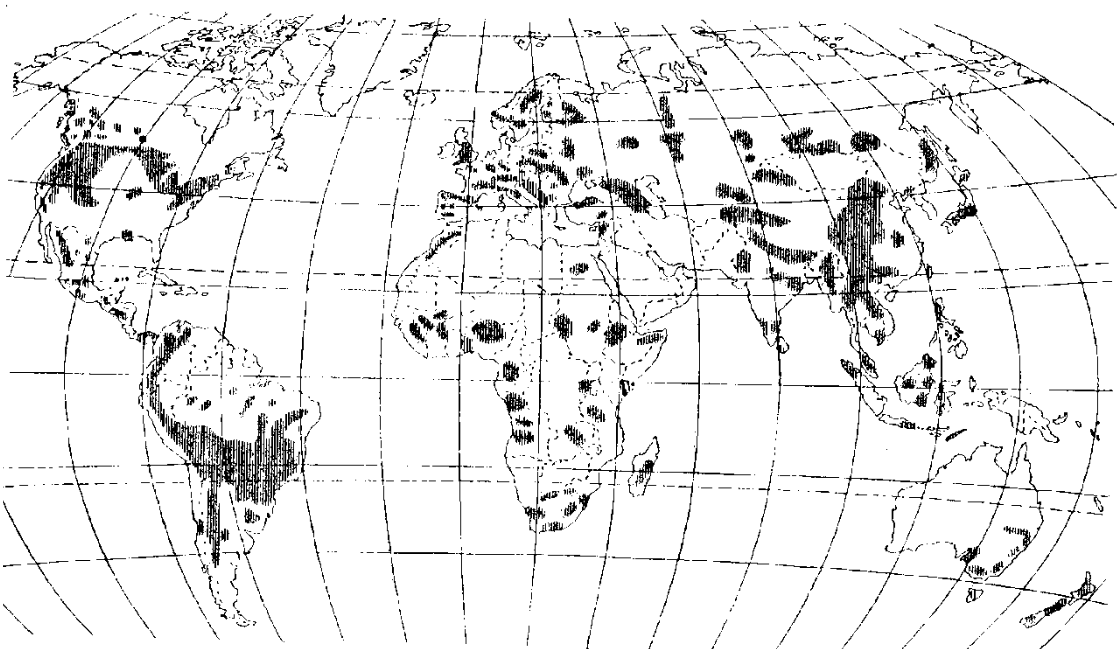


Figure 1. Biogeochemical provinces with low content of iodine in soil

Biogenic elements usually have a low atomic mass. The cause of this trend is in the fact that light elements are more widespread in Nature than heavy elements. Moreover, the abundance of radioactive isotopes for light elements is lower than that for heavy ones. Namely, organogenic elements are situated in the first (H), second (C, N, O) and third (P, S) periods of the Periodic table.

If we go down the IB group, we will see that copper (from the 4th period) is very important biogenic element, while silver is not included into active centers of enzymes, and compounds of gold are toxic. The same trend can be found in the IIB group with zinc being one of the main co-factors for enzymes, and cadmium and mercury being toxic and harmful. Of course, exceptions from this trend are known: beryllium is toxic for human body, unlike magnesium and calcium; lithium and boron are not used by our organisms, unlike sodium and carbon. One should remember that any element or compound becomes toxic taken at a high dose, while at rather low dose even toxic elements are harmless.

Hydrogen is a unique element in the Periodic table. 92 % of all the atoms in our Universe are hydrogen atoms (while 8 % of atoms are Helium atoms). There is still no agreement even about its position in the Periodic Table. Just like alkali metals it has a single electron on its valence shell. On the other hand, hydrogen needs just a single electron to complete its valence shell, just like halogens do. That is why hydrogen can demonstrate some common chemical features with both halogens and alkali metals.

Hydrogen behaves as a reducer in reactions with the most of nonmetals.

$2H_2 + O_2 \rightarrow 2H_2O$

Hydrogen can reduce metals from their oxides. Only those metals which are situated after zinc (including zinc itself) in the electrochemical series of metals may be produced from their oxides in the reaction with hydrogen at high temperature.

$CuO + H_2 \rightarrow Cu + H_2O\uparrow$

As an oxidizer hydrogen reacts with alkali and alkali-earth metals. In those reactions hydrides of metals are produced.

$2K + H_2 \rightarrow 2KH$

In normal conditions hydrogen gas can react with active metals and fluorine gas only.

Hydrides easily react with water and produce alkali and molecular hydrogen.

$KH + H_2O \rightarrow KOH + H_2\uparrow$

Hydrides also react with molecular oxygen. In those reactions hydroxides are produced.

$CaH_2 + O_2 \rightarrow Ca(OH)_2$

The most common reactions to produce hydrogen in laboratory using the Kipp’s apparatus are listed below.

$2Al + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4] + 3H_2\uparrow$

$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2\uparrow$

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$

However, the most common way is to perform electrolysis of pure water or sodium chloride solution.

$2H_2O$ (electrolysis) → $2H_2\uparrow + O_2\uparrow$

$2NaCl + 2H_2O$ (electrolysis) → $2NaOH + Cl_2\uparrow + H_2\uparrow$

One molecule of water can participate in formation of four hydrogen bonds. This feature makes melting and boiling points of water much higher than for other binary compounds of nonmetals with hydrogen.

As an oxidizer water interacts with alkali metals and alkaline-earth metals.

$2K + 2H_2O \rightarrow 2KOH + H_2\uparrow$

Water hydrates both basic and acidic anhydrates to produce basic and acidic hydroxides, respectively.

$CaO + H_2O \rightarrow CaO{\cdot}H_2O = Ca(OH)_2$

$SO_3 + H_2O \rightarrow SO_3{\cdot}H_2O = H_2SO_4$

Salts can also be hydrated by water. A salt with associated water of crystallization is known as a hydrate ($CaCl_2{\cdot}2H_2O$).

Water can hydrolyze many substances including inorganic salts, carbides and organic di- and polymeric molecules.

$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2S\uparrow$

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow$

In pharmaceutical analysis only a purified water is used. There are three types of such water: distilled water (distillation means the boiling of water and condensation of its steam without nonvolatile impurities), deionized water (deionization is a chemical process that uses specially manufactured ion-exchange resins, which exchange hydrogen and hydroxide ions for dissolved ions) and pyrogen-free water (distilled water without traces of organic compounds from bacteria which can cause hyperthermia in human).

Chains of chemical reactions

$H_2 \rightarrow HCl \rightarrow H_2 \rightarrow H_2O \rightarrow H_2$

$CaH_2 \rightarrow Ca(OH)_2 \rightarrow H_2O \rightarrow Na[Al(OH)_4] \rightarrow H_2O$

$H_2 \rightarrow NH_3 \rightarrow NH_4OH \rightarrow (NH_4)_2Cr_2O_7 \rightarrow H_2O$

$CuO \rightarrow H_2O \rightarrow Ca(OH)_2 \rightarrow (CaOH)_3PO_4 \rightarrow H_2O$

Problems

1. Calculate the mass of solid substances (see the equations) with the help of which it is possible to obtain 1L of hydrogen in vitro.

$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2\uparrow$

$2Al + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4] + 3H_2\uparrow$

$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2\uparrow$

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

2. Calculate the volume of a gas which can be obtained as a result of hydrolysis of 100 g of the following compounds: a) calcium carbide, b) aluminum carbide, c) calcium silicide, d) magnesium nitride, e) magnesium phosphide.

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow$

$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3\downarrow + 3CH_4\uparrow$

$Ca_2Si + 4H_2O \rightarrow 2Ca(OH)_2 + SiH_4\uparrow$

$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2\downarrow + 2NH_3\uparrow$

$Mg_3P_2 + 6H_2O \rightarrow 3Mg(OH)_2\downarrow + 2PH_3\uparrow$

3. What volume of hydrogen (L) is emitted in the reaction between calcium hydride and water if for neutralization of the obtained solution it is required to use 43.67 ml of hydrochloric acid with a mass fraction of HCl equal to 29.2 % (ρ =1.145 g/ml).

4. The laboratory assistant prepared 1M $MnCl_2$ solution using crystalline hydrate $MnCl_2{\cdot}4H_2O$, but he didn't consider the high hydroscopicity of this salt. What is the real concentration of Mn^{2+} ions in the prepared solution if at long storage 73 % of crystalline hydrate absorbed water and turned into $MnCl_2{\cdot}6H_2O$?

Multiple choice questions

1. Hydrogen is a product of the reaction(s) between:
a) sodium hydride and water;
b) aluminum oxide and the water solution of alkali;
c) aluminum and the water solution of alkali;
d) iron and a dilute sulfuric acid.

2. Which statements are incorrect? Hydrogen is able to react:
a) only with pure elements;
b) only with compounds;
c) only with nonmetals;
d) both with pure elements and compounds.

3. Hydride ion (H^-) and hydrogen atom differ:
a) in the number of protons;
b) in the number of neutrons;
c) in the number of electrons;
d) in oxidation-reduction properties.

4. Which solvents can’t be used to store sodium (metal)?

a) water; b) acetic acid; c) ethanol; d) kerosene.

5. Sodium hydroxide is not a product of the reaction(s):

a) the electrolysis of the sodium chloride solution;

b) the electrolysis of melted (liquid) sodium chloride;

c) the reaction between sodium hydride and water;

d) the reaction between sodium carbonate and potassium hydroxide.

6. The sodium hydroxide solution reacts with:

a) potassium chloride;

b) zinc;

c) magnesium chloride;

d) aluminum chloride.

7. Which reactions give sodium hydrogen carbonate (bicarbonate) as a product?

a) NH_4HCO_3 + NaOH (in excess) →

b) 1mole of NaOH + 1mole of CO_2 →

c) 1mole of NaOH + 2moles of CO_2 →

d) $KHCO_3$ + NaOH (in excess) →

8. Indicate the formula(s) for hydronium ion?

a) $H_4O_2^-$; b) $H_2O \cdot OH^-$; c) $H_2O \cdot H^+$; d) H_3O^+.

9. 23 g of sodium reacts with 78 g of water. The mass percentage of alkali in the produced solution is equal to:

a) 40.00; b) 39.60; c) 41.00; d) 38.50.

10. 3.42 g of an alkali metal reacts with water and produces 448 cm^3 of hydrogen. Which alkali metal is it?

a) Li; b) K; c) Na; d) Rb.

LESSONS 2–3
s-ELEMENTS AND THEIR COMPOUNDS

Main topics of the lesson:

1. *Physical properties of* s^1*- and* s^2*-elements.*
2. *Chemical properties of* s^1*- and* s^2*-elements.*
3. *Biological roles of s-elements.*
4. *The usage of compounds of s-elements in medicine and pharmaceutical analysis.*

Alkali metals can be found in the first group of the Periodic table. Alkali metals are soft enough to be cut with a knife. Alkali metals are highly reactive in normal conditions because they easily lose their single electron from the outer shell to form cations with a charge of +1. Alkaline-earth metals occupy the second group of the Periodic table. However, alkali (soluble hydroxides) can be produced from Ca, Sr and Ba only, and not from Be and Mg. Moreover, Be demonstrates amphoteric features similar for those characteristic to Al.

All the alkali and alkaline-earth metals react with water in normal conditions and produce alkali and hydrogen gas.

$2Li + 2H_2O \rightarrow 2LiOH + H_2\uparrow$

$2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$

$2K + 2H_2O \rightarrow 2KOH + H_2\uparrow$

Reaction between sodium and water produces more heat than reaction between lithium and water. Because of this, sodium melts during that reaction. Reaction between potassium and water produces so much heat that it is enough to make releasing hydrogen gas burn.

Alkali metals react with hydrogen gas at high temperatures and produce hydrides.

$2Na + H_2 \rightarrow 2NaH$

Alkali can be produced from hydrides of alkali metals.

$LiH + H_2O \rightarrow LiOH + H_2\uparrow$

$3NaH + Fe_2O_3 \rightarrow 2Fe + 3NaOH$

$2KH + O_2 \rightarrow 2KOH$

Oxides (i. e. Na_2O), peroxides (i. e. Na_2O_2) and superoxides (i. e. NaO_2) can be produced in the reaction between an alkali metal and oxygen. All those compounds are ionic: they contain metal cations and certain anions. In crystals of oxides there are O^{2-} anions, in crystals of peroxides there are O_2^{2-} anions, while in crystals of superoxides there are O_2^- anions.

Peroxides of alkali metals are used in H_2O_2 production.

$Na_2O_2 + 2HCl \rightarrow 2NaCl + H_2O_2$

Oxides can be produced from peroxides and superoxides. An excess of pure metal is needed for that purpose.

$Na_2O_2 + 2Na \rightarrow 2Na_2O$

$KO_2 + 3K \rightarrow 2K_2O$

Oxides (and so hydroxides) of alkali metals demonstrate strong basic properties: they react with acids, acidic oxides and hydroxides.

$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$

$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$

$2LiOH + H_2SO_4 \rightarrow Li_2SO_4 + 2H_2O$

Hydroxides of alkali metals (except LiOH) cannot be decomposed into oxides and water before their melting points.

$2LiOH$ (temperature) $\rightarrow Li_2O + H_2O$

$NaOH$ (temperature) $\neq$

KOH (temperature) $\neq$

Hydroxides of alkaline-earth metals can be decomposed into oxides and water before they turn to liquids (before the melting point).

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

$Ba(OH)_2$ (temperature) $\rightarrow BaO + H_2O$

Magnesium reacts with water at high temperature and produces magnesium oxide.

$Mg + H_2O \rightarrow MgO + H_2\uparrow$

Very clean magnesium ribbon has a very slight reaction with cold water. After several minutes, some bubbles of hydrogen form on its surface. However, the reaction soon stops because the magnesium hydroxide formed is almost insoluble in water and becomes a barrier on the piece of magnesium preventing further reaction.

$Mg + 2H_2O \rightarrow Mg(OH)_2\downarrow + H_2\uparrow$

Just magnesium powder (in which the area of magnesium surface is very large) can react with water and produce magnesium hydroxide and hydrogen gas.

Calcium, strontium and barium react with water in a similar way as alkali metals.

$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2\uparrow$

$Sr + 2H_2O \rightarrow Sr(OH)_2 + H_2\uparrow$

$Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2\uparrow$

Oxides (and hydroxides) of Mg, Ca, Sr and Ba show basic properties: they react with acids and acidic oxides.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$

Water solution of calcium hydroxide (so-called «limewater») reacts with carbon dioxide. When the amount of carbon dioxide is lower than the amount of calcium hydroxide white precipitate of insoluble calcium carbonate begins to form. When the amount of carbon dioxide becomes higher, $CaCO_3$ starts to react with it. As a result, white precipitate disappears because calcium bicarbonate is soluble, unlike calcium carbonate.

$CaCO_3\downarrow + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$

Common equation for limewater reaction with two times (or more) excess of carbon dioxide is written below.

$Ca(OH)_2 + 2CO_2 \rightarrow Ca(HCO_3)_2$

Hard water can be defined as a water with high concentration of calcium and magnesium cations. Water hardness can be divided into temporary hardness and permanent hardness. Temporary hardness is due to bicarbonate anions presence. That kind of hardness can be removed by the way of boiling.

$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O$

$Mg(HCO_3)_2 \rightarrow MgCO_3\downarrow + CO_2\uparrow + H_2O$

Permanent hardness is due to the presence of anions other than bicarbonate. To fight the permanent hardness one needs to add some reactants (like washing soda — Na_2CO_3 or limewater — $Ca(OH)_2$) or use special filters which can catch Ca^{2+} and Mg^{2+} ions.

$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaHCO_3$

$Mg(HCO_3)_2 + Na_2CO_3 \rightarrow MgCO_3\downarrow + 2NaHCO_3$

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$

$Mg(HCO_3)_2 + Mg(OH)_2 \rightarrow 2MgCO_3\downarrow + 2H_2O$

Cations of alkali and alkali-earth metals form aquatic complexes in water solutions $[Li(H_2O)_4]^+$; $[Na(H_2O)_6]^+$; $[Ca(H_2O)_6]^{2+}$. Na^+ cations have highest abundance among cations of the intercellular fluid and blood plasma (135–145 mmol/L). K^+ cations demonstrate much lower abundance in the blood plasma (3.0–5.5 mmol/L), while they are the most frequent cations of the intracellular fluid. The difference between Na^+ and K^+ ions concentrations inside and outside cell membranes creates the membrane potential which is important for polarization and depolarization processes.

Ions of Ca^{2+} are necessary for bones and teeth formation (the formula of the main mineral component of those tissues is calcium hydroxyapatite: $Ca_{10}(PO_4)_6(OH)_2$), for muscle contraction, for blood aggregation. Moreover, changes in Ca^{2+} level inside the cell results in activation or deactivation of different genes and enzymes. The protein called calmodulin “feels” the concentration of Ca^{2+} with the help of its domain containing EF-hands motif (alpha helix – coil – alpha helix) and then conducts this signal by the way of interactions with different proteins (figure 2).

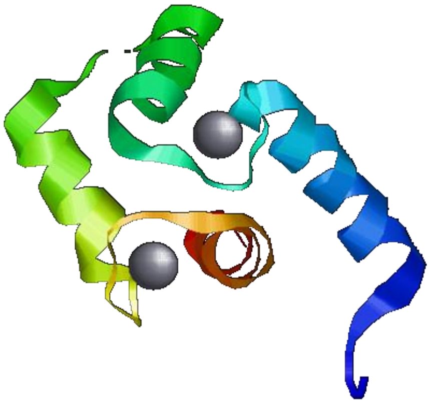


Figure 2. The fragment of N-terminal part of human calmodulin with two calcium ions bound

Ions of Mg^{2+} are necessary for numerous biochemical processes, including DNA replication, RNA transcription, phosphorylation and dephosphorylation of proteins.

Beryllium doesn't play any significant role in human organism, and its compounds are harmful because of the ability of Be^{2+} to replace Mg^{2+} in active centers of enzymes. Sr^{2+} ions are able to replace Ca^{2+} ions in bones making them more fragile.

The presence of Na^+ ions in the water solution can be revealed with the help of $K[Sb(OH)_6]$ which forms white insoluble $Na[Sb(OH)_6]$ at neutral pH. Another way to perform that qualitative analysis is to mix several drops of a sample with $Zn[(UO_2)_3(CH_3COO)_8]$ on the glass in the presence of acetic acid (yellow-green crystals are formed if there were Na^+ ions in the sample).

The presence of K^+ ions can be revealed with the help of tartaric acid which forms white precipitate of $HOOC\text{-}(CHOH)_2\text{-}COOK$. Another way to check the solution for the presence of K^+ is to mix it with $Na_3[Co(NO_2)_6]$ which turns to yellow insoluble $K_2Na[Co(NO_2)_6]$.

Characteristic reaction to reveal the presence of Mg^{2+} is the one with Na_2HPO_4 and NH_3. The resulting white insoluble $MgNH_4PO_4$ can be easily dissolved back with the help of acetic acid.

Compounds of s-elements widely used in medicine are as follows: Li_2CO_3 is used in the treatment of psychopathologies such as schizophrenia, 0.15M water solution of NaCl is used for blood replacement, $Na_2SO_4\cdot 10H_2O$ is known as laxative since the ancient times, CH_3COOK is used as diuretic, 25 % $MgSO_4$ solution is used as hypotonic and analgesic, $MgCO_3$, $CaCO_3$, $(MgOH)_2CO_3$ and MgO are antacids, $CaCl_2$ has antiallergic effect, $BaSO_4$ is used in X-ray analysis of the digestive tract, $CaSO_4\cdot 2H_2O$ is called gypsum, and it is used for immobilization of broken proximities.

Chains of chemical reactions

$NaCl \rightarrow NaHSO_4 \rightarrow Na_2SO_4 \rightarrow NaCl \rightarrow NaNO_3$

$Li \rightarrow Li_2O \rightarrow LiOH \rightarrow LiCl \rightarrow LiNO_3$

$Na \rightarrow NaOH \rightarrow Na_2CO_3 \rightarrow NaHCO_3 \rightarrow Na_2CO_3$

$KC1 \rightarrow K \rightarrow KH \rightarrow KOH \rightarrow KHCO_3$

$Na_2O \rightarrow NaOH \rightarrow Na_2CO_3 \rightarrow NaOH \rightarrow Na[A1(OH)_4]$

$Be \rightarrow BeSO_4 \rightarrow Be(OH)_2 \rightarrow K_2[Be(OH)_4] \rightarrow Be(NO_3)_2$

$MgCO_3 \rightarrow MgCl_2 \rightarrow Mg \rightarrow MgSO_4 \rightarrow Mg(NO_3)_2$

$CaH_2 \rightarrow Ca(OH)_2 \rightarrow CaCl_2 \rightarrow Ca(HCO_3)_2 \rightarrow CaCO_3$

$Ca \rightarrow CaO \rightarrow Ca(OH)_2 \rightarrow CaBr_2 \rightarrow Ca$

$BaO \rightarrow Ba(OH)_2 \rightarrow Ba(H_2PO_4)_2 \rightarrow BaHPO_4 \rightarrow Ba_3(PO_4)_2$

Problems

1. Calculate the masses of lithium carbonate, hydrochloric acid with a mass fraction of HC1 equal to 10 %, and water which are taken to prepare 30 g of lithium chloride solution with a mass fraction of LiCl equal to 10 %. Solubility of carbon (IV) oxide in water can be neglected.

2. The products of the reaction between 11.7 g of crystalline sodium chloride and concentrated sulfuric acid are sodium hydrogen sulfate and 4.0 L of hydrogen chloride. Calculate the yield (%) of hydrogen chloride.

3. 32.4 g of aluminum was added to 200 ml of potassium hydroxide solution with a mass fraction of 30 % and density of 1.29 g/ml. What is the volume of obtained hydrogen?

4. 0.56 L of CO_2 was passed through 100 g of calcium hydroxide solution with a mass fraction of 3.9 %. The precipitate ($CaCO_3$) was heated up till the constant mass equal to 1.2 g. Calculate the yield (%) of calcium carbonate in the first reaction, if the product yield in the second reaction is 100 %.

5. The sample of magnesium oxide weighing 40 g (m_1) was partially reduced by hydrogen. After the reaction the total mass of the mixture of Mg and MgO (m_2) was 32 g. Calculate the mass of obtained magnesium.

6. 5.0 g of CaO containing $CaCO_3$ as an impurity was dissolved in an acid. A gas with a volume of 140 ml was emitted as a result of the reaction. Calculate a mass fraction of $CaCO_3$.

7. What volume of SO_2 is required to transform calcium hydroxide containing in 4 L of its solution with $C_{eq}(Ca(OH)_2) = 0.5$ mol/L into calcium hydrogen sulfite?

Multiple choice questions

1. Which ions are responsible for water hardness?

a) Mg^{2+}; b) Ca^{2+}; c) Ba^{2+}; d) Sr^{2+}.

2. Which motif of the protein secondary structure is usually used for calcium ions binding?

a) beta strand – loop – beta strand;
b) alpha helix – loop – alpha helix;
c) beta strand – loop – alpha helix;
d) alpha helix – loop – beta strand.

3. The main component of a bone tissue is:

a) hydroxoapatite;
b) chloroapatite;
c) fluoroapatite;
d) carboxyapatite.

4. An excess of SO_2 gas is added to the calcium hydroxide aqueous solution. The product of this reaction is:

a) calcium oxide;
b) calcium sulfite;
c) calcium hydrogen sulfite;
d) calcium hydrogen sulfate.

5. Indicate alkalis:

a) calcium hydroxide;
b) magnesium hydroxide;
c) barium hydroxide;
d) beryllium hydroxide.

6. Indicate antacids:
a) magnesium carbonate;
b) magnesium hydroxyl carbonate;
c) magnesium oxide;
d) magnesium sulfate.

7. Salts of which ions turn the color of a flame into yellow – green?
a) calcium; b) magnesium; c) barium; d) strontium.

8. Which substances does magnesium hydroxide react with?
a) HNO_3; b) CaO; c) HCl; d) H_2O.

9. Which compound is used as an X-ray contrast substance?
a) barium carbonate;
b) calcium carbonate;
c) barium sulfate;
d) calcium sulfate.

10. What minimal mass of calcium hydroxide should be added to 200 g of phosphoric acid solution with a mass percentage of the acid equal to 2 % to produce a normal salt?
a) 8.88; b) 4.44; c) 2.96; d) 5.92.

EXPERIMENTAL WORK
"CHEMICAL PROPERTIES OF COMPOUNDS CONTAINING ELEMENTS FROM IA SUBGROUP"

The aim of the work: to perform test reactions for K^+ and Na^+ cations.

Reactants: solutions of KCl, NaCl, HCl, KOH, sodium hexanitrocobaltate (III), sodium hydrogen tartrate, potassium hydroxystibiate (V).

Experiment 1. ***Reaction between Na^+ cations and potassium hydroxystibiate (V) $K[Sb(OH)_6]$.***

Put 2–3 drops of sodium chloride in the tube, add the same volume of $K[Sb(OH)_6]$ solution and scrub the walls of the tube by a glass stick. After that action a white precipitate will be formed:

$NaCl + K[Sb(OH)_6] \rightarrow Na[Sb(OH)_6]\downarrow + KCl$

Write this reaction in ionic form:

____

Experiment 2. ***Reaction between K^+ cations and sodium hexanitrocobaltate (III) $Na_3[Co(NO_2)_6]$.***

Put 1–2 drops of slightly acidic (with low HCl concentration) solution of KCl in the tube, add 2 drops of sodium hexanitrocobaltate (III) in that tube and scrub the walls of the tube by a glass stick. Soon yellow precipitate of the double (potassium and sodium) hexanitrocobaltate (III) will be formed.

$2KCl + Na_3[Co(NO_2)_6] \rightarrow K_2Na[Co(NO_2)_6]\downarrow + 2NaCl$

Write this reaction in ionic form:

____

Experiment 3. ***Reaction between K^+ cations and sodium hydrogentartrate $NaHC_4H_4O_6$.***

Put 2–3 drops of KCl in the tube, add 2 drops of sodium hydrogentartrate solution and scrub the walls of the tube by a glass stick. Soon white precipitate will be formed.

$KCl + NaHC_4H_4O_6 \rightarrow KHC_4H_4O_6\downarrow + NaCl$

Write this reaction in ionic form:

____

Then divide the precipitate in two parts and investigate the influence of alkalis and acids on it. Add several drops of HCl into the first tube until the weak but soluble tartric acid ($H_2C_4H_4O_6$) will be formed.

$KHC_4H_4O_6 + HCl \rightarrow KCl + H_2C_4H_4O_6$

Add several drops of KOH into the second tube until soluble normal salt (potassium tartrate — $K_2C_4H_4O_6$) will be formed.

$KHC_4H_4O_6 + KOH \rightarrow H_2O + K_2C_4H_4O_6$

Write the conclusion: *“Reaction with ______________________ is better as the test for K^+ ions presence than reaction with ___________________________________, because ____”.*

EXPERIMENTAL WORK

“CHEMICAL PROPERTIES OF COMPOUNDS CONTAINING ELEMENTS FROM IIA SUBGROUP”

The aim of the work: to perform test reactions for Mg^{2+}, Ca^{2+}, and Ba^{2+} cations.

Reactants: solutions of $BaCl_2$, $CaCl_2$, $MgCl_2$, Na_2SO_4, CH_3COOH, HCl, $K_2Cr_2O_7$, CH_3COONa, Na_2CO_3, $(NH_4)_2C_2O_4$, NH_4OH, NH_4Cl.

Task 1. To perform test reactions for Mg^{2+} cations.

Experiment 1. ***Reaction of Mg^{2+} cations with soluble carbonates.***

Salts of magnesium form white precipitate of magnesium carbonate when they react with Na_2CO_3 or K_2CO_3. That precipitate ($MgCO_3$) reacts with water (it is hydrolyzed) and forms magnesium hydroxycarbonate $(MgOH)_2CO_3$.

$MgCl_2 + 2Na_2CO_3 \rightarrow MgCO_3\downarrow + 2NaCl$

$2MgCO_3 + 2H_2O \rightarrow (MgOH)_2CO_3\downarrow + H_2O + CO_2\uparrow$

Put 2–3 drops of $MgCl_2$ solution in the tube, add 2 drops of Na_2CO_3 solution. Observe white precipitate of $(MgOH)_2CO_3$.

$2MgCl_2 + 2Na_2CO_3 + H_2O \rightarrow 4NaCl + (MgOH)_2CO_3\downarrow + CO_2\uparrow$

Write this reaction in ionic form:

The precipitate — $(MgOH)_2CO_3$ — can be dissolved in acids and in the excess of NH_4Cl. Divide the precipitate in two parts.

Add acetic acid solution to the first part of the precipitate.

$(MgOH)_2CO_3\downarrow + 4CH_3COOH \rightarrow 2(CH_3COO)_2Mg + CO_2\uparrow + 3H_2O$

Write this reaction in ionic form:

Add ammonium chloride to the second part of the precipitate.

$(MgOH)_2CO_3\downarrow + 4NH_4Cl \rightarrow 2MgCl_2 + CO_2\uparrow + 4NH_3 + 3H_2O$

Write this reaction in ionic form:

Experiment 2. ***Reaction of Mg^{2+} ions with ammonium hydroxide NH_4OH.***

Put 2–3 drops of $MgCl_2$ solution in the tube, add 2 drops of NH_4OH solution to that tube and observe the formation of insoluble white amorphous $Mg(OH)_2$.

$MgCl_2 + 2NH_4OH \rightarrow Mg(OH)_2\downarrow + 2NH_4Cl$

Write this reaction in ionic form:

Remember that this precipitate will not be formed if you use the mixture of NH_4OH and NH_4Cl.

Task 2. To perform test reactions for Ca^{2+} cations.

Experiment 1. ***Reaction of Ca^{2+}cations with soluble carbonates.***

Put 2–3 drops of $CaCl_2$ solution in the tube, add 2 drops of Na_2CO_3 or K_2CO_3 solution to the same tube, observe the formation of white insoluble $CaCO_3$.

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

Write this reaction in ionic form:

The precipitate — $CaCO_3$ — can be dissolved in acids which are stronger than carbonic acid.

Add acetic acid solution to the precipitate.

$CaCO_3\downarrow + 2CH_3COOH \rightarrow (CH_3COO)_2Ca + CO_2\uparrow + 2H_2O$

Write this reaction in ionic form:

Add hydrochloric acid solution to the precipitate.

$CaCO_3\downarrow + 2HCl \rightarrow CaCl_2 + CO_2\uparrow + 2H_2O$

Write this reaction in ionic form:

Experiment 2. ***Reaction of Ca^{2+} ions with ammonium oxalate $(NH_4)_2C_2O_4$.***

Put 1–2 drops of $CaCl_2$ solution in the tube, add several drops of $(NH_4)_2C_2O_4$ solution in that tube and observe the formation of crystalline calcium oxalate precipitate.

$CaCl_2 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4\downarrow + 2NH_4Cl$

Write this reaction in ionic form:

____

The precipitate — CaC_2O_4 — can be dissolved in acids which are stronger than oxalic acid.

Add acetic acid solution to the precipitate and notice that reaction doesn't work.

Add hydrochloric acid solution to the precipitate.

$CaC_2O_4\downarrow + 2HCl \rightarrow CaCl_2 + H_2CO_4 + 2H_2O$

Write this reaction in ionic form:

____

Task 3. To perform test reactions for Ba^{2+} cations.

Experiment 1. ***Reaction of Ba^{2+} with soluble sulfates.***

Put 2–3 drops of $BaCl_2$ solution in the tube, add 2–3 drops of Na_2SO_4 solution in the same tube, observe the formation of white crystalline $BaSO_4$ precipitate.

$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + 2NaCl$

Write this reaction in ionic form:

____

The precipitate — $BaSO_4$ — cannot be dissolved in neither acetic, nor hydrochloric acid.

Experiment 2. ***Reaction of Ba^{2+} with potassium chromate and dichromate.***

Put 1–2 drops of $BaCl_2$ solution in the tube, add 2–3 drops of $(K_2Cr_2O_7)$ and 2–3 drops of sodium acetate (CH_3COONa) solutions in the same tube. Yellow crystalline precipitate of barium chromate $(BaCrO_4)$ is insoluble in acetic acid in contrast to $SrCrO_4$, while $CaCrO_4$ is soluble in water.

$2BaCl_2 + K_2Cr_2O_7 + H_2O \rightleftarrows 2BaCrO_4\downarrow + 2KCl + 2HCl$

Write this reaction in ionic form:

____

To shift the equilibrium of this process to the left one needs to remove H^+ ions. Acetate anions (from sodium acetate) are added with this aim, as well as to discriminate barium cations from strontium cations.

Write the conclusion: "*To discriminate Ba^{2+} cations from Ca^{2+} and Sr^{2+} cations I can use reaction with* ____________________ *in the presence of* _________________________".

LESSON 4
DESCRIPTION OF D-ELEMENTS. ELEMENTS FROM GROUPS IIIB–VIB AND THEIR COMPOUNDS

Main topics of the lesson:

1. *Definitions of transition metals and d-elements.*
2. *General characteristics of d-elements.*
3. *Chrome and its compounds.*
4. *Titanium, vanadium, molybdenum, tungsten and their compounds.*

Transition metals are those metals in atoms or ions of which d-subshells of pre-outer shells are not completely filled by electrons. This definition needs some explanations. If we consider just atoms in their ground state, than transition metals will occupy groups IIIB–VIIIB. To include group IB in the family of transition metals they (IUPAC) added a remark about ions. Indeed in Cu^{2+}, Ag^{3+} and Au^{3+} cations there are just 9 electrons on the 3d sublevel. However, elements from IIB subgroup cannot be classified as transition metals according to the given definition. So, in our opinion, it is better to use a term "d-block element" or "d-element" to refer to all the metals from B subgroups.

A common feature of all the elements from d-block (except those from group IIB) is that they use d-electrons for making chemical bonds. Eight from ten elements from the 4th period d-block have electron configurations which follow the general rule of the fulfillment of subshells. Two exceptional ones are chrome ($4s^1 3d^5$) and copper ($4s^1 3d^{10}$). In the d-block from the 5th period there are 6 (out of 10) elements with nonstandard ground state electron configurations. Namely, niobium has $5s^1 4d^4$ configuration, molybdenum has $5s^1 4d^5$, ruthenium has $5d^7 4s^1$, rhodium has $5d^8 4s^1$, palladium has $5d^{10} 4s^0$ and silver has $5d^{10} 4s^1$. Interestingly, in the d-block from the 6th period one can find just two exceptional elements: platinum has $6s^1 5d^9$ electron configuration and gold has $6s^1 5d^{10}$.

It is known that d-electrons shield the positive charge of the atom nucleus much worse than p- and, especially, s-electrons. However, f-electrons perform this function even worse than d-electrons. Because of this reason s- and d-electrons of d-elements from 6th period are attracted to nuclei of their atoms so strong that there is no significant difference between atomic radii of d-elements from 5th and 6th periods. This phenomenon is known as lanthanide contraction. The consequence of this atomic radii contraction is in the fact that chemical activity of d-elements decreases from top to bottom of the periodic table (table 2).

Maximal valence of a d-element is equal to its subgroup number starting from subgroup IIIB and until subgroup VIIB. Then the maximal valence decreases because of the appearance of paired d-electrons. For Fe it is equal to VI, for Co it is equal to V, for Ni it is equal to IV. Elements from the IB subgroup may have a maximal valence of III. Elements from the IIB subgroup have the maximal valence of II.

Table 2

Atomic radii (in pm) of d-elements from 4th, 5th and 6th periods

Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
162	147	134	128	127	126	125	124	128	134
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
180	160	146	139	136	134	134	137	144	151
La	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**
187	159	146	139	137	135	136	139	144	151

In complex compounds all d-elements may demonstrate high coordination numbers (up to VI). Vacant orbitals for making coordination bonds by cations of d-elements can be found not only on outer s- and pre-outer d-sublayers, but also on outer d-sublayer. In general, d-elements demonstrate the highest ability to form complex compounds compared to s- and p-elements.

The color of hydrated cations of d-elements depends on the presence of unpaired electrons. If there are no unpaired electrons in the ion (just like in Ag^+), then water solution containing it will be colorless. If there is at least one unpaired electron in the cation (just like in Ti^{3+}), then water solution will have a color. This rule doesn't work when ligands other than water make coordination bonds to metal cations.

Properties of oxides and hydroxides of d-elements largely depend on their oxidation state. Indeed, when d-element like chrome loses two electrons, remaining electrons from d-orbitals still shield the positive charge of a nucleus. When chrome makes six bonds, that shield disappears. So, in low oxidation states d-elements are prone to form ionic bonds with nonmetals, in high oxidation states they are prone to form covalent polar bonds with electronegative elements.

Chrome can be found in Nature in form of iron chromite ($Fe(CrO_2)_2$) or lead chromate ($PbCrO_4$).

Protective layer of Cr_2O_3 exists on a surface of chrome. Because of this reason inner layers of chrome are protected from further oxidation by both oxygen and other oxidizers. Chrome reacts slowly with HCl, HBr, HI and dilute H_2SO_4. In these reactions hydrogen and chrome (II) salts are produced. Then chrome (II) salts are oxidized by oxygen and form more stable chrome (III) salts.

$Cr + 2HCl \rightarrow CrCl_2 + 2H_2\uparrow$

$4CrCl_2 + O_2 + 4HCl \rightarrow 4CrCl_3 + 2H_2O$

Concentrated sulfuric and nitric acids cannot react with chrome at low temperature. At higher temperature these acids oxidize chrome to chrome (III) salts.

$2Cr + 6H_2SO_4(\text{concentrated, t°}) \rightarrow Cr_2(SO_4)_3 + 3SO_2\uparrow + 6H_2O$

Chromates (for example, K_2CrO_4) are simplest salts in which chrome (VI) is a part of the anion. These yellow salts are known as strong oxidizers. In acidic medium chromate anions are protonated. Then polycondensation of $HCrO_4^-$ anions happens. This event leads to the occurrence of orange dichromate anions: $Cr_2O_7^{2-}$. Dichromates are stable only in acidic water solutions or as dry salts.

Dichromates are used in the redox titration method which is called “dichromatometry”. That method requires specific redox indicators (such as diphenylamine) for correct estimation of the point of equivalence.

Titanium is known as the most inert metal that is biocompatible. Because of this reason and its highest strength-to-density ratio it is widely used in medicine as a material for implants and joint replacements. Usually specific alloys of titanium with other metals like aluminum, niobium or tantalum are used for this purpose.

Titanium dioxide (TiO_2) is rater atomic compound than ionic one: bonds between titanium and oxygen are covalent polar. That oxide shows amphoteric behavior. It is used in industry and pharmacy as a substance that absorbs light and protects other substances (like components of tablets) from decomposition caused by sunlight.

Vanadium, unlike titanium, is highly toxic. The layer of oxide on its surface can be removed by water. Indeed, V_2O_5 reacts with H_2O and forms metavanadic acid: HVO_3. Then HVO_3 reacts with H_2O and forms H_3VO_4 (orthovanadic acid). Orthovanadate ions are thought to replace phosphate anions in numerous processes in human body, and they really disturb normal functioning of enzymatic reactions. Ammonium metavanadate (NH_4VO_3) is used as a strong oxidizer in the redox titration method called “methavanadatometry”. That salt is a part of a specific reactant (the mixture of $(NH_4)_2MoO_4$ and NH_4VO_3) for revealing the presence of phosphate anions in water solutions. Phosphate anions are able to form salts of heteropolyacids with salts of metavanadic and molybdic acids.

Heteropolyacids are formed at low pH by the way of polycondensation between numerous protonated anions of molybdic, tungstic and metavanadic acids with an anion of phosphoric, arsenic, silicic or titanic acid. Such complex compounds usually have specific color that helps to use them to reveal the presence of different alkaloids.

Chains of chemical reactions

$Cr_2O_3 \rightarrow Cr(OH)_3 \rightarrow Na_3[Cr(OH)_6] \rightarrow Cr(NO_3)_3 \rightarrow Cr_2O_3$

$CrCl_2 \rightarrow CrCl_3 \rightarrow Cr(OH)_3 \rightarrow NaCrO_2 \rightarrow Cr_2(SO_4)_3$

$K_2Cr_2O_7 \rightarrow Cr_2(SO_4)_3 \rightarrow Cr \rightarrow CrCl_3 \rightarrow Cr(NO_3)_3$

$K_2CrO_4 \rightarrow K_2Cr_2O_7 \rightarrow CrCl_3 \rightarrow K_3[Cr(OH)_6] \rightarrow Cr(OH)_3$

Redox reactions

$K_2Cr_2O_7 + H_2S + H_2SO_4 \rightarrow$ ____________
Reduction: ____________
Oxidation: ____________
Water molecules: ____________
$Na_2CrO_4 + NaBr + HCl \rightarrow$ ____________
Reduction: ____________
Oxidation: ____________
Water molecules: ____________
$Cr + KClO_3 + KOH \xrightarrow{t}$ ____________
Reduction: ____________
Oxidation: ____________
Water molecules: ____________
$Cr_2(SO_4)_3 + Cl_2 + KOH \rightarrow$ ____________
Reduction: ____________
Oxidation ____________
Water molecules: ____________

Problems

1. A mixture of aluminum chloride and chromium (III) chloride weighing 317 g was processed by an excess of potassium hydroxide solution, and then by an excess of chlorine water. Barium nitrate solution was added to the obtained solution till the complete sedimentation of 126.5 g of a yellow precipitate. Calculate a mass fraction (%) of aluminum chloride in the initial mixture.

2. The chemical amount of the substance $CrBr_3{\cdot}6H_2O$ is 90 times lower than the amount of water, taken for this salt hydrate dissolving. Density of the obtained solution is 1.20 g/ml. Calculate molar concentration of anhydrous salt ($CrBr_3$) in this solution.

3. How many grams of chrome is possible to obtain from 2.28 kg of Cr_2O_3 in the process of reduction by aluminum, if the yield is 85 %? What mass of Al containing 4.7 % of impurities is required for this process?

4. What mass of $K_2Cr_2O_7$ and what volume (ml) of hydrochloric acid solution with a mass fraction of HCl equal to 36 % and density of 1.18 g/cm^3 should be taken to obtain chlorine which can displace 30.48 g of iodine from KI solution? It’s known that the yield at each step is equal to 80 %.

Multiple choice questions

1. Indicate the nucleus charge of the atom if its electron configuration in the ground state is $\lceil \mathrm{Ar} \rfloor 3d^34s^2$:

a) 13; b) 19; c) 23; d) 18.

2. Which chromium oxide can act as oxidizer only?

a) CrO; b) Cr_2O_3; c) CrO_3; d) Cr_2O.

3. Which oxide has the strongest acidic properties?

a) Cr_2O_3; b) CrO; c) BeO; d) CrO_3.

4. If the temperature is equal to 20 °C, chromium doesn’t react with:

a) $AgNO_3$ (solution);
b) HNO_3 (conc.);
c) HCl (solution);
d) H_2SO_4 (conc.).

5. The names of which compounds end with -ate?

a) $K_2Cr_2O_7$; b) $NaCrO_2$; c) $Na_3[Cr(OH)_6]$; d) Na_2CrO_4.

6. Which substances produce a yellow precipitate in the reaction with $BaCl_2$?

a) K_2SO_4; b) K_2CrO_4; c) K_2CO_3; d) $K_2Cr_2O_7$.

7. Which products are formed if the water solutions of $Cr(NO_3)_3$ and Na_2CO_3 are mixed together?

a) $Cr_2(CO_3)_3$; b) $NaNO_3$; c) $Cr(OH)_3$; d) CO_2.

8. Which compound is used to protect medicines from direct sunlight?

a) Cr_2O_3; b) TiO_2; c) WO_3; d) V_2O_5.

9. Phosphorous tungstic acid decomposes at pH equal to:

a) 2; b) 5; c) 7; d) 9.

10. Molybdenum vanadium reactant is used to reveal the ions:

a) phosphate ions;
b) chloride ions;
c) nitrate ions;
d) nitrite ions.

EXPERIMENTAL WORK

"THE PROPERTIES OF CHROME CONTAINING COMPOUNDS"

The aim of the work: to study acid-base and redox properties of chrome containing compounds.

Reactants: solutions of $Cr_2(SO_4)_3$, Na_2CO_3, KI, K_2CrO_4, $K_2Cr_2O_7$, starch, 2M NaOH, 2N H_2SO_4, 3 % H_2O_2.

Experiment 1. ***Production and properties of chrome (III) hydroxide.***

Produce chrome (III) hydroxide in two tubes by the way of the mixing of 3–4 drops of $Cr_2(SO_4)_3$ solution with 1–2 drops of 2M NaOH solution.

$Cr_2(SO_4)_3 + 6NaOH \rightarrow 2Cr(OH)_3\downarrow + 3Na_2SO_4$

Write this reaction in ionic form:

____

Add 2N H_2SO_4 solution to the first tube in the drop by drop manner and notice the change in color.

$2Cr(OH)_3\downarrow + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 6H_2O$

Write this reaction in ionic form:

____

Add 2M NaOH solution to the second tube in the drop by drop manner and notice the change in color.

$Cr(OH)_3\downarrow + 3NaOH = Na_3[Cr(OH)_6]$

Write this reaction in ionic form:

____

Keep the solution containing sodium hexahydroxychromate for the future experiment.

Experiment 2. ***Hydrolysis of chrome sulfate and sodium carbonate in the same tube.***

Put 2–3 drops of $Cr_2(SO_4)_3$ solution in the tube, add Na_2CO_3 solution to the same tube in the drop by drop manner until the precipitate of chrome (III) hydroxide will be formed. Notice the release of a gas.

$Cr_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O \rightarrow 2Cr(OH)_3\downarrow + 3Na_2SO_4 + 3CO_2\uparrow$

Write this reaction in ionic form:

____

Experiment 3. ***Salts of chrome (III) as reducers.***

Add 1–2 drops of NaOH and 3–5 drops of 3 % hydrogen peroxide solution to the $Na_3[Cr(OH)_6]$ solution left from one of the previous experiments. Heat the mixture until the moment when green solution will turn to yellow because of Na_2CrO_4 formation.

Balance the redox reaction using electron-ion method.

$Na_3[Cr(OH)_6] + H_2O_2 \rightarrow Na_2CrO_4 + H_2O + NaOH$

reduction: ____

oxidation: ____

water molecules:____

Experiment 4. ***Chrome (VI) compounds as oxidizers.***

Put 4–5 drops of potassium dichromate solution ($K_2Cr_2O_7$) in the tube, add 3–4 drops of potassium iodide (KI) to the same tube. Notice the change in color. To approve that molecular iodine has been formed in that reaction put one drop of the resulting solution into the tube with 5–6 drops of starch solution.

Balance the redox reaction using electron-ion method. Keep in your mind that the initial solution of potassium dichromate contained sulfuric acid.

$K_2Cr_2O_7 + KI + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + I_2 + H_2O$

reduction: ____

oxidation: ____

water molecules:____

Experiment 5. ***Chromates and dichromates***

a) *Conversion of potassium chromate to dichromate*

Put 3–4 drops of potassium chromate (K_2CrO_4) in the tube, add 2N H_2SO_4 solution to that tube in the drop by drop manner. Notice the change in color.

$2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$

Write this reaction in the ionic form:

____

b) *Conversion of potassium dichromate to chromate*

Put 3–4 drops of potassium dichromate $K_2Cr_2O_7$ solution in the tube, add 2M NaOH solution in the drop by drop manner. Notice the change in color.

$K_2Cr_2O_7 + 2NaOH \rightarrow K_2CrO_4 + Na_2CrO_4 + H_2O$

Write this reaction in the ionic form:

____

Write the conclusion: "*dichromate ions are stable in* ___________________ *medium, while chromate ions are stable in* ____ *medium*".

LESSON 5
ELEMENTS FROM GROUP VIIB AND THEIR COMPOUNDS

Main topics of the lesson:

1. *Overall description of elements from VIIB subgroup.*
2. *Chemical properties of manganese and its compounds.*
3. *The usage of manganese compounds in pharmacy and medicine.*

Manganese, technetium and rhenium are situated in the VIIB subgroup of the Periodic table. These elements have the same electronic configuration $ns^2(n-1)d^5$. Manganese is the most studied element from this subgroup, since all technetium isotopes are radioactive and rhenium is a very rare metal. These elements may demonstrate wide range of oxidation states from +2 to +7. In specific complex compounds which are called carbonyls (for example, $Mn_2(CO)_{10}$) manganese (and other metals) demonstrate the oxidation state equal to 0. Such compounds are used for production of very pure metals. The most stable oxidation states for manganese are +2 (in salts) and +4 (in the oxide), while for technetium and rhenium such stable oxidation state should be +7. Indeed, in Nature manganese can be found in $MnCO_3$ (rhodochrosite) and in MnO_2 (pyrolusite). Technetium cannot be found in Nature — it is the first technically synthesized chemical element.

Manganese is a hard, silvery-gray metal that is easily oxidized in the air. Manganese reacts with the most nonmetals, except hydrogen. At normal temperature manganese slowly reacts with water, while at higher temperature the velocity of this reaction increases. Cold concentrated nitric and sulfuric acids cannot react with manganese, while at higher temperature they do react. Complex compounds of manganese are not very stable in water solutions, except manganese hexacyanides.

Manganese (II) oxide cannot react with water. Manganese (II) hydroxide is not stable. It reacts with oxygen and forms manganese (III) metahydroxide and then, finally, manganese (IV) oxide.

$$4Mn(OH)_2 + O_2 \rightarrow 4MnO(OH)\downarrow + 2H_2O$$

$$4Mn(OH)_2 + 2O_2 \rightarrow 4MnO_2\downarrow + 4H_2O$$

Manganese (II) cations exist in water solutions in form of $[Mn(H_2O)_6]^{2+}$ complexes which have very pale pink color. Dry salts of Mn^{2+} are prone to form hydrates with water vapor from the air. Mn^{2+} ions are important co-factors for numerous enzymes. For example, mitochondrial superoxide dismutase uses Mn^{2+} in its catalytic center to convert O_2^- radical into less hazardous H_2O_2. In many enzymes Mn^{2+} can substitute Mg^{2+} ions and modify their velocities. In proteins Mn^{2+} cations are usually coordinated by oxygen atoms from carboxylic groups of aspartic and glutamic acids and by imidazole nitrogen atoms from histidine side chain. There is a motif for Mn^{2+} coordination that can be described as “beta strand – binder – random coil”. Such motif is also used (but less frequently) for Mg^{2+} coordination.

Insufficiency of manganese in the diet leads to the decrease of steroid hormones synthesis. Manganese intoxication results in the development of Parkinson-like symptoms.

Manganese (IV) oxide is dark brown or black substance that is insoluble in water. Since manganese has a transition oxidation state in that oxide, it can act as both reducer and oxidizer.

$3MnO_2 + KClO_3 + 6KOH \rightarrow 3K_2MnO_4 + KCl + 3H_2O$

$MnO_2 + 2NaCl + 3H_2SO_4 \rightarrow MnSO_4 + 2NaHSO_4 + 2H_2O + Cl_2\uparrow$

Salts which contain manganese in the oxidation state of +6 are called manganates. These salts have green color. They are relatively stable only in basic medium. Manganates disproportionate into MnO_2 and permanganates.

$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + MnO_2\downarrow + 4KOH$

Permanganates are strong oxidizers: manganese in those salts exists in its highest possible oxidation state equal to +7. Redox potential of potassium permanganate depends on the pH of the water solution. In acidic medium $KMnO_4$ shows strongest oxidative properties and turns to Mn^{2+} salts after reduction.

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

In neutral medium $KMnO_4$ shows weaker oxidative potential and the product of its reduction is MnO_2.

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

If the same reaction with sodium sulfite proceeds in basic medium, permanganate turns to manganate.

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

In the method of redox titration that is called “permanganometry” $KMnO_4$ is used as a titrant. Obviously, all the reactions in this method require acidic medium (dilute H_2SO_4 is used for this purpose). Since $KMnO_4$ has a violet or deep purple color, it plays not just the role of a titrant, but also the role of an indicator. Before the point of equilibrium drops of colored $KMnO_4$ solutions are becoming colorless in the flask with the excess of reducer. When the point of equilibrium is reached, the drop of $KMnO_4$ keeps its color and makes the solution in the flask pink.

Permanganometry may be used to measure the amount of both inorganic and organic substances: Fe^{2+} salts, unsaturated hydrocarbons, aldehydes.

$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$

$5CH_2 = CH_2 + 2KMnO_4 + 3H_2SO_4 + 2H_2O \rightarrow 2MnSO_4 + K_2SO_4 + 5CH_2OH\text{-}CH_2OH$

$2KMnO_4 + 5HCOOH + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5CO_2$

Potassium permanganate is used in medicine as antiseptic because of its strong oxidative properties. Very dilute $KMnO_4$ solutions are used for stomach (gastric) lavage in case of food poisoning. That solution also helps in case of alkaloids intake, since it can oxidize them.

Chains of chemical reactions

$KMnO_4 \rightarrow MnO_2 \rightarrow MnCl_2 \rightarrow HMnO_4 \rightarrow KMnO_4$

$KMnO_4 \rightarrow MnSO_4 \rightarrow MnCO_3 \rightarrow MnO \rightarrow Na_2MnO_4$

$Na_2MnO_4 \rightarrow NaMnO_4 \rightarrow MnCl_2 \rightarrow MnO_2 \rightarrow Na_2MnO_4$

Redox reactions

$KMnO_4 + K_2SO_3 + KOH \rightarrow$
Reduction:
Oxidation:
Water molecules:
$KMnO_4 + H_2S + H_2O \rightarrow$
Reduction:
Oxidation:
Water molecules:
$KMnO_4 + HCl$(conc.) →
Reduction:
Oxidation:
Water molecules:
$MnO_2 + HCl$(conc.) →
Reduction:
Oxidation:
Water molecules:
$MnSO_4 + NaBrO_3 + HNO_3 \rightarrow$
Reduction:
Oxidation:
Water molecules:

$MnSO_4 + Br_2 + NaOH \rightarrow$ ____________________

Reduction: ____________________

Oxidation: ____________________

Water molecules: ____________________

Problems

1. To titrate 25.0 ml of 0.05N $KMnO_4$ solution in the acidic medium it is required to use 10.2 ml of sodium nitrite solution. What mass of $NaNO_2$ is contained in 100 ml of its solution?

2. 2.5 g of hydrogen peroxide solution is diluted with water to the volume of 200 ml. To titrate 5.0 ml of this solution in the acidic medium it is required to use 20.00 ml of 0.05N $KMnO_4$ solution. What is a mass fraction of H_2O_2 in the initial concentrated solution?

3. There are two $KMnO_4$ solutions, each with the volume of 100 ml. For the first solution $C_{eq}(KMnO_4)$ = 0.1 mol/L, for the second solution $C_{eq}(KMnO_4)$ = 0.1 mol/L. Calculate the mass of $KMnO_4$ in each solution.

4. A sample of $FeSO_4 \cdot 7H_2O$ salt weighing 27.8 g was used to prepare 200 ml of iron (II) sulfate solution. What volume of 0.1N $KMnO_4$ solution is required to titrate 50 ml of this solution in the acidic medium?

Multiple choice questions

1. Which statements are correct?

a) Mn^{2+} ions activate many enzymes;

b) manganese (II) oxide is a basic oxide;

c) potassium permanganate can be hydrolyzed;

d) the highest oxides and corresponding hydroxides of the elements with the same group number (VIIA and VIIB) have a lot of similar chemical properties.

2. How do the acidic and basic properties change in the series $MnO – MnO_2 – MnO_3 – Mn_2O_7$?

a) the basic properties increase; c) the acidic properties increase;
b) don't change; d) the acidic properties decrease.

3. Complete the equation and calculate the sum of all coefficients in the redox reaction

$$Na_2SO_3 + KMnO_4 + H_2O \rightarrow \ldots$$

a) 12; b) 13; c) 11; d) 10.

4. Indicate the compounds in which manganese atoms are found in anions:

a) $MnSO_4$; b) $K_3[Mn(C_2O_4)_3]$; c) $KMnO_4$; d) K_2MnO_4

5. The chain is given: 2 moles K_2MnO_4 (t) → MnOx (+4HCl) → Y ($+PbO_2 + H_2SO_4$) → Z. Which substance is Z if it is a manganese containing compound?

a) manganic acid; c) permanganic acid;
b) a basic oxide; d) amphoteric oxide.

6. Indicate electron half – reactions for the oxidation – reduction reaction

$$Na_2SO_3 + KMnO_4 + KOH \rightarrow \ldots$$

a) $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$;
b) $MnO_4^- + e \rightarrow MnO_4^{2-}$;
c) $SO_3^{2-} + 2OH^- - 2e \rightarrow SO_4^{2-} + H_2O$;
d) $SO_3^{2-} + H_2O - 2e \rightarrow SO_4^{2-} + 2H^+$.

7. Indicate metal enzymes normally containing Mn^{2+} cations:

a) arginase; c) carboxypeptidase;
b) carbonic anhydrase; d) pyruvate carboxylase.

8. Permanganic acid and its salts are strong oxidizers:

a) in basic medium; b) in neutral medium; c) in acidic medium.

9. Which substances are formed spontaneously in water solutions of manganates?

a) permanganic acid salts; c) manganese (II) oxide;
b) manganese (III) oxide; d) manganese (IV) oxide.

10. Which substances don't participate in the process of hydrolysis?

a) sodium permanganate; c) potassium permanganate;
b) manganese (II) sulfate; d) manganese (II) chloride.

EXPERIMENTAL WORK

"CHEMICAL PROPERTIES OF MANGANESE CONTAINING COMPOUNDS"

The aim of the work: to study acid-base and redox properties of manganese containing compounds.

Dry substances: manganese (IV) oxide, manganese (II) sulfate, manganese (II) chloride, sodium bithmutate.

Solutions: 0.1M HCl, 0.1M H_2SO_4, 0.1M HNO_3, 0.1M CH_3COOH, 0.5M manganese sulfate, 0.5M manganese chloride, 0.1M potassium permanganate, 0.5M sodium sulfite, 0.1M sodium hydroxide, 0.5M sodium nitrite, iron (II) sulfate.

Exercise 1. ***Test reaction for*** Mn^{2+} ***cations.***

Put several drops of manganese (II) sulfate solution in the tube, add 5–6 drops of nitric acid in the same tube. Then add a small portion of sodium bithmutate ($NaBiO_3$) in the same tube. Notice the color change.

Balance the redox reaction using electron-ion method.

$MnSO_4 + NaBiO_3 + HNO_3 \rightarrow HMnO_4 + Bi(NO_3)_3 + Na_2SO_4 + NaNO_3 + H_2O$

reduction: ____

oxidation: ____

water molecules: ____

Exercise 2. ***Production and chemical properties of manganese (II) hydroxide.***

Put several drops of manganese (II) chloride in the tube, add NaOH solution in the drop by drop manner until the formation of pale pink precipitate of manganese (II) hydroxide.

$MnCl_2 + 2NaOH \rightarrow 2NaCl + Mn(OH)_2\downarrow$

Write this reaction in ionic form:

____

Divide the precipitate in two parts and keep in separate tubes. Add HCl solution in the first tube in the drop by drop manner until the disappearance of the precipitate.

$Mn(OH)_2 + 2HCl \rightarrow MnCl_2 + 2H_2O$

Write this reaction in ionic form:

____

Add NaOH solution to the second tube in the drop by drop manner and mix that solution by a glass stick. In alkaline solution manganese (II) hydroxide turns to metahydroxide (brown) and then to manganese (IV) oxide (dark brown).

Balance both equations.

$Mn(OH)_2 + O_2 \rightarrow MnO(OH)\downarrow + H_2O$

$MnO(OH) + O_2 \rightarrow MnO_2\downarrow + H_2O$

Experiment 3. ***Oxidative properties of manganese (IV) oxide.***

Put 2 small spoons of MnO_2 in the tube, add solutions of sulfuric acid and iron (II) sulfate to the same tube.

Balance the redox reaction using electron-ion method.

$MnO_2 + FeSO_4 + H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + H_2O$

reduction: ____

oxidation: ____

water molecules: ____

Experiment 4. ***Oxidative properties of potassium permanganate depend on the pH of a solution.***

Take 3 tubes and add 3–4 drops of potassium permanganate solution in each of them. Add sulfuric acid in the first tube, water in the second tube, and alkali in the third tube. Then add the same amount (5–6 drops) of sodium nitrite in each of the three tubes.

Balance the redox reactions using electron-ion method.

$KMnO_4 + KNO_2 + H_2SO_4 \rightarrow MnSO_4 + KNO_3 + K_2SO_4 + H_2O$

reduction: ____

oxidation: ____

water molecules: ____

$KMnO_4 + KNO_2 + H_2O \rightarrow MnO_2\downarrow + KNO_3 + KOH$

reduction: ____

oxidation: ____

water molecules: ____

$KMnO_4 + KNO_2 + KOH \rightarrow K_2MnO_4 + KNO_3 + H_2O$

reduction: ____

oxidation: ____

water molecules: ____

Keep the last tube for the next experiment.

Exercise 5. ***Disproportioning of potassium manganate (K_2MnO_4).***

Add 3 drops of acetic acid solution in the tube with potassium manganate. Notice the change in color and precipitation.

Balance the redox reaction using electron-ion method.

$K_2MnO_4 + H_2O \rightarrow KMnO_4 + MnO_2 + KOH$

reduction: ____

oxidation: ____

water molecules: ____

Experiment 6. ***Hydrolysis of manganese (II) salts***

Put several crystals of manganese (II) sulfate in the tube with distilled water. Notice the change in pH level with the help of indicator paper.

Write the equation of stepwise hydrolysis for manganese chloride.

Step 1 (complete form): ____

Step 1 (ionic form): ____

Step 2 (complete form): ____

Step 2 (ionic form): ____

Write the conclusion: “*The higher the oxidation state of manganese in its compound, the stronger its* ____ *properties*”

LESSON 6

ELEMENTS FROM GROUP VIIIB AND THEIR COMPOUNDS

Main topics of the lesson:

1. *Overall description of elements from VIIIB subgroup.*
2. *Chemical properties of iron and its compounds.*
3. *The usage of iron compounds in pharmacy and medicine.*

The VIIIB subgroup includes three columns of the Periodic table. In the 4th period that subgroup includes iron, cobalt and nickel. These elements have much in common and usually they go under the name “iron family”. Elements from 5th and 6th periods which can be found in VIIIB subgroup are usually included in the “platinum family”.

Iron has one of the highest abundances in the Earth crust. It can be found in pyrite (FeS_2), siderite ($FeCO_3$), hematite (ferric oxide: Fe_2O_3), magnetite (the mixture of ferric and ferrous oxides: $Fe_3O_4 = Fe_2O_3 \cdot FeO$).

Cobalt can be found in CoAsS mineral (cobaltite) and polymetallic minerals, as well as nickel. Metals from platinum family are very rare, but since they are more inert than metals from iron family, they can be found as native pure chemical elements.

Iron is stable in the dry air, while in the presence of water it turns to rust.

$4Fe + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_3$

Disperse iron reacts with oxygen at normal temperature, while solid iron requires higher temperature to be burnt. The higher the temperature, the higher the percentage of Fe^{2+} relative to the percentage of Fe^{3+} among the products of this reaction.

$4Fe + 3O_2 \rightarrow 2Fe_2O_3$

$3Fe + 2O_2 \rightarrow Fe_3O_4$ (t° = 570 °C)

$2Fe + O_2 \rightarrow 2FeO$ (t° = 1200–1300 °C)

Carbides and sulfides of iron, cobalt and nickel are nonstoichiometric compounds. Hydrogen can be dissolved in metals from group VIIIB. This phenomenon is used in the standard hydrogen electrode that is composed of platinum with dissolved hydrogen. Iron is oxidized by chlorine gas and forms $FeCl_3$.

At normal temperature iron cannot react with water in the absence of oxygen. At higher temperature it reacts with water in a way similar to other metals situated in the reactive series of metals after magnesium. Again, the higher the temperature, the lower the oxidation state of iron.

$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2\uparrow$ (t° = 570 °C)

$Fe + H_2O \rightarrow FeO + H_2\uparrow$ (t° = 900 °C)

Iron, cobalt and nickel cannot react with concentrated nitric and sulfuric acids at normal temperature. At higher temperature that passivation doesn’t work.

Iron, unlike cobalt and nickel, is able to react with a concentrated solution of alkali.

$Fe + 4NaOH$ (concentrated) $+ 2H_2O \rightarrow Na_4[Fe(OH)_6] + H_2$

Oxides of iron, cobalt and nickel in the oxidation state of +2 show mostly basic properties (they react with acids and produce salts and water). FeO reacts with NaOH only at very high temperature and in the absence of water.

$FeO + 4NaOH \rightarrow 2H_2O + Na_4FeO_3$

CoO is able to react just with boiling concentrated alkalis.

$CoO + 2NaOH + H_2O \rightarrow Na_2[Co(OH)_4]$

It is important to highlight that the most stable oxidation state for iron is +3, but for cobalt and nickel the most stable oxidation state is +2. Iron (II) hydroxide is oxidized by oxygen. Resulting compound is usually written as $Fe(OH)_3$, while this formula is not the one that describes its content well, unlike $nFe_2O_3 \cdot mH_2O$. $Ni(OH)_2$ and $Co(OH)_2$ cannot react with oxygen.

Acidic properties of $Fe(OH)_2$ and $Co(OH)_2$ are weak, while they still can react with concentrated alkali, unlike $Ni(OH)_2$.

$2NaOH + Fe(OH)_2 \rightarrow Na_2[Fe(OH)_4]$

$2NaOH + Co(OH)_2 \rightarrow Na_2[Co(OH)_4]$

The salts of Fe^{2+} are easily oxidized by the oxygen from the air or water solution.

$4FeSO_4 + O_2 + 2H_2O \rightarrow 4Fe(OH)SO_4$

$4FeSO_4 + O_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + 2H_2O$

The Mohr's salt ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) shows better resistance to oxidation than other salts of Fe^{2+}.

Compounds of nickel and cobalt in the oxidation state of +3 are strong oxidizers.

If iron (III) oxide (or hydroxide) reacts with solid sodium hydroxide at high temperature sodium ferrite and water are formed.

$Fe_2O_3 + 2NaOH_{\text{(solid)}} \rightarrow 2NaFeO_2 + H_2O$

$Fe(OH)_3 + NaOH_{\text{(solid)}} \rightarrow NaFeO_2 + 2H_2O$

If iron (III) oxide (or hydroxide) reacts with concentrated sodium hydroxide solution a complex salt (sodium hexahydroxoferrate) will be formed.

$Fe_2O_3 + 3H_2O + 6NaOH \rightarrow 2Na_3[Fe(OH)_6]$

$Fe(OH)_3 + 3NaOH \rightarrow Na_3[Fe(OH)_6]$

Concentrated alkali solutions are able to react with pure iron as well.

$2Fe + 2NaOH + 6H_2O \rightarrow 3H_2\uparrow + 2Na[Fe(OH)_4]\downarrow$

Ferrates are formed in reactions between iron and iron containing compounds with strong oxidizers.

$Fe + KClO_3 + 2KOH \rightarrow KCl + K_2FeO_4 + H_2O$

$2Fe(OH)_3 + 4NaOH + 3NaClO \rightarrow 3NaCl + 5H_2O + 2Na_2FeO_4$

Iron demonstrates the oxidation state of +6 in ferrates. These salts oxidize water and ammonia.

$2Na_2FeO_4 + 10H_2O \rightarrow 4Fe(OH)_3 + 4NaOH + O_2$

$3NH_3 + 8K_2FeO_4 + 14H_2O \rightarrow 3KNO_3 + 8Fe(OH)_3 + 13KOH$

Iron is essential chemical element that is necessary for numerous proteins and enzymes. It can be bound by amino acids of proteins directly (for example, in ferritin), or it can be a part of the heme (in hemoglobin).

Cobalt is the part of the vitamin B_{12} that is necessary for metabolism.

Reaction with gold blood salt is used to detect the presence of Fe^{3+} cations in the water solution.

$FeCl_3 + K_4[Fe(CN)_6] \rightarrow KFe[Fe(CN)_6]\downarrow + 3KCl$

Resulting insoluble complex has deep blue color.

The same compound is formed in the reaction between red blood salt and Fe^{2+} cations.

$K_3[Fe(CN)_6] + Fe^{2+} \rightarrow KFe[Fe(CN)_6] + 2K^+$

Reaction with dimethylglyoxime is used for the detection of Ni^{2+} ions. In this reaction ruby red complex (figure 3) is formed.

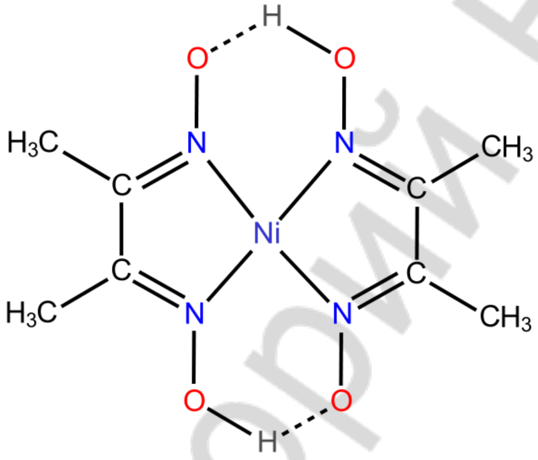


Figure 3. The complex of Ni^{2+} cation and two molecules of dimethylglyoxime

Chains of chemical reactions

$Fe \rightarrow FeCl_2 \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \rightarrow Na_2FeO_4$

$Na_2FeO_4 \rightarrow Fe(OH)_3 \rightarrow NaFeO_2 \rightarrow Fe(OH)_3 \rightarrow Fe_2O_3$

$Fe_3O_4 \rightarrow Fe \rightarrow FeCl_2 \rightarrow FeCl_3 \rightarrow FeS$

$FeSO_4 \rightarrow Fe_2(SO_4)_3 \rightarrow Fe(OH)_3 \rightarrow FeBr_3 \rightarrow Fe$

Redox reactions

$FeSO_4 + KBrO_3 + H_2SO_4 \rightarrow$

Reduction:

Oxidation:

Water molecules:

$K_2FeO_4 + H_2O \rightarrow$

Reduction:

Oxidation:

Water molecules:

$K_2FeO_4 + HCl(conc.) \rightarrow$

Reduction:

Oxidation:

Water molecules:

Problems

1. When cooling 0.2 L ($\rho = 1.23$ g/ml) of iron (III) nitrate solution with a mass fraction of the salt equal to 25.0 %, there was a precipitate of crystalline hydrate of this salt weighing 40.32 g. Define its composition if in the solution over the precipitate the mass fraction of the dissolved substance is 18.16 %.

2. Calculate the mass of heptahydrate of iron (II) sulfate and the volume of water, necessary for preparation 0.6 L of the solution in which molar concentration of equivalent of the salt will be equal to 0.5 mol/L ($\rho = 1.06$ g/ml). The prepared solution will be used for the reaction: $2FeSO_4 + H_2O_2 = 2Fe(OH)SO_4$

3. An unknown iron oxide weighing 4.5 g was reduced by hydrogen. The mass of obtained iron is equal to 3.5 g. Find the formula of the initial oxide.

4. 8 g of a mixture of iron (II) and iron (III) oxides was dissolved in sulfuric acid solution taken in excess. To titrate the obtained solution it was required to use 31.6 g of $KMnO_4$ solution with a mass fraction of 5 %. Define the mass fractions of the oxides in the initial mixture.

5. 14 g of iron was melted with sulfur weighing 4.8 g. Hydrochloric acid solution taken in excess was added to the obtained mixture. Define the emitted gases and their volumes.

Multiple choice questions

1. Which statements are correct?

a) powders of iron, cobalt and nickel form Fe_3O_4, CoO, NiO oxides in the process of burning;

b) electron configurations in the ground state of the iron family metals differ in the number of d-electrons;

c) chemical activity of metals increases from iron to nickel;

d) when iron family metals are heated up, their passivation by concentrated sulfuric and nitric acids is removed.

2. Which salt is used to reveal Fe^{2+} ions in aqueous solutions?

a) potassium hexacyanoferrate (II);

b) potassium hexacyanoferrate (III);

c) potassium thiocyanate;

d) sodium hydroxide.

3. The chain is given: $Ni(OH)_2$ (+X) → NiO(OH) (+HCl) → Y. Which substances are X and Y?

a) H_2O and $NiCl_3$;

b) Cl_2 and $NiCl_2$

c) Cl_2 and $NiCl_3$;

d) O_2 and $NiCl_2$

4. Co^{3+} ions are:

a) weak oxidizers;

b) weak complex formers;

c) strong oxidizers;

d) strong reducers.

5. Which two substances are reactants if iron (III) metahydroxide is the product of the reaction?

a) Fe_2O_3 and H_2O;

b) Fe and H_2O;

c) $Fe(OH)_2$ and H_2O_2;

d) Fe_3O_4 and H_2O_2

6. The chain is given: Ni (+HCl) → X (+NaOH + Br_2) → Y (+NaOH + Cl_2) → Z. Indicate the oxidation states of nickel in X, Y, Z compounds respectively?

a) +3, +2, +3; b) +3, +3, +3; c) +2, +2, +3; d) +2, +3, +3.

7. Indicate the metal, which doesn't dissolve in sodium hydroxide solution at room temperature, but reacts with hot concentrated sodium hydroxide solution?

a) Mn; b) Co; c) Fe; d) Ni.

8. Calculate the sum of all coefficients in the reaction: CoO(OH) + HCl → $CoCl_2$ + + Cl_2 + H_2O.

a) 14; b) 15; c) 8; d) 10.

9. Indicate electron half-reactions for the redox reaction in the melt:

$$Fe_2O_3 + KNO_3 + KOH \rightarrow$$

a) $2Fe^{+3} - 6e \rightarrow 2Fe^{6+}$;

b) $N^{+5} + 2e \rightarrow N^{+3}$;

c) $2Fe^{+3} + 2e \rightarrow 2Fe^{2+}$;

d) $N^{+5} + 5e \rightarrow N^{0}$.

10. Nickel deficiency in a human body leads to:

a) the inhibition of certain liver enzymes;

b) the disruption of respiratory processes in the mitochondria;

c) the changes in lipid content in the liver;

d) the emergence of malignancies.

EXPERIMENTAL WORK
“IRON, NICKEL, COBALT AND THEIR COMPOUNDS”

The aim of the work: to study chemical properties of compounds containing iron, cobalt and nickel.

Reactants: bromine water, Mohr’s salt, solutions of: iron (II) sulfate (0.1M), iron (III) chloride, potassium thiocyanate (0.1M), potassium permanganate (0.1M), cobalt (II) sulfate, nickel (II) sulfate, potassium hexacyanoferrate (III) (0.1M), potassium hydroxide (0.1M), sulfuric acid (0.1M), nitric acid (0.1M), potassium iodide (0.1M), colorimetric indicator paper.

Experiment 1. ***Test reaction for Fe^{2+} and Fe^{3+} ions.***

a) *Reaction between iron (II) salts and “red blood salt” — potassium hexacyanoferrate (III).*

Add the solution of potassium hexacyanoferrate (III) ($K_3[Fe(CN)_6]$) to the tube with iron (II) salt solution in the drop by drop manner and notice the color change. In this reaction iron (III) from complex anion oxidizes iron (II) from the solution.

$Fe^{2+} + [Fe(CN)_6]^{3-} \rightarrow Fe^{3+} + [Fe(CN)_6]^{4-}$

Then a new insoluble complex is formed.

$Fe^{3+} + K^{+} + [Fe(CN)_6]^{4-} \rightarrow KFe^{3+}\ [Fe^{2+}(CN)_6]\downarrow$

The name of the resulting complex $KFe[Fe(CN)_6]$ is «Prussian blue» because of the deep blue color.

This reaction works good only in acidic medium (it prevents hydrolysis of iron salts). Remember that complex precipitate reacts with alkali.

The complete equation is written below:

$FeSO_4 + K_3[Fe(CN)_6] \rightarrow KFe[Fe(CN)_6]\downarrow + K_2SO_4$

b) *Reaction between iron (III) salts and “gold blood salt” — potassium hexacyanoferrate (IV).*

Add the solution of gold blood salt ($K_4[Fe(CN)_6]$) to the tube with iron (III) chloride solution in the drop by drop manner. As a result, the same blue precipitate (Prussian blue) will be formed.

$FeCl_3 + K_4[Fe(CN)_6] = KFe[Fe(CN)_6]\downarrow + 3KCl$

$Fe^{3+} + K^{+} + [Fe(CN)_6]^{4-} = KFe[Fe(CN)_6]\downarrow$

c) *Reaction between iron (III) salts and potassium thiocyanate.*

Add the solution of potassium thiocyanate to the tube with iron (III) chloride. Notice blood red color of the resulting solution.

$FeCl_3 + 3KSCN = Fe(SCN)_3 + 3KCl.$

Experiment 2. ***Formation of iron (II) and iron (III) hydroxides.***

a) Add KOH solution to the tube with iron (II) salt in the drop by drop manner until white precipitate of $Fe(OH)_2$ will be formed. Notice that after some period of time the color of the precipitate will turn to green. Then green will turn to red brown (because of $Fe(OH)_3$ formation).

$FeSO_4 + 2KOH = K_2SO_4 + Fe(OH)_2$

Write this reaction in ionic form:

____

b) Add KOH solution to the tube with iron (III) salt in the drop by drop manner until red brown precipitate will be formed.

$FeCl_3 + 3NaOH = Fe(OH)_3\downarrow + 3NaCl$

or

$FeCl_3 + 3NaOH = FeO(OH)\downarrow + 3NaCl + H_2O$

Experiment 3. ***Reductive properties of iron (II) slats.***

a) Add the excess of the solution of iron (II) salt in the tube with potassium permanganate solution in acidic medium. Notice that solution became colorless.

Balance the redox reaction using electron-ion method.

$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + K_2SO_4 + MnSO_4 + H_2O$

reduction: ____

oxidation: ____

water molecules: ____

Confirm the presence of Fe^{3+} ions in the resulting solution with the help of KSCN solution.

b) Add hydrogen peroxide solution to the tube with iron (II) salt in the acidic medium.

Balance the redox reaction using electron-ion method.

$H_2O_2 + FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$

reduction: ____

oxidation: ____

water molecules: ____

Confirm the presence of Fe^{3+} ions in the resulting solution with the help of KSCN solution.

Experiment 4. ***Oxidative properties of iron (III) compounds***

Add 1–2 drops of potassium iodide (KI) to the tube with iron (III) chloride solution. Observe the release of molecular iodine and color change.

Balance the following equation.

$FeCl_3 + KI \rightarrow FeCl_2 + I_2 + KCl$

Experiment 5. ***Hydrolysis of iron salts.***

a) Hydrolysis of iron (II) salts. With the help of indicator paper check the pH level in the water solution of iron (II) sulfate.

Write equations of the stepwise hydrolysis of iron (II) sulfate.

Step 1 (complete form): ______________________________

Step 1 (ionic form):______________________________

Step 2 (complete form): ______________________________

Step 2 (ionic form):______________________________

b) Hydrolysis of iron (III) salts. With the help of indicator paper check the pH level in the water solution of iron (III) chloride.

Write equations of the stepwise hydrolysis of iron (III) chloride.

Step 1 (complete form): ______________________________

Step 1 (ionic form):______________________________

Step 2 (complete form): ______________________________

Step 2 (ionic form):______________________________

Step 3 (complete form): ______________________________

Step 3 (ionic form):______________________________

Experiment 6. ***Production of ferrates and their properties.***

a) Pour 10–15 drops of concentrated KOH solution into the tube. Then add 4–5 drops of iron (III) chloride and 1–2 drops of bromine. Carefully heat the tube in the fume hood. Notice the appearance of red color.

Balance the redox reaction using electron-ion method.

$Fe(OH)_3 + KOH + Br_2 \rightarrow K_2FeO_4 + KBr + H_2O$.

reduction: ______________________________

oxidation: ______________________________

water molecules:______________________________

Add water to the tube and divide the solution into two tubes.

b) Add barium chloride solution to the potassium ferrate solution in the drop by drop manner. Notice the precipitation:

$K_2FeO_4 + BaCl_2 = BaFeO_4\downarrow + 2KCl$

c) Add sulfuric acid solution (0.1 mol/L) to the potassium ferrate solution. Notice the release of a gas.

Balance the following reactions.

$K_2FeO_4 + H_2O \rightarrow FeO(OH) + KOH + O_2$

$FeO(OH) + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$.

Experiment 7. ***Production of cobalt (II) hydroxide and cobalt (III) hydroxide.***

Add potassium hydroxide solution to the tube with cobalt (II) chloride solution in the drop by drop manner. Notice blue precipitate of CoOHCl. Continue the addition of KOH solution and notice the formation of pink precipitate $Co(OH)_2$.

$CoCl_2 + NaOH = CoOHCl\downarrow + NaCl$

Write this reaction in ionic form:

____

$CoOHCl + NaOH = Co(OH)_2\downarrow + NaCl$

Write this reaction in ionic form:

____

Add several drops of hydrogen peroxide to the same tube and notice the formation of brown CoO(OH) precipitate.

$2Co(OH)_2 + H_2O_2 = 2CoO(OH)\downarrow + 2H_2O$.

Experiment 8. ***Production of nickel (II) hydroxide and nickel (III) hydroxide.***

Add potassium hydroxide solution to the tube with nickel (II) chloride solution in the drop by drop manner. Notice green precipitate of $Ni(OH)_2$.

$NiCl_2 + 2KOH \rightarrow Ni(OH)_2 + 2KCl$

Write this reaction in ionic form:

____

Add 3–5 drops of bromine water to the same tube in the fume hood. Notice black precipitate of NiO(OH).

$2Ni(OH)_2 + Br_2 + 2NaOH = 2NiO(OH)\downarrow + 2NaBr + 2H_2O$.

Write the conclusion: “*The higher the oxidation state of iron in its compound, the stronger its* ____ *properties*”

LESSON 7
ELEMENTS FROM GROUP IB AND THEIR COMPOUNDS

Main topics of the lesson:

1. *Overall description of elements from IB subgroup.*
2. *Chemical properties of elements from IB subgroup and their compounds.*
3. *Biological roles, the usage in medicine and pharmaceutical analysis of compounds containing elements from IB subgroup.*

The common electronic configuration of copper, silver and gold is $ns^1(n–1)d^{10}$. Those metals are quite inert. Because of this reason they can be found in Nature as pure chemical elements. Copper, silver and gold can also be found in minerals made up from sulfides and arsenides. Silver forms stable compounds with chlorine. The most chemically active metal from IB subgroup is copper, the less active one is gold. All the three metals are known since ancient times. Gold and silver have been discovered by mankind sometimes in V century B.C. Copper has been discovered later in III century B.C.

Copper slowly reacts with oxygen, water and carbon dioxide. Thus, sculptures made from copper are usually covered by green layer of copper hydroxycarbonate.

$2Cu + H_2O + CO_2 + O_2 \rightarrow (CuOH)_2CO_3$

Interestingly, there is a mineral called malachite that has a formula of $CuCO_3{\cdot}Cu(OH)_2$ that is actually the same as $(CuOH)_2CO_3$.

Silver slowly reacts with hydrogen sulfide and oxygen at normal temperature. As a result, the surface of silver becomes black.

$4Ag + 2H_2S + O_2 \rightarrow 2Ag_2S + 2H_2O$

Gold is resistant to oxygen from the air, but it can be dissolved in the solution of potassium cyanide in the presence of oxygen.

$4Au + 8KCN + 2H_2O + O_2 \rightarrow 4K[Au(CN)_2] + 4KOH$

The resulting complex compound (dicyanoaurate of potassium) can react with zinc to produce gold back.

$2K[Au(CN)_2] + Zn \rightarrow K_2[Zn(CN)_4] + 2Au\downarrow$

Copper reacts with oxygen and produces copper (II) oxide at lower temperature, while copper (I) oxide is produced at higher temperature.

$2Cu + O_2\ (400–500\ °C) \rightarrow 2CuO$

$4Cu + O_2\ (> 800\ °C) \rightarrow 2Cu_2O$

The same tendency has been discovered for the reaction between copper and sulfur.

$Cu + S\ (t_1°) \rightarrow CuS$

$2Cu + S\ (t_2° > t_1°) \rightarrow Cu_2S$

Copper cannot react with so-called non-oxidizing acids. Reaction with oxidizing acids is possible.

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

$3Cu + 8HNO_3$ (40 %) → $Cu(NO_3)_2 + 2NO + 4H_2O$

$Cu + 2H_2SO_4$ (conc.) → $CuSO_4 + SO_2 + 2H_2O$

Copper reacts with iodine and forms copper (I) iodide instead of copper (II) iodide.

$2Cu + I_2 \rightarrow 2CuI$

Compounds of copper in the oxidation state of +1 are less stable than compounds of copper in the oxidation state of +2. For example, copper (I) oxide reacts with sulfuric acid and forms copper (II) sulfate and pure copper.

$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + H_2O + Cu\downarrow$

Thermal decomposition of copper (I) salts also leads to the formation of copper (II) salt and pure copper.

$2CuCl$ (t°) → $2Cu + CuCl_2$

$CuSO_4$ (t°) → $Cu + CuSO_4$

Copper (I) hydroxide is oxidized by oxygen and forms copper (II) hydroxide.

$4CuOH + O_2 + 2H_2O \rightarrow 4Cu(OH)_2$

Both copper (I) and copper (II) cations are prone to form complexes with ammonia.

$CuOH + 2NH_3$(water solution) → $[Cu(NH_3)_2]OH$

$CuCl_2 + 4NH_3 \rightarrow [Cu(NH_3)_4]Cl_2$

In the excess of chloride anions copper (II) chloride turns to complex tetrachlorocuprate anion.

$CuCl_2 + 2NaCl$(concentrated) → $Na_2[CuCl_4]$

Silver reacts with concentrated sulfuric and nitric acids.

$2Ag + 2H_2SO_4$ (concentrated) → $Ag_2SO_4 + SO_2\uparrow + 2H_2O$

$Ag + 2HNO_3$ (concentrated) → $AgNO_3 + NO_2\uparrow + H_2O$

$3Ag + 4HNO_3$ (dilute) → $3AgNO_3 + NO\uparrow + 2H_2O$

Silver nitrate is one of the very few soluble silver salts. In the reaction with an alkali silver nitrate produces silver hydroxide that decomposes into silver oxide and water.

$AgNO_3 + NaOH \rightarrow AgOH + NaNO_3$

$2AgOH \rightarrow Ag_2O\downarrow + H_2O$

With the help of silver nitrate one can check the presence of chloride, bromide and iodide anions in a solution. Silver chloride is a white precipitate, silver bromide is a pale yellow precipitate, while silver iodide is a deep yellow precipitate. Interestingly, silver fluoride is soluble.

In the presence of ammonia silver nitrate forms complex compound known as diaminesilver chloride.

$AgNO_3 + 2NH_3 \rightarrow [Ag(NH_3)_2]NO_3$

Diaminesilver cations as a main component of Tollens' reactant are used in the silver mirror test that helps to reveal the presence of the aldehyde group in an organic compound. Fresh copper (II) oxide can also oxidize aldehyde groups of organic compounds into carboxylic groups.

Gold can be oxidized by a few substances like ozone or halogens. Interestingly, gold can act as oxidizer itself in the reaction with cesium (CsAu is an ionic compound).

Gold can react with just one acid. That acid is selenic acid.

$2Au + 6H_2SeO_4 \rightarrow Au_2(SeO_4)_3 + 3H_2SeO_3 + 3H_2O$

However, gold can be dissolved in the mixture of acids (1 part of HNO_3 and 2 parts of HCl by mass) know as “aqua regina”. In that mixture such strong oxidative agents as atomic chlorine and NO are formed. Those oxidative agents oxidize gold, while chloride anions make a complex with Au^{3+}.

$Au + 4HCl + HNO_3 \rightarrow H[AuCl_4] + NO\uparrow + 2H_2O$

Resulting complex compound (hydrogen tetrachloroaurate (III)) is soluble in water. Gold can be obtained from such solution with the help of reducers like Fe^{2+} ions or hydrazine.

$2[AuCl_4]^- + 3Fe^{2+} \rightarrow 3Fe^{3+} + 8Cl^- + 2Au\downarrow$

$4[AuCl_4]^- + 3N_2H_4 \rightarrow 3N_2 + 12H^+ + 16Cl^- + 4Au\downarrow$

Copper is an important microelement that plays the role of co-factor for numerous enzymes. The biological role of silver is unclear. Compounds of gold are toxic. Copper and silver cations are used as bactericide agents. Silver is usually administered as colloid solution in form of nasal drops. Auranophine is a compound of gold that is used in treatment of autoimmune diseases (like rheumathoid arthritis). Alloys of gold are traditionally used in dentistry to make tooth crowns.

Chains of chemical reactions

$Cu_2S \rightarrow CuO \rightarrow Cu(OH)_2 \rightarrow CuCl \rightarrow [Cu(NH_3)_4]Cl_2$

$Cu_2O \rightarrow CuCl_2 \rightarrow CuO \rightarrow CuCl \rightarrow CuSO_4$

$Ag \rightarrow Ag_2SO_4 \rightarrow Ag_2O \rightarrow [Ag(NH_3)_2]OH \rightarrow Ag_2S$

$Au \rightarrow AuCl_3 \rightarrow Au(OH)_3 \rightarrow NaAuO_2 \rightarrow AuCl_3$

Redox reactions

$Cu + HNO_3$(dilute) →
Reduction: ____________________
Oxidation: ____________________
Water molecules: ____________________
$Cu + H_2SO_4$(conc.) →
Reduction: ____________________
Oxidation: ____________________
Water molecules: ____________________
$CuO + NH_3$ →
Reduction: ____________________
Oxidation: ____________________
Water molecules: ____________________
$CuCl_2 + KI$ →
Reduction: ____________________
Oxidation: ____________________
Water molecules: ____________________
$Au + HCl + HNO_3$ →
Reduction: ____________________
Oxidation: ____________________
Water molecules: ____________________

Problems

1. A mixture of copper (II) nitrate and silver nitrate was heated up until the constant mass of 5.92 g. What is the total volume of the produced gases?

____
____
____
____

2. A copper plate weighing 10 g was immersed in 200 g of iron (III) chloride solution with a mass fraction equal to 22 %. After a while the mass of a plate decreased twice. What are mass fractions of the salts in the obtained solution?

____
____
____
____

3. A sample of copper weighing 24 g was dissolved in nitric acid solution with a mass fraction equal to 8 %. What volume of the acid solution was used for the reaction? What is the volume of the obtained gas?

4. A sample of alloy of copper, tin, and zinc weighing 1.6645 g was tested. Two substances were obtained: 1.3466 g of $Cu(SCN)_2$ and 0.0840 g of SnO_2. Calculate mass fractions of copper, tin, and zinc in the initial alloy.

Multiple choice questions

1. The most stable oxidation states of Cu, Ag and Au in their compounds are equal to (respectively):

a) +1, +2, +3; b) +3, +2, +1; c) +2, +1, +3; d) +2, +2, +3.

2. How do the acidic properties change in the line CuO – Ag_2O – Au_2O_3?

a) decrease;
b) increase;
c) first decrease, and then increase;
d) first increase, and then decrease.

3. Which reactions are impossible?

a) $Cu + H_2SO_4(\text{dilute}) \rightarrow CuSO_4 + H_2$;
b) $Cu + H_2SO_4(\text{conc.}) \rightarrow CuSO_4 + SO_2 + H_2O$;
c) $Ag + HNO_3(\text{dilute}) \rightarrow AgNO_3 + NO + H_2O$;
d) $Ag + HNO_3(\text{conc.}) \rightarrow AgNO_3 + NO_2 + H_2O$;
e) $Ag + Cu(NO_3)_2 \rightarrow AgNO_3 + Cu$;
f) $AgNO_3 + KOH \rightarrow AgOH + KNO_3$;
g) $Ag_2S + O_2 \rightarrow Ag_2O + SO_2$.

4. Indicate the least common multiple coefficients in the balance of the redox reaction of gold dissolution in aqua regia:

a) 2; b) 3; c) 4; d) 6.

5. Write the reaction of silver bromide with sodium thiosulfate, and calculate the sum of the coefficients in the short ionic equation:

a) 7; b) 5; c) 4; d) 3.

6. Calculate the sum of all coefficients in the reaction of copper (II) sulfate with potassium iodide, if molecular iodine is formed:

a) 11; b) 9; c) 8; d) 7.

7. The chain is given: $Cu(NO_3)_2$ (t°) → A ($+H_2SO_4$) → B (+NaOH dilute in excess) → → C ($+HNO_3$ in excess) → D. Calculate the sum of molar masses (g/mol) of the copper containing substances A, C, and D.

a) 321; b) 366; c) 481; d) 526.

8. The chain is given: 1 mole Cu_2S ($+O_2$ (in excess) t°) → A ($+HNO_3$ (in excess)) → → B (+2 moles KOH (solution)) → C (+2 moles HNO_3 (dilute)) → D. Calculate the sum of molar masses (g/mol) of the copper containing substances C and D.

a) 268; b) 286; c) 331; d) 376.

9. Copper (II) nitrate weighing 4.68 g was heated up. 4.02 g of the solid remain was obtained, determine the degree of copper nitrate decomposition (%).

a) 25; b) 14; c) 30; d) 50.

10. 3 g of copper hydroxide reacts with 150 ml of ammonia solution in water (density is equal to 0.907 g/ml). Tetraamincopper (II) hydroxide solution is formed. Calculate the mass fraction (%) of this substance in the resulting solution.

a) 6.8; b) 5.7; c) 3.9; d) 4.7.

EXPERIMENTAL WORK
“CHEMICAL PROPERTIES OF COMPOUNDS CONTAINING ELEMENTS FROM IB GROUP”

The aim of the work: to study the properties of IB elements and their compounds.

Reactants: copper (swarf). Solutions: starch, 2M nitric acid; 2N sulfuric acid; 2M hydrochloric acid; 2M sodium hydroxide; 2M ammonia; 0.5N and 0.1N copper (II) sulfate; 0.5N potassium iodide; 0.5N sodium thiosulfate; 0.5N sodium sulfite; 0.1N silver nitrate; 0.5M potassium chloride; 0.5M potassium bromide; 0.5N potassium chromate.

Experiment 1. ***Reaction of copper with dilute and concentrated acids.***

Put a piece of copper in each of the three tubes. Add 5–6 drops of ***dilute*** HCl in the first tube. Add 5–6 drops of concentrated H_2SO_4 in the second tube. Add 5–6 drops of concentrated HNO_3 in the third tube. In which of the tubes the solution became blue due to the formation of Cu^{2+} ions?

Repeat the experiment with ***concentrated*** acids. Carefully heat each of the three tubes. Describe your observations.

$Cu + HCl(dilute) \neq$

$Cu + H_2SO_4(dilute) \neq$

$3Cu + 8HNO_3(dilute) = 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$

$Cu + HCl(concentrated) \neq$

$Cu + 2H_2SO_4(\text{concentrated}) \xrightarrow{t} CuSO_4 + 2SO_2\uparrow + 2H_2O$

$Cu + 4HNO_3(\text{concentrated}) = Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$

Experiment 2. ***Production of copper (II) hydroxide, its properties.***

a) *Production of copper (II) hydroxide and its thermal decomposition*.

Add sodium hydroxide into the tube with 3–4 drops of copper (II) sulfate solution in the drop by drop manner. Notice the color of the precipitate. ***Carefully*** heat the tube with the precipitate. Notice the change in color.

$CuSO_4 + 2NaOH = Cu(OH)_2\downarrow + Na_2SO_4$

$Cu(OH)_2 \xrightarrow{t} CuO + H_2O$

b) *Reactions of copper (II) hydroxide with acids and alkalis*

Make copper (II) hydroxide in two tubes. Add 5–6 drops of 2N sulfuric acid solution to the first tube and 5–6 drops of 2M NaOH solution to the second tube.

Notice that precipitate has been dissolved only in the first tube.

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

$Cu(OH)_2\downarrow + NaOH(\text{dilute}) \neq$

Reaction between $Cu(OH)_2$ and alkali is possible only if alkali has very high concentration.

Experiment 3. ***Production of copper (I) iodide.***

Put 3 drops of copper (II) sulfate solution in the tube and add 3 drops of 0.5N potassium iodide solution to that tube. Notice the precipitation and yellow color of the solution. Add a drop of starch solution to the same tube and notice the blue color.

Add 0.5N sodium sulfite solution to the same tube in the drop by drop manner until the disappearance of yellow color. Observe the color of precipitate. Keep the tube for the next experiment.

$2CuSO_4 + 4KI = 2CuI\downarrow + I_2 + 2K_2SO_4$

Balance the redox reaction using electron-ion method.

$I_2 + Na_2SO_3 + H_2O = NaI + Na_2SO_4 + H_2SO_3$

reduction: ____

oxidation: ____

water molecules: ______________________________________

Experiment 4. ***Complex compounds of copper.***

a) *Production of complex copper (II) thiosulfate*

Add several drops of sodium thiosulfate solution into the tube from the experiment № 3. Notice the complete dissolving of the precipitate due to the formation of a complex salt.

$CuI\downarrow + Na_2S_2O_3 = Na[Cu(S_2O_3)_2] + NaI$

b) *Production of copper (II) ammonia complex*

Add 2M ammonia solution into the tube with copper (II) sulfate solution in the drop by drop manner. After first drops insoluble $(CuOH)_2SO_4$ will be formed but then it will be dissolved. Notice the color of the precipitate.

$2CuSO_4 + 2NH_3 + 2H_2O = (CuOH)_2SO_4\downarrow + (NH_4)_2SO_4$

$(CuOH)_2SO_4\downarrow + 8NH_3 = [Cu(NH_3)_4]SO_4 + [Cu(NH_3)_4](OH)_2$

Experiment 5. ***Production of silver (I) oxide.***

Add several drops of 2M sodium hydroxide into the tube with silver nitrate solution. Keep the precipitate for the next experiment. Notice the color of the precipitate.

$2AgNO_3 + 2NaOH = Ag_2O\downarrow + 2NaNO_3 + H_2O$

Experiment 6. ***Insoluble and complex compounds of silver.***

a) *Production of silver (I) ammonia complexes*

Put 2 drops of silver nitrate into each of the four tubes. Add 2 drops of 0.5M potassium chloride into the first tube, 2 drops of 0.5M potassium bromide in the second tube, 2 drops of 0.1M potassium iodide in the third tube, 2 drops of 0.5N potassium chromate in the fourth tube. Notice the colors of precipitates.

$AgNO_3 + KCl = AgCl\downarrow + KNO_3$

$AgNO_3 + KBr = AgBr\downarrow + KNO_3$

$AgNO_3 + KI = AgI\downarrow + KNO_3$

$2AgNO_3 + K_2CrO_4 = Ag_2CrO_4\downarrow + 2KNO_3$;

Add 3 drops of 25 % ammonia solution in each of the four tubes. Notice that in the tube № 3 precipitate has not been dissolved.

$AgCl\downarrow + 2NH_3 = [Ag(NH_3)_2]Cl$

$AgBr\downarrow + 2NH_3 = [Ag(NH_3)_2]Br$

$AgI\downarrow + 2NH_3 \neq$

$Ag_2CrO_4\downarrow + 2NH_3 = [Ag(NH_3)_2]CrO_4$

Constants of solubility are the following.

$K_s\ (AgCl\downarrow) = 1{,}8 \cdot 10^{-10}$

$K_s\ (AgBr\downarrow) = 6{,}0 \cdot 10^{-13}$

$K_s\ (AgI\downarrow) = 1{,}1 \cdot 10^{-16}$

$K_s\ (Ag_2CrO_4\downarrow) = 1{,}1 \cdot 10^{-12}$

b) *Production of a complex silver (I) hydroxide*

Add 2M ammonia solution to the tube left from experiment №5. Notice the dissolving of precipitate due to the formation of diaminesilver (I) hydroxide.

$Ag_2O + 4NH_3 + H_2O = 2[Ag(NH_3)_2]OH$

Write the conclusion: “*AgI did not dissolve in ammonia solution because* ____”

LESSON 8

ELEMENTS FROM GROUP IIB AND THEIR COMPOUNDS

Main topics of the lesson:

1. *Overall description of elements from IIB subgroup.*
2. *Chemical properties of elements from IIB subgroup and their compounds.*
3. *Biological role, the usage in medicine and pharmaceutical analysis of compounds containing elements from IIB subgroup.*

The common electronic configuration of zinc, cadmium and mercury is $ns^2(n\text{-}1)d^{10}$. It is important to state that these elements have completed d-sublevels of their pre-outer layers and 2 s-electrons on their outer layers. Electrons from completed d-sublevel don’t take part in chemical bonds formation. Because of this reason they all can demonstrate oxidation states which are not higher than +2. Zinc and cadmium demonstrate the oxidation state of +2, while mercury can exist in both +1 and +2 oxidation states. Even when the oxidation state of mercury is +1, it demonstrates the valence of II: two Hg^+ cations form covalent nonpolar bond between each other. The structure of mercury (I) chloride, for example, can be described like: “Cl – Hg – Hg – Cl” (figure 4). The ability of mercury to form such cation as Hg_2^{2+} is the consequence of lanthanide contraction: mercury is more prone to form covalent bonds that ionic.

In nature zinc, cadmium and mercury are usually found in form of sulfides. Zinc also can be found in form of carbonate. Metals from IIB subgroup react with oxygen and form oxides. Sulfides are formed in their reactions with sulfur. Interestingly, mercury is able to react with sulfur even at room temperature. At lower temperature mercury forms $HgCl_2$ (corrosive sublimate) with chlorine gas, while at higher temperature Hg_2Cl_2 (calomel) is formed.

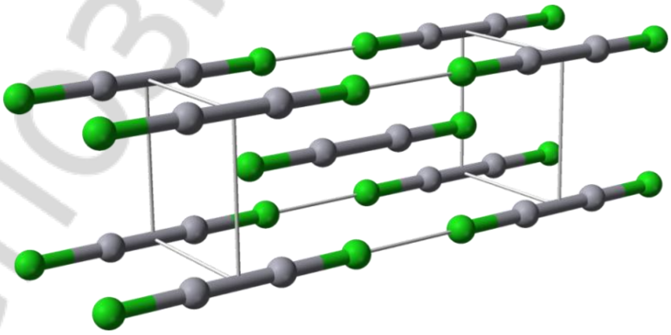


Figure 4. The crystal structure of mercury (I) chloride. Mercury atoms are gray, chlorine atoms are green

Zinc slowly reacts with oxygen and water vapor from the air, as well as with carbon dioxide. As a result, the surface of zinc is covered by its hydroxide and hydroxycarbonate.

$2Zn + O_2 + 2H_2O \rightarrow 2Zn(OH)_2$

$2Zn + O_2 + CO_2 + H_2O \rightarrow (ZnOH)_2CO_3$

Mercury cannot react with water at any temperature, while zinc and cadmium react with H_2O at high temperature in the way similar to other inactive metals.

$Zn + H_2O\ (t°) \rightarrow ZnO + H_2\uparrow$

Zinc and cadmium react with nonoxidizing acids and produce corresponding acids and hydrogen, unlike mercury which cannot be oxidized by H^+ cations.

$Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$

Mercury can react with oxidizing acids (HNO_3 and concentrated H_2SO_4). When nitric acid is taken at high concentration, salts of Hg (II) are formed, while at lower concentration HNO_3 can oxidize mercury just to the state of Hg_2^{2+}.

$Hg + 2H_2SO_{4\ (concentrated)} \rightarrow HgSO_4 + SO_2\uparrow + 2H_2O$

$Hg + 4HNO_{3\ (concentrated)} \rightarrow Hg(NO_3)_2 + 2NO_2\uparrow + 2H_2O$

$6Hg + 8HNO_{3\ (dilute)} \rightarrow 3Hg_2(NO_3)_2 + 2NO\uparrow + 4H_2O$

Zinc can be easily dissolved in alkali.

$Zn + 2H_2O + 2OH^– \rightarrow [Zn(OH)_4]^{2–} + H_2\uparrow$

Moreover, that metal can be dissolved in the water solution of ammonia.

$Zn + 4NH_3 + 2H_2O \rightarrow [Zn(NH_3)_4](OH)_2 + H_2\uparrow$

Zinc oxide and hydroxide are amphoteric: they can react with both acids and bases.

$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$

$ZnO + 2OH^– + H_2O$ (in water solution of alkali) $\rightarrow [Zn(OH)_4]^{2–}$

$ZnO + 2NaOH$ (with solid alkali at high temperature) $\rightarrow Na_2ZnO_2 + H_2O$

$Zn(OH)_2 + 2H^+ \rightarrow Zn^{2+} + 2H_2O$

$Zn(OH)_2 + 2OH^–$ (in water solution of alkali) $\rightarrow [Zn(OH)_4]^{2–}$

$Zn(OH)_2 + 2NaOH$ (with solid alkali at high temperature) $\rightarrow Na_2ZnO_2 + 2H_2O$

Cadmium hydroxide shows weaker amphoteric properties than zinc hydroxide. Reaction between $Cd(OH)_2$ and alkali is possible only if the alkali solution is concentrated enough. Cadmium oxide cannot react with alkali of any concentration. Reaction between solid alkali and cadmium hydroxide is possible at high temperature.

$Cd(OH)_2 + 4NaOH$ (in water solution of concentrated alkali) $\rightarrow Na_4[Cd(OH)_6]$

$Cd(OH)_2 + 4KOH$ (with solid alkali at high temperature) $\rightarrow K_2CdO_2 + 2H_2O$

Zinc and cadmium hydroxides can be thermally decomposed into oxides and water. Mercury hydroxide is instable: it decomposes right after the moment of its formation. Mercury oxides are decomposed at high temperature.

In complex compounds Zn^{2+} has coordination number of 4, Cd^{2+} has coordination number of 6, while mercury can demonstrate both 4 and 6.

Mercury can form complexes with ammonia only in the presence of ammonium salts. Otherwise mercury amidochloride ($HgNH_2Cl$) will be formed.

Complexes of mercury and halide ions are especially stable.

$HgS\downarrow + 4KI \rightarrow K_2[HgI_4] + K_2S$

Many binary compounds of mercury are rather molecules then ionic compounds. This is the consequence of the high electronegativity of mercury.

Compounds of mercury (I) are prone to disproportioning.

$Hg_2Cl_2 \rightarrow HgCl_2 + Hg$

They can act as both reducers and oxidizers.

$2Hg_2(NO_3)_2 + O_2 + 4HNO_3 \rightarrow 4Hg(NO_3)_2 + 2H_2O$

$Hg_2(NO_3)_2 + Zn \rightarrow Zn(NO_3)_2 + 2Hg\downarrow$

Calomel can be produced from $HgCl_2$ in the reaction with $H_2[SnCl_4]$.

$2HgCl_2 + H_2[SnCl_4] \rightarrow Hg_2Cl_2 + H_2[SnCl_6]$

Zinc plays important roles in biochemical processes. For example, it acts as a co-factor for carbonic anhydrase, alcohol dehydrogenase and carboxypeptidase.

Zinc cations are also necessary for numerous transcription factors which have a specific motif entitled “Zinc finger”. That motif contains cysteine and histidine residues which coordinate Zn^{2+} cation by sulfur and nitrogen atoms, respectively. However, the percentage of coordination spheres for zinc binding similar to zinc finger (those with cysteine residues) is equal to 35.51 %. Other binding sites for Zn^{2+} include aspartic and glutamic acid residues together with histidine.

Cadmium and mercury cations are able to replace zinc cations in their binding sites on numerous proteins. Cadmium and mercury cations oxidize –SH groups instead of forming coordination bonds with them. Because of this cadmium and mercury compounds are highly toxic. Nowadays mercury compounds are not used in medicine.

Zinc oxide, sulfate and chloride are used in medicine as antiseptic agents.

Nessler’s reagent is used in pharmaceutical analysis to detect ammonia in the solution. Yellow or brown precipitate is formed in this reaction.

$NH_4^+ + 2[HgI_4]^{2-} + 4OH^- \rightarrow HgO{\cdot}Hg(NH_2)I\downarrow + 7I^- + 3H_2O$

The sensitivity of this test is about 0.3 μg of NH_3 in 2 μL.

Chains of chemical reactions

$Zn(OH)_2 \rightarrow Zn \rightarrow ZnOHNO_3 \rightarrow K_2ZnO_2 \rightarrow Zn(OH)_2$

$Na_2[Zn(OH)_4] \rightarrow ZnO \rightarrow (ZnOH)_2SO_4 \rightarrow Zn \rightarrow Na_2ZnO_2$

$CdSO_4 \rightarrow Cd \rightarrow [Cd(NH_3)_6]SO_4 \rightarrow CdS \rightarrow Cd(OH)_2$

$Hg \rightarrow HgSO_4 \rightarrow HgCl_2 \rightarrow K_2[HgI_4] \rightarrow HgS$

Redox reactions

$Zn + HNO_3$ (dilute) →

Reduction:

Oxidation:

Water molecules:

$Cd + H_2SO_4$(con.) $\xrightarrow{t}$

Reduction:

Oxidation:

Water molecules:

Reactions with complex compounds

$Zn + KOH + H_2O \rightarrow$

$K_2[Zn(OH)_4] + CO_2 \rightarrow$

$Zn(OH)_2 + NH_3 \rightarrow$

$CdCl_2 + NH_4I$(excess) →

$Hg + HCl + HNO_3 \rightarrow$

$Hg(NO_3)_2 + KI$(excess) →

Reactions during the fusion

$ZnO + NaOH \xrightarrow{t}$

$ZnO + K_2CO_3 \xrightarrow{t}$

Problems

1. Calculate the minimal mass of zinc which is added to 100 g of sulfuric acid solution with a mass fraction equal to 19.6 % to obtain zinc sulfate solution. H_2S is a subproduct of this reaction. What is the mass fraction of the salt in the final solution?

2. A mixture of zinc oxide and zinc sulfide weighing 33.15 g was put into 200 g of hydrochloric acid solution with an excess of HCl. A solution of zinc salt with a mass fraction equal to 21.35 % was obtained. Calculate mass fractions of zinc oxide and zinc sulfide in the initial mixture.

3. A mixture of zinc and cadmium was dissolved in a dilute solution of sulfuric acid. A gas with a volume of 6.72 L was produced. In the obtained solution there was a mixture of zinc sulfate and cadmium sulfate with the total mass equal to 53.00 g. Calculate the mass of initial mixture.

Multiple choice questions

1. Indicate the elements whose atoms have constant oxidation state in their compounds:

a) Zn and Fe; b) Zn and Hg; c) Zn and Cd; d) Zn and Be.

2. Indicate the number of electrons in the pre-outer electron level of cadmium atom in the ground state:

a) 2; b) 18; c) 8; d) 6.

3. Which types of chemical bonds may exist in mercury salts?

a) metallic; b) covalent; c) ionic.

4. Which interaction corresponds to the short ionic equation $Cd^{2+} + S^{2-} = CdS$?

a) Cd and S; c) $Cd(OH)_2$ and K_2S (solution);

b) $Cd(OH)_2$ and H_2SO_4 (solution); d) $CdSO_4$ and Na_2S (solution).

5. Plates of gold, silver and zinc are kept in the copper sulfate solution. Where the red precipitate will be formed?

a) on the gold and silver plates; c) on the gold and zinc plates;

b) only on the zinc plate; d) on the zinc and silver plates.

6. Which reactions are impossible?

a) $Zn + HCl$ (solution) $\rightarrow ZnCl_2 + H_2$;

b) $Hg + HCl$ (solution) $\rightarrow HgCl_2 + H_2$;

c) $Zn + H_2SO_4$ (conc.) $\rightarrow ZnSO_4 + H_2$;

d) $Cd + H_2SO_4$ (dilute) $\rightarrow CdSO_4 + H_2$;

e) $Zn + MgSO_4$ (sol.) $\rightarrow ZnSO_4 + Mg$;

f) $Cd + CuSO_4$ (solution) $\rightarrow CdSO_4 + Cu$.

7. Me_2ZnO_2 salt is formed as a product of the reactions between:

a) Zn and $Ca(OH)_2$ (solid), (t^0);
b) ZnO and KOH (solid), (t^0);
c) $Zn(OH)_2$ and NaOH (solution);
d) $Zn(OH)_2$ and KOH (solid), (t^0).

8. Calculate the sum of the coefficients in the short ionic equation of the reaction between 0.1 mole of $K_2[Zn(OH)_4]$ solution and 0.2 mole of HNO_3 solution.

a) 9; b) 11; c) 6; d) 5.

9. 0.92 g of sodium is completely dissolved in 1.36 g of $ZnCl_2$ solution. Which product is obtained?

a) 0.01 mole of Na_2ZnO_2;
b) 0.01 mole of $Zn(OH)_2$;
c) 0.04 mole of $Na_2[Zn(OH)_4]$;
d) 0.01 mole of $Na_2[Zn(OH)_4]$.

10. The chain is given: ZnO (+KOH (solution, in excess)) → A (+HNO_3 (in excess)) → → B (t°) → C (+$Ba(OH)_2$ (solid), t°) → D. Calculate the sum of molar masses (g/mol) of zinc containing substances B and D.

a) 423; b) 288; c) 333; d) 380.

EXPERIMENTAL WORK

“CHEMICAL PROPERTIES OF COMPOUNDS CONTAINING ELEMENTS FROM IIB GROUP”

The aim of the work: to study chemical properties of the elements from IIB group, and their compounds.

Reactants: zinc (powder and granules); litmus (neutral solution); zinc sulfate; cadmium sulfate. Solutions: sulfuric acid (2N and concentrated one with the density equal to 1.84 g/ml); 1M hydrochloric acid; 2M sodium hydroxide; 2N ammonia; 2N cadmium sulfate; 2N zinc sulfate; ammonium sulfate (concentrated); 0.1M potassium permanganate; 0.1M potassium dichromate.

Experiment 1. ***The dissolving of zinc in acids and bases.***

Pour 4–5 drops of 2N sulfuric acid into the tube and add 1 small spoon of zinc powder, then heat it up. Repeat the same experiment with concentrated acid and notice a specific smell of sulfur dioxide.

Which reaction happened in the tube № 1, which reaction happened in the tube № 2?

$Zn + H_2SO_4(dilute) \rightarrow ZnSO_4 + H_2\uparrow$

$4Zn + 5H_2SO_4(average\ concentration) \rightarrow 4ZnSO_4 + H_2S\uparrow + 4H_2O$

$Zn + 2H_2SO_4(concentrated) \rightarrow ZnSO_4 + SO_2\uparrow + 2H_2O$

Experiment 2. ***Reductive properties of zinc.***

Put granules of zinc in the tube with acidic potassium permanganate solution and in the tube with acidic potassium dichromate solution. Notice the changes in color for each tube.

Balance the redox reactions using electron-ion method.

$Zn + KMnO_4 + H_2SO_4 \rightarrow ZnSO_4 + MnSO_4 + H_2O + K_2SO_4$

reduction: ____

oxidation: ____

water molecules: ______________________________________

$Zn + K_2Cr_2O_7 + H_2SO_4 \rightarrow ZnSO_4 + Cr_2(SO_4)_3 + H_2O + K_2SO_4$

reduction: ____

oxidation: ____

water molecules: ______________________________________

$Zn + Cr_2(SO_4)_3 \xrightarrow{pH<7} ZnSO_4 + CrSO_4$

reduction: ____

oxidation: ____

Experiment 3. ***Zinc hydroxide and cadmium hydroxide, their properties.***

Pour 3–4 drops of zinc sulfate in one tube and 3–4 drops of cadmium sulfate in the second tube. Add 2M sodium hydroxide solution in each of the tubes in the drop by drop manner until white precipitate will appear.

$ZnSO_4 + 2NaOH \rightarrow Zn(OH)_2\downarrow + Na_2SO_4$

Write this reaction in ionic form:

$CdSO_4 + 2NaOH \rightarrow Cd(OH)_2\downarrow + Na_2SO_4$

Write this reaction in ionic form:

Add sodium hydroxide solution in the first tube until the precipitate will be dissolved.

$Zn(OH)_2\downarrow + 2NaOH \rightarrow Na_2[Zn(OH)_4]$

Try to repeat this experiment with the second tube and notice that cadmium hydroxide cannot be dissolved in dilute sodium hydroxide solution.

$Cd(OH)_2\downarrow + NaOH(dilute) \neq$

Experiment 4. ***Zinc and cadmium sulfides.***

Pour 3–4 drops of zinc sulfate solution in the first tube and 3–4 drops of cadmium sulfate solution in the second tube. Add 2–3 drops of concentrated ammonium sulfide solution in each of the tubes. Notice the color of each precipitate.

$ZnSO_4 + (NH_4)_2S \rightarrow ZnS\downarrow + (NH_4)_2SO_4$

Write this reaction in ionic form:

$CdSO_4 + (NH_4)_2S \rightarrow CdS\downarrow + (NH_4)_2SO_4$

Write this reaction in ionic form:

Add several drops of hydrochloric acid solution to each of the two tubes.

$ZnS\downarrow + 2HCl \rightarrow ZnCl_2 + H_2S\uparrow$

Write this reaction in ionic form:

____

$CdS\downarrow + 2HCl \rightarrow CdCl_2 + H_2S\uparrow$

Write this reaction in ionic form:

____

Solubility constants for zinc and cadmium sulfides are as follows:

$K_s(ZnS) = 1.6 \cdot 10^{-24}$

$K_s(CdS) = 7.9 \cdot 10^{-27}$

Why ZnS reacts with HCl faster than CdS?

____

Experiment 5. ***Hydrolysis of zinc and cadmium salts.***

Put several crystals of zinc sulfate in the first tube and several crystals of cadmium sulfate in the second tube. Dissolve each of these salts in 2 drops of water. Add 2–3 drops of litmus in each tube and heat them. Use the third tube as a control (put just drops of water in that tube). Notice the color of litmus in each of the three tubes.

Write the equation of the first step of hydrolysis for $ZnSO_4$

Complete form: ____

Short ionic form: ____

Write the equation of the first step of hydrolysis for $CdSO_4$

Complete form: ____

Short ionic form: ____

Experiment 6. ***Complex compounds of zinc and cadmium.***

Put 1 drop of zinc sulfate solution in the tube and add 2 drops of 2M ammonia solution to that tube. Notice the precipitate.

$ZnSO_4 + 2NH_3 \cdot H_2O \rightarrow Zn(OH)_2\downarrow + (NH_4)_2SO_4$

Add more ammonia solution to the tube and notice the dissolving of the precipitate.

$Zn(OH)_2 + 4NH_3 \cdot H_2O \rightarrow [Zn(NH_3)_4](OH)_2 + 4H_2O$

$Zn(OH)_2$ can be dissolved in ammonium solution, unlike $Al(OH)_3$.

The constant of instability for the complex ion can be written like this:

$[Zn(NH_3)_4]^{2+} \rightleftarrows Zn^{2+} + 4NH_3$

$$K_I([Zn(NH_3)_4]^{2+}) = \frac{[Zn^{2+}][NH_3]^4}{[Zn(NH_3)_4]^{2+}}$$

$Cd(OH)_2$ cannot be dissolved in ammonia solution.

Conclusion: *“Amphoteric properties of $Cd(OH)_2$ are ______________________ than those of $Zn(OH)_2$”*

LESSON 9

COLLOQUIUM ON THE CHEMICAL PROPERTIES OF ELEMENTS FROM s- AND d-BLOCKS OF THE PERIODIC SYSTEM

Main types of tasks:

1. *Chains of chemical reactions.*
2. *Reactions with complex compounds.*
3. *Hydrolysis reactions.*
4. *Redox reactions.*
5. *Short ionic equations.*
6. *Problems.*
7. *Theoretical questions.*

LESSON 10

ELEMENTS FROM GROUP IIIA AND THEIR COMPOUNDS

Main topics of the lesson:

1. *Overall description of elements from IIIA subgroup.*
2. *Chemical properties of boron and its compounds.*
3. *Chemical properties of aluminum and its compounds.*
4. *Biological role, the usage in medicine and pharmaceutical analysis of compounds containing elements from IIIA subgroup.*

The common electronic configuration for elements from IIIA group is ns^2np^1. So, there are 3 electrons and 4 (for boron) or 9 (for aluminum, gallium, zinc, indium and thallium) electron orbitals on their outer layers. This situation is called electron deficiency. Empty electron orbitals are frequently used by boron and aluminum for making covalent donor-acceptor bonds. Atomic radius of aluminum is higher than that for boron, while the atomic radius of gallium is lower than that for aluminum. This phenomenon is usually explained by d-contraction. Indeed, gallium has already completed d-sublevel of the third layer. It is known that d-orbitals shield the positive charge of nucleus worse than s- and p-orbitals. Because of this reason valence electrons of gallium are attracted to the nucleus even stronger than those of aluminum.

Main minerals of boron are borax ($Na_2B_4O_7{\cdot}10H_2O$) and sassolite (H_3BO_3). Boron also forms diamond-like compound with nitrogen (BN). Boron cannot be found in nature as a pure chemical element. One of the ways to produce it includes reaction between borax and sulfuric acid in which weak boric acid is formed. Boric acid then is thermally decomposed into boron oxide and water. Boron oxide reacts with magnesium and produces pure boron and magnesium oxide.

Boron cannot react with hydrogen, even so there are numerous compounds made from boron and hydrogen known under the common name “boranes”. Boron reacts with nitrogen, oxygen, sulfur and halogens producing nitride, oxide, sulfide and halides, respectively. Halides of boron have a planar structure: boron exists in the sp^2 hybridization state with one empty p-orbital.

Boron reacts with water only at high temperature. In that reaction boron oxide and hydrogen are formed. Boron cannot react with hydrogen halides. With oxidizing acids boron forms boric acid.

$2B + 3H_2SO_{4\ (concentrated)} \rightarrow 2H_3BO_3 + 3SO_2\uparrow$

$2B + 6HNO_{3\ (concentrated)} \rightarrow 2H_3BO_3 + 6NO_2\uparrow$

Boron reacts with concentrated alkali and with solid alkali at high temperature in the presence of oxygen, and forms metaborates.

$2B + 2KOH_{\ (concentrated)} + 2H_2O \rightarrow 2KBO_2 + 3H_2\uparrow$

$4B + 4NaOH_{\ (solid)} + 3O_2\ (t°) \rightarrow 4NaBO_2 + 2H_2O$

Boron forms numerous different binary compounds with metals which are mostly nonstoichiometric. These borides of metals can react with acids and form different boranes.

$6MgB_2 + 12HCl \rightarrow H_2 + B_4H_{10} + 6MgCl_2 + 8B$

Boranes may be described by the common formulas like B_nH_{n+4} and B_nH_{n+6}. Diborane and tetraborane are gases in normal conditions. The structure of diborane (and other boranes) contains specific type of covalent bonds which are called “banana bonds” (figure 5). Actually, the ring made from two boron and two hydrogen atoms (a characteristic part of the structure of boranes) is kept together by just four electrons (instead of eight). Hydrogen is more electronegative than boron. So, hydrogen completes its outer shell with one electron from one of the two boron atoms and that pair of electrons makes a donor-acceptor bond with empty p-orbital of another boron atom.

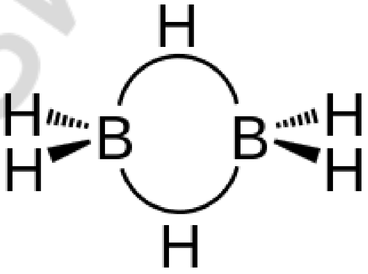


Figure 5. Schematic structure of diborane. “Banana bonds” are shown by curved lines

The products of the combustion of boranes are boron oxide and water. Diborane can react with water and form boric acid and hydrogen.

$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2\uparrow$

Halides of boron can react with water and form boric acid and hydrogen halides.

$BF_3 + 3H_2O \rightarrow H_3BO_3 + 3HF$

Namely, hydrogen fluoride can then react with boron fluoride and form a complex compound: tetrafluoroboride of hydrogen.

$BF_3 + HF \rightarrow H[BF_4]$

Boric acid is not a real Arrhenius acid which dissociates into H^+ and an anion. Instead of this, H_3BO_3 forms $[B(OH)_4]^-$ complex with OH- ions. In this process an empty orbital of boron plays a main role. As a result, an excess of H^+ ions occurs in the water solution.

Boric acid reacts with alkali solutions forming tetraborates.

$4H_3BO_3 + 2NaOH + 3H_2O \rightarrow Na_2B_4O_7 \cdot 10H_2O$

That acid is also able to form ethers with alcohols. Such ethers can be burnt down with a green cool flame.

$B(OH)_3 + 3C_2H_5OH \rightarrow B(OC_2H_5)_3 + 3H_2O$

Boric acid is used as antiseptic in medicine. However, its usage is not recommended for children and pregnant women.

Sodium tetraborate decahydrate (borax) is used as a primary standard for acids in acid-base titration. Indeed, borax has a regular structure that stays the same during long period of time. The reaction between HCl and $Na_2B_4O_7$ includes initial hydrolysis of borax.

$Na_2B_4O_7 + 7H_2O \rightleftarrows 2NaOH + 4H_3BO_3$

$2NaOH + 2HCl \rightarrow 2NaCI + 2H_2O$

The resulting reaction is written below.

$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3$

Aluminum is widespread in the Earth crust. Among numerous minerals we can mention bauxite ($nAl_2O_3{\cdot}mH_2O$), sapphire (Al_2O_3) and ruby (Al_2O_3).

Aluminum cannot react with hydrogen (as well as boron), but it reacts with oxygen, sulfur, halogens, nitrogen, phosphorus and carbon. The surface of aluminum is covered by its own oxide. The oxide protects aluminum from further oxidation and from reaction with water. However, that passivation layer cannot protect aluminum from acids and bases.

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

$Al_2O_3 + 2KOH + 3H_2O \rightarrow 2K[Al(OH)_4]$

When thin protective layer is removed, aluminum starts its reaction with water that is similar to the reaction between active metals and H_2O.

$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2\uparrow$

Resulting reaction with hydrochloric acid is written below.

$2Al + 6HCl + 12H_2O \rightarrow 2[Al(H_2O)_6]Cl_3 + 3H_2\uparrow$

Resulting reaction with potassium hydroxide produces not aquatic, but hydroxyl complex of Al^{3+} cation.

$2Al + 6KOH + 6H_2O \rightarrow 2K_3[Al(OH)_6] + 3H_2\uparrow$

Aluminum is prone to form numerous complex compounds.

$AlF_3 + 3NaF \rightarrow Na_3[AlF_6]$

$AlCl_3 + NaCl \rightarrow Na[AlCl_4]$

Just like boron, aluminum is prone to form banana bonds. For example, aluminum chloride (if it is not dissolved in water) and aluminum hydride are not ionic compounds, but molecules with formulas Al_2Cl_6 and Al_2H_6, respectively.

When solid aluminum and sodium hydroxides are heated together, sodium metaaluminate ($NaAlO_2$) and water are formed.

$Al(OH)_3(solid) + NaOH(solid) \rightarrow NaAlO_2 + 2H_2O$

When aluminum hydroxide is added to the water solution of alkali, a complex salt will be formed. If the ratio between $Al(OH)_3$ and NaOH is equal to 1 : 1, the resulting complex salt will be $Na[Al(OH)_4]$ — sodium tetrahydroxyaluminate.

$Al(OH)_3 + NaOH \rightarrow Na[Al(OH)_4]$

If the ratio between $Al(OH)_3$ and NaOH is 1 : 3, then resulting complex salt will be $Na_3[Al(OH)_6]$ — sodium hexahydroxyaluminate.

$Al(OH)_3 + 3NaOH \rightarrow Na_3[Al(OH)_6]$

Aluminum hydride cannot be produced directly from aluminum and hydrogen. Aluminum chloride first forms complex compound with lithium hydride. Then resulting complex reacts with the excess of aluminum chloride.

$4LiH + AlCl_3 \rightarrow Li[AlH_4] + 3LiCl$

$3Li[AlH_4] + AlCl_3 \rightarrow 4AlH_3 + 3LiCl$

Aluminum is resistant to concentrated cold solutions of nitric and sulfuric acids, as well as to cold acetic and phosphoric acids.

Aluminum is able to reduce the most of metals from their oxides.

$8Al + 3Fe_3O_4 \rightarrow 4Al_2O_3 + 9Fe$

Among aluminum salts we can mention potassium alum: the double salt (sulfate) of potassium and aluminum. This salt $KAl(SO_4)_2 \cdot 12H_2O$ is used in medicine as an antiseptic.

Insoluble aluminum compounds are used as adjuvants for vaccines. Such compounds as aluminum hydroxide, aluminum hydroxophosphate and hydroxophosphate-sulfate of aluminum form gels which bind antigens. This binding helps to increase the time of the contact between an antigen and immune system. As a result, the quality of the immune response becomes better.

Chains of chemical reactions

$B \rightarrow Mg_3B_2 \rightarrow B_2H_6 \rightarrow B_2O_3 \rightarrow Na_2B_4O_7$

____

____

____

____

$Na_3[Al(OH)_6] \rightarrow Al_2(SO_4)_3 \rightarrow Al_2O_3 \rightarrow Al(OH)_3 \rightarrow Al_2O_3$

$Al \rightarrow Na[Al(OH)_4] \rightarrow Al_2O_3 \rightarrow [Al(OH)_2]_2SO_4 \rightarrow AlCl_3$

$B_2O_3 \rightarrow B \rightarrow H_3BO_3 \rightarrow Na_2B_4O_7 \rightarrow B(OH)_3 \rightarrow B(OC_2H_5)_3$

Finish chemical reactions

$B + HNO_3$(con.) →

$B_2H_6 + NaH \rightarrow$

$Na_3[Al(OH)_6] + CO_2 \rightarrow$

$Na[Al(OH)_4(H_2O)_2] \xrightarrow{t}$

$Al_2S_3 + H_2O + KOH$(in excess) →

$Na_2B_4O_7 + H_2SO_4 + H_2O \rightarrow$

$H_3BO_3 + NaOH \rightarrow$

$K_3AlO_3 + HNO_3$(in excess) →

Problems

1. A mixture of aluminum and aluminum sulfide was divided into two equal parts. Upon reaction of the first part of the mixture with water, 0.672 L of a gas was obtained. Upon reaction of the other part of the mixture with hydrogen chloride solution taken in excess, 1.344 L of a gas mixture was obtained. Calculate the mass of the initial mixture and mass fractions of its components.

2. 1 L of a solution, used for houseplants fertilizing, contains boron weighing $5 \cdot 10^{-4}$ g. Calculate the mass of the salt $Na_2B_4O_7 \cdot 10H_2O$ which is necessary for preparation of 10 L of such a solution.

3. Amorphous boron weighing 20 g reacts with 50 ml of nitric acid solution with mass fraction of the acid equal to 65 % (ρ = 1.4 g/ml). What amount of boric acid can be obtained, if HNO_3 is reduced to NO?

4. A solution containing 14 g of NaOH was added to a solution containing 13.35 g of $AlCl_3$. What is the mass of produced precipitate?

Multiple choice questions

1. Which solution can not be boiled in an aluminum vessel?

a) $NaNO_3$; b) $Hg(NO_3)_2$; c) Na_2CO_3; d) KCl.

2. Which compound is produced if boron reacts with concentrated nitric acid?

a) $B(NO_3)_3$; b) B_2O_3; c) $H_2B_4O_7$; d) H_3BO_3.

3. Indicate the number of substances both aluminum and aluminum oxide react with: hydrogen, sodium hydroxide, water, calcium oxide, concentrated nitric acid, carbon dioxide, concentrated sulphuric acid, calcium hydroxide:

a) 4; b) 8; c) 3; d) 6.

4. Choose the pairs of the reaction schemes in which both chemical transformations produce aluminum hydroxide:

a) $Al_2(SO_4)_3 + H_2O \rightarrow$ and $Al_4C_3 + H_2O \rightarrow$
b) $Al_2S_3 + H_2O \rightarrow$ and Al (amalgam) + $H_2O \rightarrow$
c) $AlCl_3 + Na_2CO_3 \rightarrow$ and $Na_3[Al(OH)_6] + 3HCl \rightarrow$
d) $Al_2O_3 + H_2O \rightarrow$ and $AlCl_3 + NH_3 \cdot H_2O \rightarrow$

5. Choose the correct statements:

a) all the highest oxides and hydroxides of IIIA group elements are amphoteric and insoluble in water;

b) both aluminum hydroxide and tin (II) hydroxide dissociate stepwise in water forming only hydroxide ions as anions;

c) for a more complete aluminum hydroxide precipitation from water solutions of salts, it’s better to use ammonium hydroxide solution, not alkaline solutions;

d) of the metals belonging to the p-electron family, only IIIA group metals form oxides E_2O_3.

6. Indicate the number of characteristics, which correctly describe the properties of pure aluminum:

1) it’s the most abundant metal in the Earth’s crust;

2) it belongs to p-electron family;

3) both corundum and silicon carbide contain aluminum;

4) it has a constant oxidation state in its compounds;

5) it’s a light metal;

6) it has lower ionization energy than magnesium and barium;

7) it’s a corrosion-resistant metal with good electrical conductivity;

8) aluminum is used for producing amalgam.

a) 3; b) 4; c) 5; d) 6.

7. Which two substances interact with each other?

a) $Al(OH)_3$ and KNO_3;

b) B_2O_3 and H_2O;

c) $NaAlO_2$ and HNO_3;

d) $B(OH)_3$ and NaOH.

8. Which substances does diborane react with in certain conditions?

a) O_2; b) $KMnO_4$; c) H_2O; d) NaH.

9. Which substances are formed if boron oxide is fused with alkalis?

a) KBO_2; b) $NaBO_2$; c) K_3BO_3; d) $NaBO_3$.

10. Aluminum reacts with magnetite and produces 1 mole of iron. What is the mass of obtained aluminum oxide?

a) 51; b) 5.1; c) 45.3; d) 43.5.

EXPERIMENTAL WORK
“CHEMICAL PROPERTIES OF COMPOUNDS CONTAINING ELEMENTS FROM IIIA GROUP”

The aim of the work: to study chemical properties of compounds containing elements from IIIA group.

Reactants: Boric acid, sodium chloride, potassium iodide, silver nitrate, aluminum chloride, aluminum sulfate. Solutions of borax (concentrated), boric acid, 0.5M sulfuric acid, 0.1M ammonia, ethanol, litmus (neutral solution), silver nitrate, copper sulfate, ammonium sulfide, sodium hydroxide.

Experiment 1. ***Production of orthoboric acid.***

Add 2–3 drops of concentrated sulfuric acid in the tube with 5–6 drops of hot concentrated borax solution $Na_2B_4O_7 \cdot 10H_2O$ (rub the walls of the tube by a glass stick). Notice the formation of orthoboric acid crystals.

$2Na_2B_4O_7 + H_2SO_4 + 12H_2O \rightarrow 8H_3BO_3\downarrow + Na_2SO_4 + 2NaOH$

Experiment 2. ***Production and burning of triethyl borate.***

Put several crystals of boric acid in the porcelain cap and add 2–3 drops of concentrated sulfuric acid (density is 1.84 g/ml) together with 10–15 drops of ethanol. Mix the solution by a glass stick and then burn it. Notice the color of the flame.

$H_3BO_3 + 3C_2H_5OH \rightarrow B(OC_2H_5)_3 + 3H_2O$

What is the role of sulfuric acid in this reaction?

Experiment 3. ***Production of insoluble borates.***

Add 3–4 drops of concentrated borax ($Na_2B_4O_7$) solution in the tube with silver nitrate solution and in the tube with aluminum sulfate solution.

$Na_2B_4O_7 + 2AgNO_3 + 3H_2O \rightarrow 2H_3BO_3 + 2AgBO_2\downarrow + 2NaNO_3$

$Na_2B_4O_7 + CuSO_4 + 5H_2O \rightarrow 3H_3BO_3 + CuOHBO_2\downarrow + 2Na_2SO_4$

$3Na_2B_4O_7 + Al_2(SO_4)_3 + 21H_2O \rightarrow 12H_3BO_3 + 2Al(OH)_3\downarrow + 3Na_2SO_4$

In the first tube there is silver metaborate precipitate, in the second tube there is copper hydroxyborate precipitate, and aluminum hydroxide is the precipitate from the third tube.

Experiment 4. ***Production and properties of aluminum.***

Make aluminum hydroxide precipitate in two tubes (mix 2–3 drops of aluminum salt solution with 2–3 drops of 2M sodium hydroxide solution). Add 3–5 drops of 2M hydrochloric acid solution to the first tube and 3–5 drops of 2M sodium hydroxide solution to the second one.

$AlCl_3 + 3NaOH \rightarrow Al(OH)_3\downarrow + 3NaCl$

Write this reaction in ionic form:

$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$

Write this reaction in ionic form:

____

$Al(OH)_3 + 3NaOH \rightarrow Na_3[Al(OH)_6]$

Write this reaction in ionic form:

____

Experiment 5. ***Hydrolysis of aluminum salts.***

a) Put several crystals of aluminum chloride in the first tube and several crystals of aluminum sulfate in the second tube. Dissolve each of these salts in 2 drops of water. Add 2–3 drops of litmus in each tube. Use the third tube as a control (put just drops of water in that tube). Notice the color of litmus in each of the three tubes.

Write the equation of the first step of hydrolysis for $AlCl_3$

Complete form:____

Short ionic form:____

Write the equation of the first step of hydrolysis for $Al_2(SO_4)_3$

Complete form:____

Short ionic form:____

b) Mix two solutions together: aluminum sulfate and ammonium sulfide. Notice the release of hydrogen sulfide (sense the smell) and the formation of insoluble aluminum hydroxide.

Write the equation of the first step of hydrolysis for $(NH_4)_2S$

Complete form:____

Short ionic form:____

The processes proceed to the end.

$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2SO_4$

$(NH_4)_2S + 2H_2O \rightarrow H_2S\uparrow + 2NH_4OH$

Write the conclusion: *“Chemical properties of boron containing compounds are* ________________________________ *the properties of aluminum containing compounds”.*

LESSONS 11–12
ELEMENTS FROM GROUP IVA AND THEIR COMPOUNDS

Main topics of the lessons:

1. *Overall description of elements from IVA subgroup.*
2. *Chemical properties of carbon and its inorganic compounds.*
3. *Chemical properties of silicon and its compounds.*
4. *Chemical properties of germanium, tin and lead.*
5. *Biological role, the usage in medicine and pharmaceutical analysis of compounds containing elements from IVA subgroup.*

The common electronic configuration for elements from IVA group is ns^2np^2. In that subgroup one can find both nonmetals (carbon and silicon) and metals (germanium, tin and lead). Germanium, just like gallium from IIIA subgroup, is an exceptional element with consequences of d-contraction (its electronegativity is higher than that for silicon).

Carbon can be found in nature as a main component of living organisms, as well as in form of minerals such as limestone ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$). These minerals are (partially) the products of degradation of ancient living organisms (mollusks). The other types of the remains of ancient organisms are: coal (from plants), natural oil and gas (from animals). Moreover, atoms of carbon can be found in carbon dioxide produced by living organisms.

There are several allotropic modifications of carbon. The best known ones are graphite and diamond. Diamond is the hardest naturally occurring material known, while graphite is soft enough to form a streak on paper (that is why it is used in pencils).

Electron orbitals of carbon atoms in diamond are in the state of sp^3 hybridization. Each carbon atom makes four identical bonds to other atoms. In graphite each carbon atom makes three bonds to other atoms. Each layer of graphite is the combination of numerous planar hexagons in which electron orbitals of carbon atoms exist in the state of sp^2 hybridization. The bonds between those layers are much weaker than the bonds within layers. There are numerous artificial allotropic modifications of carbon. The most of them are based on carbon hexagons (graphite-like ones) arranged as football (soccer) balls, as tubes (nanotubes), spheres or ellipsoids. Their common name is fullerenes. In carbyne (linear acetylenic carbon) there are alternating single and triple bonds $(-C{\equiv}C-C{\equiv}C-)_n$. So, electron orbitals in carbon atoms from carbyne are in sp^1 hybridization state.

The most reactive forms of carbon are amorphous soot and coal. Carbon in form of soot is used in metallurgy with the aim to produce metals from their oxides.

$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO\uparrow$

$CuO + C \rightarrow Cu + CO\uparrow$

In case with calcium the final product of this process is carbide.

$3C + CaO \rightarrow CaC_2 + CO$

Carbides of metals can be divided into several groups according to the product of their hydrolysis. For example, methanides (like Al_4C_3) produce methane, while acetylides (like CaC_2) produce acetylene.

$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3\downarrow + 3CH_4\uparrow$

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow$

Soot also reacts with concentrated sulfuric and nitric acids.

$C + 2H_2SO_{4\ (concentrated)} \rightarrow CO_2\uparrow + 2SO_2\uparrow + 2H_2O$

$C + 4HNO_{3\ (concentrated)} \rightarrow CO_2\uparrow + 4NO_2\uparrow + 2H_2O$

Carbon reacts with oxygen and forms carbon dioxide. Then CO_2 can react with the excess of carbon and form carbon monoxide. Normally CO reacts with oxygen, while when the amount of oxygen is limited, this reaction doesn't work well.

Carbon monoxide is the molecule with a triple bond: two bonds between carbon and oxygen are made by the way of electron sharing; while the third one is made by the way of donor-acceptor mechanism (oxygen is the donor of electron pair). CO is a good ligand in complex compounds. Indeed, it makes strong bonds with hemoglobin and produce carboxyhemoglobin. Oxygen is unable to replace CO in the carboxyhemoglobin, so the transport of oxygen to body tissues fails.

CO is a neutral oxide that cannot form salts. In chemical reactions it usually plays a role of reducer.

$Ag_2O + CO \rightarrow 2Ag\downarrow + CO_2$

$CO + CuO \rightarrow Cu + CO_2$

$CO + Cl_2 \rightarrow COCl_2$

Water solution of the hydrogen cyanide (HCN) is called prussic acid. HCN can be produced from cyanogen in its reaction with hydrogen.

$NCCN + H_2\ (t^\circ) \rightarrow 2HCN$

Another way to produce it is to perform reaction between methane, ammonia and oxygen.

$2CH_4 + 2NH_3 + 3O_2\ (t^\circ) \rightarrow 2HCN + 6H_2O$

HCN (as well as its salts prone to hydrolysis) is toxic because one of its isoforms (H-N=C: and not H-C≡N) binds cytochrome C oxidase and stops the process of oxidative phosphorylation in mitochondria. Glucose is known as an antidote for prussic acid because HCN reacts with aldehyde groups.

Carbon dioxide is a linear nonpolar molecule with two double bonds. This gas reacts with water and forms bicarbonate and hydronium ions. The corresponding carbonic acid decomposes right after its formation into carbon dioxide and water.

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2\uparrow + H_2O$

The salts of carbonic acid are called carbonates. They all (except carbonates of all alkali metals but not a lithium carbonate) can be decomposed into oxides of corresponding metals and CO_2 before the melting points.

$CaCO_3 \rightarrow CaO + CO_2\uparrow$

Acidic salts of carbonic acid are called bicarbonates. Bicarbonates of alkali-earth metals show better solubility in water then carbonates.

Carbon reacts with fluorine and forms CF_4. This gas is used in refrigerators. CCl_4 can be produced just indirectly — by the way of reaction between methane and chlorine gas.

Silicon forms more than 400 minerals. Disperse SiO_2 is nothing but the main component of sand. There are several ways to produce pure silicon. One of them is the reaction between silicon dioxide and magnesium.

$SiO_2 + 2Mg\ (t°) \rightarrow 2MgO + Si$

Silicon also can be reduced by carbon or hydrogen.

$SiO_2 + 2C\ (t°) \rightarrow Si + 2CO$

$SiCl_4 + 2H_2\ (t°) \rightarrow Si + 4HCl$

At normal temperature silicon can react just with fluorine. At higher temperature silicon reacts with other halogens, with oxygen, carbon and metals.

Silicon reacts with water solutions of alkali and forms silicates. Hydrogen is released in such reactions.

$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2\uparrow$

Silicon dioxide has atomic (diamond-like) crystal structure. This oxide is acidic, even though it cannot react with water. The corresponding silicic acid is also insoluble in water. The formula of silicic acid is usually written as H_2SiO_3, while it is more appropriate to write it as $mSiO_2{\cdot}nH_2O$. Some salts of silicic acid (like sodium or potassium silicate) are soluble in water. Silicic acid can be produced in the reaction between such salts and stronger acids.

$Na_2SiO_3 + 2HCl \rightarrow 2NaCl + H_2SiO_3\downarrow$

Hydrides of silicon (silanes) are numerous, but not as numerous as hydrocarbons. The reason of this difference is in the fact that silanes are highly reactive (unlike hydrocarbons). One of the ways to produce silanes is to perform the reaction between metal silicide and water.

$Mg_2Si + 4HCl \rightarrow 2MgCl_2 + SiH_4$

Newly formed silanes are burning immediately in the air.

$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$

Halides of silicon are hydrolyzed and form H_2SiO_3 and hydrogen halides.

$SiCl_4 + 3H_2O \rightarrow H_2SiO_3 + 4HCl$

In case with hydrofluoric acid the process may be continued with the formation of $H_2[SiF]_6$.

$3SiF_4 + 3H_2O \rightarrow H_2SiO_3 + 2H_2[SiF]_6$

There are several reasons why the Nature ones chosen carbon and not silicon to build up the molecules of life. First of all, the number of valence electrons in carbon is the same as the number of orbitals. Carbon can form single, double and triple bonds. Partial negative charge exists on carbon atoms of hydrocarbons, while in silanes it exists on hydrogen atoms. Hydrocarbons have neither acidic, nor basic properties.

Metals from germanium family (germanium, tin and lead) are amphoteric. They all react with oxidizing acids. However, germanium forms just acidic hydroxide in such reaction, and lead forms just salt. Tin can form both acidic hydroxide (with concentrated nitric acid) and salt (with dilute nitric acid).

$Ge + 4HNO_{3\ (concentrated)} \rightarrow H_2GeO_3 + 4NO_2 + H_2O$

$Sn + 4HNO_{3\ (concentrated)} \rightarrow H_2SnO_3 + 4NO_2 + H_2O$

$Sn + 4HNO_{3\ (concentrated)} \rightarrow Sn(NO_3)_2 + NO + H_2O$

$Pb + 4HNO_{3\ (concentrated)} \rightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$

Tin and lead can also react with nonoxidizing acids and solutions of alkali, unlike germanium.

$Sn + 2NaOH + 4H_2O \rightarrow Na_2[Sn(OH)_6] + 2H_2$

$Pb + NaOH + 2H_2O \rightarrow Na[Pb(OH)_3] + H_2$

Halides of germanium, tin and lead in their higher oxidation state (+4) are instable. They are prone to hydrolysis and formation of complexes.

Halides of the abovementioned metals in the oxidation state of +2 are typical salts.

Monoxides of metals from germanium family are more basic than dioxides. Obviously, monoxides are good reducers, while dioxides are strong oxidizers. Hydroxides of metals from IVA subgroup are amphoteric.

Activated coal is used in medicine as sorbent. Carbonates and bicarbonates are used as antacids. Fullerenes are promising candidates for the specific deliverance of drugs to certain cell types. Silicon-based materials are used as implants.

Chains of chemical reactions

$CO_2 \rightarrow NH_4HCO_3 \rightarrow BaCO_3 \rightarrow CO_2 \rightarrow CO$

$Si \rightarrow Na_2SiO_3 \rightarrow H_4SiO_4 \rightarrow SiO_2 \rightarrow SiCl_4$

$H_2SiO_3 \rightarrow SiO_2 \rightarrow Si \rightarrow K_2SiO_3 \rightarrow$ glass

$Pb(OH)_2 \rightarrow PbO_2 \rightarrow Pb_3O_4 \rightarrow PbCl_2 \rightarrow H_2[PbCl_6]$

$SnCl_2 \rightarrow Sn \rightarrow Sn(NO_3)_2 \rightarrow Sn(OH)_2 \rightarrow K_2[Sn(OH)_4]$

$Pb \rightarrow PbO \rightarrow Pb(NO_3)_2 \rightarrow Pb(OH)_2 \rightarrow Na_2[Pb(OH)_4]$

Finish chemical reactions

$Si + NaOH + H_2O \rightarrow$
$Na_2SiO_3 + NH_4Cl \rightarrow$
H_2SO_4 (conc.) + C →
HNO_3 (conc.) + Si →
$Mg_2Si + H_2SO_4$ (dilute) →
$Pb + H_2SO_4$ (conc.) →
$Na_2PbO_2 + HCl \rightarrow$
$Sn + KOH + H_2O \rightarrow$
$Ge + HNO_3 + HCl \rightarrow$
$Na_2[Sn(OH)_6] + CO_2 \rightarrow$

Problems

1. At 18 °C potassium cyanide hydrolyzes by 1.2 % in a solution with a concentration of 0.1 mol/dm^3. Calculate the constant of hydrolysis (K_h) of this salt.

2. Calculate the constant of HCN dissociation, considering that at 18 °C it dissociates by 0.002 % in a solution with a concentration of 1 mol/L. How does carbon dioxide of the air influences water solutions of alkaline cyanides? Why do cyanides have to be stored in densely closed vessels?

3. 180 g of $Na_2CO_3 \cdot 10H_2O$ salt was dissolved in 1300 g of water. Density of the solution is 1.16 g/cm^3. Define the mass fraction (%) of the anhydrous salt in the solution. Calculate molar and normal concentration of the solution.

4. Upon reaction of a mixture of silicon, aluminum carbonate and calcium carbonate with an alkali solution, 8.96 L of a gas (in normal conditions) was obtained. Upon reaction of the same sample of the initial mixture with HCl solution, 8.96 L of a gas was obtained. This gas reacts with $Ca(OH)_2$ solution and 8.1 g of $Ca(HCO_3)_2$ is produced. Define quantitative composition of the initial mixture.

5. 100 g of lead nitrate was heated up till the constant mass. Which gases were produced? What were their volumes?

6. There are Sn^{2+} ions in the solution. Besides, there are 0.05 moles of Pb^{2+} ions in the same solution. What is the volume of the solution of potassium iodide with concentration equal to 2 mol/L required to separate these ions?

7. 100 g of an alloy with mass fractions of Sn and Pb equal to 70 % and 30 % respectively was dissolved in nitric acid solution with mass fraction equal to 20 %. Calculate the volume of the acid solution if one of the products of the reaction is nitrogen (II) oxide.

8. A sample of lead weighing 6.9 g was dissolved in the concentrated nitric acid. Hydrogen sulfide taken in excess reacts with the obtained solution. What is the mass of the produced precipitate?

9. 40 ml of $SnCl_2$ solution was used to reduce potassium dichromate from 20 ml of its 0.2 N solution (acetic medium). Calculate the molar concentration of $SnCl_2$ solution.

Multiple choice questions

1. Choose the correct statements for the IVA group elements:

a) the maximum valence of all elements of the group corresponds to the group number;

b) silicon is the most abundant element in the Earth crust;

c) germanium has a diamond-like atomic lattice;

d) relative electronegativity of the elements monotonically decreases from silicon to lead.

2. With many metals carbon monoxide forms complex compounds (metal carbonyls). Choose the correct statements to characterize these compounds:

a) these substances have the molecular structure;

b) high purity metals are obtained as a result of their thermal decomposition;

c) they are not formed by the direct interaction of metal with CO, but only indirectly;

d) they are inert complex compounds.

3. Which substances can be hydrolyzed?

a) CCl_4; b) $SiCl_4$; c) $GeCl_4$; d) $SnCl_4$.

4. Choose the method for low-purity silicon production:
a) $SiO_2 + Mg \rightarrow$
b) $SiO_2 + C \rightarrow$
c) $SiCl_4 + H_2 \rightarrow$
d) $SiH_4 \rightarrow$

5. Indicate the ionic carbides:
a) CS_2; b) CaC_2; c) SiC; d) Na_2C_2.

6. Silicon dissolves in nitric acid in the presence of HF producing:
a) silane; c) silicic acids;
b) silicon tetrafluoride; d) fluorosilicic acid.

7. The largest amount of H_2 (in moles) is released in the reaction:
a) 1 mole Si + $H_2O \rightarrow$
b) 1 mole Si + NaOH + $H_2O \rightarrow$
c) 1 mole Si + 1 mole HF →
d) 1 mole Si + 1 mole SiH_4 + H_2O + NaOH →

8. Choose the inequalities that correctly reflect the ratio of the energies of single bonds:
a) E (C – C) bond > E (Si – Si) bond;
b) E (C – H) bond < E (Si – H) bond;
c) E (C – Cl) bond > E (Si – Cl) bond;
d) E (C – O) bond > E (Si – O) bond.

9. Complete the statements correctly: 'Hydrocyanic acid ….'
a) is stronger than carbonic acid;
b) has a linear structure;
c) mixes with water unlimitedly;
d) forms intermolecular hydrogen bonds.

10. Choose the correct series to correspond to the change in the substance properties:
a) basic properties increase in the series GeO, SnO, PbO;
b) reductive properties decrease in the series GeO, SnO, PbO;
c) acidic properties increase in the series GeO_2, SnO_2, PbO_2;
d) oxidizing properties increase in the series GeO_2, SnO_2, PbO_2.

11. Indicate the mixed oxides:
a) PbO; b) Pb_3O_4; c) SnO_2; d) Pb_2O_3.

12. Which substances are used as (enterosorbents) chelators in medicine?
a) activated carbon; c) highly dispersed silica;
b) sodium carbonate; d) aspirin.

13. Which medicines are used as antacids?

a) almagelum;	c) activated carbon;
b) sodium hydrogen carbonate;	d) calcium gluconate.

14. Which enzyme decreases the CN ions concentration in a human body?

a) carbonic anhydrase;	c) catalase;
b) cytochrome oxidase;	d) rodanase.

15. Which halides are salts?

a) $PbCl_4$; b) $PbCl_2$; c) $GeCl_4$; d) $SnCl_2$;

16. How do properties change in the series GeO_2 – SnO_2 – PbO_2?

a) the stability of substances decreases;

b) the oxidizing properties increase;

c) the acidic properties (acidity) increase.

17. Indicate the typical oxidizers:

a) $SnCl_2$; b) PbO_2; c) GeO; d) Pb_3O_4.

18. Which substances react with the alkali solution only in the presence of an oxidizer?

a) Si; b) Ge; c) Sn; d) Pb.

19. Indicate the schemes of reactions which prove amphoteric properties of PbO_2:

a) $PbO_2 + NaOH\ (conc.) + H_2O \rightarrow Na_2[Pb(OH)_6]$

b) $PbO_2 + CH_3COOH \rightarrow Pb(CH_3COO)_4 + H_2O$

c) $PbO_2 + HCl\ (conc.) \rightarrow H_2[PbCl_4] + Cl_2 + H_2O$

d) $PbO_2 + CaO \rightarrow Ca_2PbO_4$

20. At low temperature, white tin turns into gray tin. This process (phenomenon) is called.

a) sublimation;	c) allotropic transformation;
b) melting;	d) tin pest.

EXPERIMENTAL WORK
"CHEMICAL PROPERTIES OF COMPOUNDS CONTAINING ELEMENTS FROM IVA GROUP"

The aim of the work: to study chemical properties of coal, compounds of silicon and lead.

Reactants: fuchsine solution, activated coal, solutions of salts: Na_2CO_3, $NaHCO_3$, Na_2SiO_3, NH_4Cl, $Pb(CH_3COO)_2$, KI; solution of HCl (ρ = 1.19 g/ml), solution of phenolphthalein, cool water.

Experiment 1. ***Adsorption of fuchsine on the coal*.**

Pour fuchsine solution in the tube (fill 1/2 of its volume). Add 1 g (two small spoons) of activated coal to that tube. Mix it and wait for 20 minutes. Describe the resulting solution.

Experiment 2. *Hydrolysis of salts of carbonic and silicic acids*.

Pour several drops of $NaHCO_3$ solution to the first tube, pour several drops of Na_2CO_3 solution to the second tube, pour several drops of Na_2SiO_3 to the third tube. Add 2 drops of phenolphthaleine to each of these three tubes. Arrange the salts in the order of the increase of their hydrolysis degree.

Write the equation of the first step of hydrolysis for $NaHCO_3$

Complete form: ____

Short ionic form: ____

Write the equation of the first step of hydrolysis for Na_2CO_3

Complete form: ____

Short ionic form: ____

Write the equation of the first step of hydrolysis for Na_2SiO_3

Complete form: ____

Short ionic form: ____

Add 3–5 drops of NH_4Cl to the tube with Na_2SiO_3 solution. Notice precipitation and the release of a gas.

Write the equation of NH_4Cl and Na_2SiO_3 hydrolysis in the same tube

Complete form: ____

Experiment 3. *Production of silicic acid*.

Pour Na_2SiO_3 solution in the tube (fill ½ of its volume). Add 6–7 drops of concentrated HCl solution ($\rho = 1.19$ g/ml). Close the tube by a finger and shake it. Notice precipitation.

Write the reaction happened in the tube in complete and short ionic form.

____

____

Experiment 4. *Amphoteric properties of $Pb(OH)_2$*

Pour lead (II) acetate solution in two tubes. Add NaOH solution in each of them in the drop by drop manner until the formation of a precipitate.

Write the reaction in complete and short ionic form.

____

____

Add the excess of NaOH solution in the first tube.

Write the reaction in complete and short ionic form.

____

____

Add the excess of HNO_3 solution in the second tube.

Write the reaction in complete and short ionic form.

____

____

Experiment 5. ***Production of slightly soluble lead iodide PbI_2.***

Fill 2/3 of the volume of a tube with lead (II) acetate solution. Add several drops of potassium iodide solution to that tube. Notice the color of a precipitate. Write the equation of chemical reaction in complete and short ionic form.

Heat the tube (after the addition of a small portion of acetic acid solution) until the complete dissolving of a precipitate. Then put that tube in the glass with cool water.

Write the conclusion: *“The higher the temperature, the* ________________________ *the solubility of a solid substance in water”*

EXPERIMENTAL WORK
“CHEMICAL PROPERTIES OF TIN, LEAD AND THEIR COMPOUNDS”

The aim of the work: to study chemical properties of tin, lead and their compounds.

Reactants: flakes of Zn, bromine water; solutions of salts: $SnCl_2$, $K_2Cr_2O_7$, $(CH_3COO)_2Pb$, $Pb(NO_3)_2$; solutions of acids: 2M HCl, 2N H_2SO_4, 2M HNO_3, concentrated H_2SO_4 (density 1.84 g/ml), concentrated HNO_3 (density 1.4 g/ml).

Experiment 1. ***Production of metallic tin.***

Put a small piece of zinc in the solution of tin (II) chloride.

Write the reaction in complete and short ionic form.

Experiment 2. ***Reactions of tin with acids.***

Put metallic tin in tubes with the following acids (2M HCl; 2N H_2SO_4; concentrated H_2SO_4; dilute HNO_3; concentrated HNO_3). Write chemical reactions.

Experiment 3. ***Reductive properties of Sn^{2+} ions.***

Pour several drops of tin (II) chloride in the tube and add bromine water (Br_2) inside it in the drop by drop manner. Write the chemical reaction.

Add several drops of HCl solution to the tube with $SnCl_2$ solution and add $K_2Cr_2O_7$ solution inside the same tube in the drop by drop manner. Write the chemical reaction.

Experiment 4. ***Production of metallic lead.***

Put a zinc plate in the lead acetate solution (($(CH_3COO)_2Pb$.

Write this reaction in complete and short ionic form.

____

____

Experiment 5. ***Reactions of lead with acids.***

Put metallic lead in tubes with the following acids (2M HCl; 2N H_2SO_4; concentrated H_2SO_4; dilute HNO_3; concentrated HNO_3). Heat those tubes and write chemical reactions if they are possible.

____

____

____

____

Experiment 6. ***Production of hardly soluble lead (II) salts.***

Produce 1) lead (II) chloride; 2) lead (II) chromate; 3) lead (II) sulfide; lead (II) hydroxycarbonate in four separate tubes by the way of the exchange reaction between lead (II) nitrate and respective salts. Notice the colors of precipitates. Write chemical reactions happened in each of the four tubes.

____

____

____

____

Experiment 7. ***The confirmation of the fact that Pb_3O_4 is really made from 2 portions of PbO and 1 portion of PbO_2.***

Dissolve Pb_3O_4 in nitric acid. Notice a brown precipitate. Write the corresponding chemical reaction.

____

Heat the same tube and notice that the color of precipitate has changed to red. Write the corresponding chemical reaction.

____

Take the solution upon the precipitate from the same tube and pour it into another tube, then add K_2CrO_4 to it. Write the corresponding chemical reaction.

____

Write the conclusion: *"I approved that Pb_3O_4 really contains Pb^{2+} and Pb^{4+} cations, because* ____

____"

LESSONS 13–14
ELEMENTS FROM GROUP VA AND THEIR COMPOUNDS

Main topics of the lessons:

1. *Overall description of elements from VA subgroup.*
2. *Chemical properties of nitrogen and its inorganic compounds.*
3. *Chemical properties of phosphorus and its compounds.*
4. *Biological role, the usage in medicine and pharmaceutical analysis of compounds containing elements from VA subgroup.*

The common electronic configuration for elements from VA group is ns^2np^3. In that subgroup one can find both nonmetals (nitrogen and phosphorus) and metals (arsenic, antimony and bismuth). Arsenic and antimony are good examples of semimetals if we divide elements into three categories (metals, nonmetals and semimetals), instead of two (metals and nonmetals).

Nitrogen can be found in nature as the component of nitrates: Chile saltpeter ($NaNO_3$), Indian saltpeter (KNO_3), Norwegian saltpeter ($Ca(NO_3)_2$). Nitrogen gas (N_2) is the “solvent” of the air: its volume percentage is about 78 %. This gas is very stable and inert because two nitrogen atoms in its molecule are bound with each other by the triple bond. At normal temperature nitrogen reacts just with lithium.

In the laboratory N_2 can be produced during decomposition of ammonium nitrite or ammonium dichromate.

$NH_4NO_2 \rightarrow 2H_2O + N_2\uparrow$

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

Copper oxide can oxidize ammonia and produce nitrogen together with metallic copper.

$3CuO + 2NH_3 \rightarrow 3Cu + N_2\uparrow + 3H_2O$

At certain concentration of nitric acid it can react with metals forming N_2 as the prevailing product of nitrogen reduction.

$5Mg + 12HNO_3 \rightarrow 5Mg(NO_3)_2 + N_2\uparrow + 6H_2O$

Nitrides of metals react with water and produce ammonia.

$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2\downarrow + 2NH_3\uparrow$

Nitrides indeed may be described as salts of ammonia in which all the three atoms of hydrogen are replaced by metal atoms. If just two hydrogen atoms are replaced, the compound is called imide (K_2HN). When just one of the hydrogen atoms is replaced, the compound is called amide ($NaNH_2$).

Ammonia behaves as a weak base in water solutions.

$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^-$

However, equilibriums of both processes described above are shifted towards reactants (ammonia and water). For this reason, water solution of ammonia may be described as $NH_3{\cdot}H_2O$.

Ammonium cation (NH_4^+) is formed due to donor-acceptor bond formation between hydrogen atom (acceptor of the electron pair) and nitrogen from ammonia (donor of the electron pair). As a result, all the bonds in the NH_4^+ cation have the same length.

Ammonium hydroxide (NH_4OH) demonstrates all the properties of a weak base. In the mixture of ammonium salt and alkali newly produced NH_4OH decomposes into ammonia and water.

$NH_4NO_3 + NaOH \rightarrow NaNO_3 + H_2O + NH_3\uparrow$

Ammonia can react with oxygen at high temperature only. In the absence of catalyst N_2 is formed in this reaction.

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

In the presence of catalyst the products of that reaction are different. Actually, N_2 is oxidized by the excess of oxygen and forms nitric oxide (NO).

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Ammonium nitrate decomposes at high temperature into water and nitrogen (I) oxide.

$NH_4NO_3 \rightarrow 2H_2O + N_2O\uparrow$

At higher temperatures nitrogen (I) oxide decomposes as well.

$2NH_4NO_3 \rightarrow 4H_2O + 2N_2\uparrow + O_2\uparrow$

Nitrous oxide (N_2O) is known under the name “laughing gas” (figure 6) because of its ability to bind numerous receptors in the nervous system causing unstoppable laughing and narcolepsy (at high concentration).

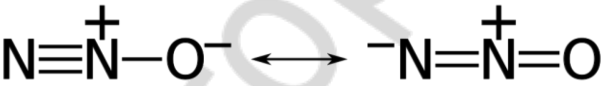


Figure 6. Resonant structures of N_2O

Laughing gas is a strong oxidizer.

$Cu + N_2O = CuO + N_2$

Both N_2O and NO cannot form corresponding acids and salts. NO plays important function in the human organism: it is the secondary messenger produced by NO-synthases. One of the effects of NO release is the dilatation of vessels. NO is oxidized by the oxygen from the air into the nitrogen dioxide (NO_2).

Dinitrogen trioxide (N_2O_3) is stable only at low temperatures (in solid and liquid phases). If the temperature is higher than 3.5 °C, N_2O_3 breaks down into two molecules: NO and NO_2. Dinitrogen trioxide is an acidic one: it reacts with water and forms nitrous acid (HNO_2).

HNO_2 is a weak acid and relatively strong oxidizer.

$2HNO_2 + 2HI = I_2 + 2NO + 2H_2O$

$2HNO_2 + H_2S = S + 2NO + 2H_2O$

Nitrogen dioxide (NO_2) forms dimeric molecules of dinitrogen tetraoxide (N_2O_4) at lower temperatures.

Nitrogen (IV) oxide (brown gas) forms nitric acid in the reaction with water in the presence of oxygen.

$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$

In the absence of oxygen both nitrous and nitric acids are produced in the reaction between NO_2 and H_2O.

$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

Anyway, the reaction between NO_2 and water is the oxidation-reaction process.

Dinitrogen pentoxide (N_2O_5) in the solid state is a salt, consisting of separated anions and cations. The cation is the linear nitronium ion NO_2^+ and the anion is the planar nitrate NO_3^- ion. In the gaseous state this substance has a molecular structure.

Nitrogen (V) oxide forms just nitric acid in the reaction with water.

$N_2O_5 + H_2O \rightarrow 2HNO_3$

Nitric acid may demonstrate regular properties of acids in reactions with bases, salts and oxides. However, this substance is a strong oxidizer. It can release different products in the reaction with a metal (NO_2, NO, N_2O, N_2, NH_3 or NH_4NO_3). The more active the metal, the lower the oxidation state of the nitrogen atom in the product of the reduction. The concentration of the nitric acid also plays significant role in its behavior. The highly concentrated acid (80 % and more) releases mostly NO_2 with all the metals (except Pt and Au which cannot react with it). The acid with lower concentration (45–80 %) releases NO_2 with metals situated after hydrogen in the electrochemical series of metals and, mostly, NO with less active metals, as well as, mostly, N_2O with very active metals. Dilute nitric acid forms, mostly, ammonia with very active metals. Very dilute (less than 5 %) HNO_3 cannot react with metals situated after hydrogen in the electrochemical series. In such dilute solutions HNO_3 can produce H_2 in the reaction with a metal, while that hydrogen is then oxidized by NO and N_2O (they are produced simultaneously) into H_2O and N_2.

Concentrated nitric acid is also able to oxidize some nonmetals.

$6HNO_3\text{(concentrated)} + S \rightarrow H_2SO_4 + 6NO_2\uparrow + 2H_2O$

$5HNO_3\text{(concentrated)} + P \rightarrow H_3PO_4 + 5NO_2\uparrow + H_2O$

$4HNO_3\text{(concentrated)} + C \rightarrow CO_2\uparrow + 4NO_2\uparrow + 2H_2O$

Nitrates (salts of nitric acid) of alkali (except lithium) and alkali-earth metals can be decomposed into nitrites (salts of nitrous acid) and oxygen gas.

$2NaNO_3 \rightarrow 2NaNO_2 + O_2\uparrow$

Nitrates of metals situated between magnesium and copper in the reactivity series (including those two metals) decompose into corresponding metal oxides, nitric (IV) oxide and oxygen.

$4Al(NO_3)_3 \rightarrow 2Al_2O_3 + 12NO_2\uparrow + 3O_2\uparrow$

Nitrates of metals situated after the copper in the reactivity series produce pure metals, nitric (IV) oxide and oxygen in the decomposition reaction.

$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2\uparrow$

Industrial method of nitric acid production includes three steps:

1. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
2. $2NO + O_2 \rightarrow 2NO_2$
3. $4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$

The presence of nitrate anions in the solution can be detected with the help of diphenylamine (it will become deep blue).

Phosphorus exists as several forms with strikingly different properties. The two most common allotropes are white phosphorus and red phosphorus. Black phosphorus is obtained by the way of heating white phosphorus under high pressures. White phosphorus is a molecular substance with P_4 molecules. Red phosphorus is amorphous, while black phosphorus has an atomic crystal structure. The most reactive allotropic modification of phosphorus is white phosphorus, the most stable one is black phosphorus.

The most important mineral of phosphorus is calcium hydroxyapatite $Ca_5(PO_4)_3(OH)$. This substance makes up 70 % (by mass) of human bones. Hydroxyl group in this substance can be replaced by chloride, fluoride or carbonate.

The industrial method to produce phosphorus is to heat up the mixture of calcium phosphate with sand and coal.

$Ca_3(PO_4)_2 + 5C + 3SiO_2 \rightarrow 3CaSiO_3 + 2P + 5CO$

Phosphorus can react with concentrated nitric and sulfuric acids. Phosphoric acid is one of the products of those reactions.

$5HNO_{3(concentrated)} + P \rightarrow H_3PO_4 + 5NO_2\uparrow + H_2O$

$2P + 5H_2SO_{4(concentrated)} \rightarrow 2H_3PO_4 + 5SO_2\uparrow + 2H_2O$

Phosphorus reacts with metals and produces phosphides of metals.

$Al + P \rightarrow AlP$

Those phosphides of metals can react with water and acids to produce phosphine.

$Mg_3P_2 + 6H_2O \rightarrow 3Mg(OH)_2\downarrow + 2PH_3\uparrow$

Phosphine has a similar structure to ammonia, while PH_3 is much less stable (it reacts with oxygen from the air). Moreover, PH_3 cannot make an ion like NH_4^+ with water.

Halides of phosphorus are hydrolyzed in water and form two corresponding acids.

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

There are several acids in which phosphorus plays the role of a central atom.

In the hypophosphorus acid (H_3PO_2) just one hydrogen is connected to the oxygen, so it is a monoprotic acid. In the phosphorous acid (H_3PO_3) two hydrogen atoms are connected to oxygen atoms and can dissociate in water solutions. Orthophosphoric acid (H_3PO_4) has three protons for the participation in acid-base reactions.

Phosphorus trioxide (P_2O_3) corresponds to phosphorus acid, while phosphorus pentoxide (P_2O_5) corresponds to orthophosphoric acid and the set of polymeric acids described below.

Polyphosphoric acids are made by the way of H_3PO_4 molecules polycondensation. The dimeric one is known as the pyrophosphoric acid ($H_4P_2O_7$). Polyphosphoric acids are not cyclic, unlike metaphosphoric acids. The last ones have the common formula of $(HPO_3)_n$.

The biological role of nitrogen and phosphorus cannot be overestimated. Nitrogen is the part of DNA, RNA, proteins and many bioactive molecules. Phosphorus (in the form of remains of orthophosphoric acid) is the component of DNA, RNA and nucleotide mono-, di-, tri- and cyclophosphates. Proteins can undergo posttranslational phosphorylation (and then dephosphorylation). These actions can “switch on” or “switch off” the enzyme. Phosphorylation can be described as the formation of ester between phosphoric acid and hydroxyl group of serine, threonine or tyrosine.

Chains of chemical reactions

$N_2 \rightarrow NH_3 \rightarrow NO \rightarrow Cu(NO_3)_2 \rightarrow NO_2$

$NH_4NO_2 \rightarrow N_2 \rightarrow NO_2 \rightarrow NaNO_3 \rightarrow HNO_3$

$NH_3 \rightarrow NH_4OH \rightarrow NH_4Cl \rightarrow NH_4NO_3 \rightarrow N_2O$

$HNO_3 \rightarrow NH_3 \rightarrow (NH_4)_2Cr_2O_7 \rightarrow N_2 \rightarrow Na_3N$

$P_4 \rightarrow Ca_3P_2 \rightarrow PH_3 \rightarrow P_4O_{10} \rightarrow Ca_3(PO_4)_2$

$Ca_3(PO_4)_2 \rightarrow P \rightarrow H_3PO_4 \rightarrow (NH_4)_2HPO_4 \rightarrow Ca_3(PO_4)_2$

$As_2O_3 \rightarrow As_2S_3 \rightarrow (NH_4)_3AsS_4 \rightarrow As_2S_5 \rightarrow H_3AsO_4$

$Sb_2O_5 \rightarrow Na[Sb(OH)_6] \rightarrow Sb_2S_5 \rightarrow (NH_4)_3SbS_4 \rightarrow Sb_2S_5$

$Bi \rightarrow Bi(NO_3)_3 \rightarrow NaBiO_3 \rightarrow HBiCl_4 \rightarrow BiOCl$

Finish chemical reactions

$NO_2 + H_2O$ (cool) → ____

$NH_4Cl + CuO \xrightarrow{t}$ ____

$KNO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow$ ____

$PH_3 + KMnO_4 + H_2SO_4 \rightarrow$ ____

$P_4 + KOH + H_2O \rightarrow$ ____

$Sb + HNO_3$(conc.) → ____

$AsH_3 + KMnO_4 + H_2SO_4 \rightarrow H_3AsO_4 +$ ____

$Bi(OH)_2 + Br_2 + KOH \rightarrow KBiO_3 +$ ____

$Na_3AsO_4 + H_2S + HCl \rightarrow$ ____

$K[Sb(OH)_6] + H_2S + HCl \rightarrow$ ____

Problems

1. When heating up the mixture of $Pb(NO_3)_2$, $CaCO_3$, and KNO_3, 51.34 g of a solid mixture of oxides has been obtained, and 17.92 L (in normal conditions) of a gas mixture has been collected. The volume percentage of CO_2 in that mixture is equal to 25 %. Calculate the mass of the initial mixture.

2. Upon reaction of 12.8 g of a metal with nitric acid solution with a mass percentage equal to 60 % (ρ = 1.375 g/ml), 8.96 L (in normal conditions) of a brown gas and a metal (II) salt were produced. Find out the metal and calculate the volume of the spent nitric acid solution.

3. The phosphorus, which was quantitatively obtained from 31.0 g of calcium phosphate, was oxidized by the excess of oxygen and the product was dissolved in 200 ml of KOH solution with molar concentration of alkali equal to 1.5 mol/L. Which salts and in what amounts (moles) are now in the solution?

4. The phosphorus oxide, produced by burning down 62 g of phosphorus, was added to 400 g of orthophosphoric acid solution with mass percentage equal to 24.5 %. The obtained solution was boiled. Calculate the volume of sodium hydroxide solution with mass percentage of NaOH equal to 5 % (ρ = 1.05 g/ml) required for transformation of all acid containing in the solution into sodium hydrogen phosphate.

5. Upon reaction of metallic bismuth with 200 ml of nitric acid solution, a gas was obtained. Define the gas and its volume if for the first reaction a dilute solution of nitric acid with concentration equal to 0.8 mol/L was used; for the second reaction the concentrated solution with a mass fraction of nitric acid equal to 48 % was used.

Multiple choice questions

1. Chemical elements from VA group differ:

a) in the number of atomic valence orbitals;

b) in the value of minimal valence;

c) in the value of maximal valence;

d) in the maximal oxidation state.

2. Choose the correct statements for all elements of VA group:

a) the formula for the highest oxide is E_2O_5;

b) the formula for the volatile hydrogen compound is EH_3;

c) there are three unpaired electrons in the outer level in the ground state;

d) the formula for the acidic hydroxide in the highest oxidation state is H_3EO_4.

3. Choose the correct statements for nitrogen as a substance:

a) in nature nitrogen can be found both as chemical element and in compounds;

b) its highest oxidation state is equal to +4;

c) chemical activity of nitrogen is lower than that of white phosphorus;

d) nitrogen is a part of the air.

4. Choose the pair of substances, if you know that the interaction between them is a redox process at room temperature:

a) NO and H_2O; c) NO_2 and H_2O;

b) N_2O_3 and H_2O; d) N_2O_5 and H_2O.

5. Indicate the substance in which nitrogen has the oxidation state equal to +5 only:

a) NH_4NO_3; b) N_2O_4; c) NH_4NO_2; d) $Sr(NO_3)_2$.

6. The iron and copper alloy was treated with the concentrated nitric acid solution at room temperature. Indicate the line with the main products of the reaction:

a) $Fe(NO_3)_2$, $Cu(NO_3)_2$, NO_2, H_2O;

b) $Cu(NO_3)_2$, NO_2, H_2O;

c) $Fe(NO_3)_3$, $Cu(NO_3)_2$, NO_2, H_2O;

d) $Fe(NO_3)_3$, NO, H_2O.

7. 4.6 g of nitrogen (IV) oxide reacts with hot potassium hydroxide solution. Calculate the amount of substance of potassium nitrate.

a) 0.05 mole; b) 0.0667 mole; c) 0.1 mole; d) 0.4 mole.

8. The nature of products of the reaction between nitric acid and metals depends on the acid concentration and the metal activity. Besides salt and water, there may be:

a) N_2; b) NO; c) NO_2; d) N_2O.

9. How many substances: Cl_2, H_3PO_4, CH_3COOH, H_2SO_4 (conc.), H_2O, CaO, H_2S does ammonia react with as a reducer?

a) 3; b) 4; c) 5; d) 2.

10. How many moles of electrons transferred from the reducing agent to the oxidizing agent in complete thermal decomposition of 72 g of iron (II) nitrate?

a) 0.8; b) 0.4; c) 1.6; d) 1.0.

11. Choose the differences between red phosphorus and white phosphorus:

a) it's chemically less active;

b) it has a molecular lattice;

c) when heated to 250°, it sublimates;

d) it has a characteristic garlic smell.

12. Phosphorus has the oxidation state equal to –3 in the compounds:

a) PBr_3; b) Ca_3P_2; c) HPO_3; d) PH_3.

13. How many substances: Cl_2, S, O_2, H_2, Li, HNO_3, H_2SO_4 (dilute), $KClO_3$ does phosphorus react with as a reducer?

a) 4; b) 5; c) 6; d) 7.

14. Phosphorus (III) oxide differs from phosphorus (V) oxide:

a) in its aggregation state in normal conditions;

b) in the type of the lattice;

c) in the number of σ-bonds in their molecules;

d) in the number of π-bonds in their molecules.

15. Phosphoric acid:

a) is a solid at room temperature;

b) produces two types of salts;

c) reacts with alcohols producing esters;

d) cannot be an oxidizer.

16. Which substances does ammonium dihydrogen phosphate react with?

a) potassium hydroxide; c) sulfuric acid;

b) ammonia; d) barium hydroxide.

17. Which substances does phosphorus (V) oxide react with?

a) CO_2; b) Li_2O; c) CsOH; d) $BaCO_3$.

18. Choose the correct statements. Distinctive properties of arsine are:

a) it's a strong oxidizer; c) it's thermally unstable;

b) it's a strong reducer; d) it's toxic.

19. Typical oxidation states of arsenic and antimony in their compounds are:

a) -3; b) +1; c) +3; d) +5.

20. The products of bismuth (III) chloride hydrolysis are:

a) HCl, $Bi(OH_3)$; c) $HClO_2$;

b) HClO, $Bi(OH)_2Cl$; d) HCl, BiOCl.

EXPERIMENTAL WORK
"NITROGEN AND NITROGEN CONTAINING COMPOUNDS"

The aim of the work: production and chemical properties of nitrogen containing compounds.

Reactants: phenolphthalein, neutral litmus solution, diphenylamine, solutions: NH_4OH, $Al_2(SO_4)_3$, NH_4Cl, 2M NaOH, NH_4NO_3, CH_3COONH_4, $CuSO_4$, $NaNO_2$, 2N H_2SO_4, 25 % NH_3, $KMnO_4$, $K_2Cr_2O_7$, KI.

Experiment 1. ***The equilibrium in water solution of ammonia.***

Pour 6 drops of NH_4OH solution in each of the 2 tubes. Add a drop of phenolphthalein in the first tube. Notice a color of the solution. Add 3 small spoons of ammonium chloride in the same tube and mix them. Notice the change in color. Write the equilibrium describing ammonia in water solution.

____

Add 5–6 drops of aluminum sulfate solution in the second tube. Notice precipitation and the disappearance of ammonia smell.

$6NH_4OH + Al_2(SO_4)_3 \rightarrow 2Al(OH)_3\downarrow + 3(NH_4)_2SO_4$

Why the smell of ammonia disappeared?

____

Experiment 2. ***Test reaction for NH_4^+ ions.***

Pour 2–3 drops of NH_4Cl solution in the tube. Then add 2 drops of 2N NaOH solution. Cover the tube by a wet litmus paper. Notice the color of that paper. Write the corresponding chemical reaction.

Complete form:____

Short ionic form:____

Experiment 3. ***Hydrolysis of ammonium salts.***

Pour 5–6 drops of neutral litmus solution in two tubes. Put 2 small spoons of ammonium nitrate in the first tube. Mix the solution. Notice the change in color. Write hydrolysis reaction.

Complete form:____

Short ionic form:____

Put 2 small spoons of ammonium acetate in the second tube. Mix the solution. Notice, was there a change in color or not. Write hydrolysis reaction.

Complete form:____

Short ionic form:____

Experiment 4. ***Chemical properties of ammonia and ammonium cations (in the fume hood).***

Pour 5 drops of $CuSO_4$ solution in the tube. Add 1–2 drops of concentrated ammonia solution in that tube. Notice the precipitation. Continue the addition of concentrated ammonia solution until the dissolving of the precipitate.

$CuSO_4 + 2NH_3 + 2H_2O \rightarrow Cu(OH)_2\downarrow + (NH_4)_2SO_4$

Short ionic form:____

$Cu(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4](OH)_2$

Short ionic form:____

Experiment 5. ***Reductive properties of ammonia.***

Pour 3–4 drops of potassium permanganate solution ($KMnO_4$) to the tube. Add 3–5 drops of concentrated ammonia solution to the same tube. Heat the solution until the change in color will happen.

Balance the redox reaction using electron-ion method.

$NH_3 + KMnO_4 \rightarrow N_2\uparrow + MnO_2\downarrow + H_2O + KOH$

reduction: ____

oxidation: ____

water molecules:____

Experiment 6. ***Nitrogen (III) oxide and salts of nitrous acid.***

a) *Production of nitrogen (III) oxide and its decomposition*.

Put 3–4 drops of concentrated sodium nitrite ($NaNO_2$) solution in the tube, add 2 drops of 2N sulfuric acid solution in the same tube. Notice the appearance of blue color of the solution. Then notice the appearance of a brown gas upon the solution.

$2NaNO_2 + H_2SO_4 = Na_2SO_4 + NO_2\uparrow + NO\uparrow + H_2O$

$N_2O_3 \rightleftarrows NO_2 + NO$

b) *Redox properties of nitrites*

Pour 3–4 drops of potassium iodide solution in the first tube and 3–4 drops of potassium permanganate solution in the second tube. Add 2–4 drops of 2N sulfuric acid solution in both tubes. Then add 4–5 drops of sodium nitrite solution in both tubes. Notice the change in color in each of the tubes.

Balance the redox reaction using electron-ion method.

$KI + NaNO_2 + H_2SO_4 \rightarrow I_2 + NO + K_2SO_4 + Na_2SO_4 + H_2O$

reduction: ____

oxidation: ____

water molecules:____

Balance the redox reaction using electron-ion method.

$KMnO_4 + NaNO_2 + H_2SO_4 \rightarrow NaNO_3 + MnSO_4 + K_2SO_4 + H_2O$

reduction: ____

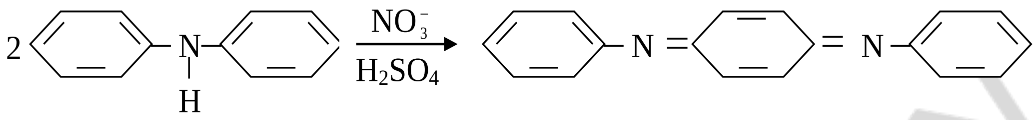
oxidation: ____

water molecules:____

In the first reaction sodium nitrite acted as ____________________________, while in the second reaction it acted as ____.

Experiment 7. ***Test reaction for nitrate anions***

Put a drop of diphenylamine $(C_6H_5)_2NH$ solution in the tube with sodium nitrate solution. Notice the appearance of intense blue color.



Write the conclusion: *“Ammonium salts can act as reducers only, while nitrites can be either reducers, or oxidizers, because* ____

____*”*

EXPERIMENTAL WORK
“PHOSPHORUS AND ITS COMPOUNDS”

The aim of the work: to study chemical properties of phosphorus containing compounds.

Reactants: water solutions of: $CaCl_2$, Na_2HPO_4, $Al_2(SO_4)_3$, CH_3COONa, $BaCl_2$, $AgNO_3$, neutral litmus; crystals of: Na_3PO_4, NaH_2PO_4, red phosphorus; concentrated HNO_3, concentrated ammonium molybdate ($(NH_4)_2MoO_4$) solution with nitric acid.

Experiment 1. ***Production of phosphates and hydrogen phosphates of some metals.***

a) *Production of hydrogen phosphate and phosphate of calcium*

Pour 4–5 drops of calcium chloride solution in two tubes. Add 4–5 drops of sodium hydrogen phosphate in the first tube. Add 4–5 drops of sodium phosphate in the second tube. Notice the colors of precipitates.

$CaCl_2 + Na_2HPO_4 \rightarrow CaHPO_4\downarrow + 2NaCl$

Write this reaction in ionic form:

____

$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 6NaCl$

Write this reaction in ionic form:

____

b) *Production of aluminum phosphate ($AlPO_4$) in the presence of sodium acetate (CH_3COONa).*

Put 3–4 drops of aluminum sulfate solution in the tube. Add 2–3 drops of sodium acetate solution in each tube. Then add 2–3 drops of sodium hydrogen phosphate solution Na_2HPO_4 in each tube. Notice the color of precipitate. Notice the role of acetate anions in this reaction.

$Al_2(SO_4)_3 + 2Na_2HPO_4 + 2CH_3COONa \rightarrow 2AlPO_4\downarrow + 2CH_3COOH + 3Na_2SO_4$

Write this reaction in ionic form:

____

Experiment 2. *Hydrolysis of sodium orthophosphate and sodium dihydrogen phosphate.*

Pour 5–6 drops of neutral litmus solution in each of the three tubes. The first tube is the control one. Put a few crystals of Na_3PO_4 in the second tube and mix the solution. Put a few crystals of NaH_2PO_4 in the third tube and mix the solution. Notice the change in color in both tubes.

Increased acidity in the NaH_2PO_4 solution is the consequence of the fact that the dissociation of dihydrogen phosphate anion overwhelms the hydrolysis of dihydrogen phosphate anion:

$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-}$

$H_2PO_4^- + H_2O \rightleftarrows H_3PO_4 + OH^-$

Experiment 3. *Production of orthophosphoric acid.*

Put one small spoon of red phosphorus in the tube. Add 3–5 drops of concentrated nitric acid (density is 1.4 g/ml) in that tube. Heat the tube until the release of a gas.

$3P + 5HNO_3\text{(concentrated)} + 2H_2O \rightarrow 3H_3PO_4 + 5NO\uparrow$

Cool down the tube. Then perform the test reaction for PO_4^{3-} anions with ammonium molybdate solution: pour 5–6 drops of ammonium molybdate solution in the separate tube, add 1 drop of your own solution to it and heat it. Notice the appearance of yellow precipitate of ammonium molybden phosphate.

$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = (NH_4)_2H_4[P(Mo_2O_7)_6] + 21NH_4NO_3 + 10H_2O$

Experiment 4. *Test reactions for phosphate anions.*

a) *Reaction with $BaCl_2$*: barium chloride ($BaCl_2$) forms white precipitate of barium hydrogen phosphate $BaHPO_4$ with the solution of Na_2HPO_4. That precipitate is soluble in acids (except H_2SO_4).

$BaCl_2 + Na_2HPO_4 \rightarrow BaHPO_4\downarrow + 2NaCl$

Write this reaction in ionic form:

____

To produce a normal salt one has to add some alkali or ammonium to the solution.

b) *Reaction with $AgNO_3$*: silver nitrate ($AgNO_3$) forms yellow precipitate of silver phosphate with solutions of phosphates and hydrogen phosphates. That precipitate is soluble in nitric acid.

$2Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4\downarrow + 3NaNO_3 + NaH_2PO_4$

Write this reaction in ionic form:

____

Write the conclusion: *"Precipitates of hydrogen phosphates are usually soluble in nitric acid because ____*
____".

LESSON 15

ELEMENTS FROM GROUP VIA AND THEIR COMPOUNDS

Main topics of the lesson:

1. *Overall description of elements from VIA subgroup.*
2. *Chemical properties of oxygen and its inorganic compounds.*
3. *Chemical properties of sulfur and its compounds.*
4. *Biological role, the usage in medicine and pharmaceutical analysis of compounds containing elements from VIA subgroup.*

The common electronic configuration for elements from VIA group is ns^2np^4. In that subgroup all the elements (oxygen, sulfur, selenium and tellurium), except polonium, are classified as nonmetals.

Oxygen as a pure chemical element exists in two allotropic modifications: oxygen gas (O_2) and ozone (O_3).

The common allotrope of elemental oxygen on the Earth is called dioxygen, O_2. This is the form that is used by complex forms of life, such as animals, in cellular respiration and is the form that is an important part of the atmosphere of our planet. It is important to remind that dioxygen is a nonpolar molecule that has rather low solubility in water: 3.15 ml of dioxygen can be dissolved in 100 ml of water at 20 °C. Because of this reason it is transferred in the blood of chordates with the help of hemoglobin.

Ozone (Trioxygen, O_3) is a very reactive allotrope of oxygen that is damaging to lung tissue. It demonstrates higher reactivity than oxygen and can even react with such inactive metals as gold and platinum. Ozone is a polar molecule of the angular shape (figure 7).

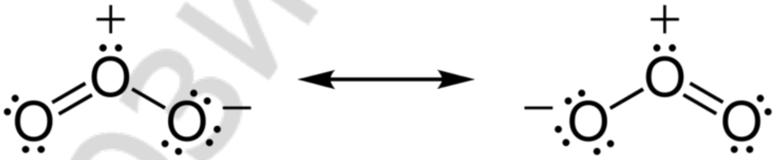


Figure 7. Resonant structures of ozone molecule

Ozone is produced in the upper layer of atmosphere when O_2 combines with atomic oxygen made by the splitting of O_2 by ultraviolet (UV) radiation. Since ozone absorbs strongly in the UV region of the spectrum, the ozone layer of the upper atmosphere functions as a protective radiation shield for the planet.

Oxygen is able to form three types of compounds with alkali metals: oxides, peroxides and superoxides.

In oxides the oxidation state of oxygen is equal to –2, as well as in the most of oxygen containing compounds.

$4Na + O_2 \rightarrow 2Na_2O$

In peroxides oxygen atoms have the oxidation state of –1.

$2Na + O_2 \rightarrow Na_2O_2$

In superoxides oxygen demonstrates fractional oxidation state of $-{}^{1}/_{2}$. Actually, superoxide is a compound that contains the superoxide anion with the chemical formula O_2^-.

$K + O_2 \rightarrow KO_2$

In fact, a mixture of oxide and peroxide (in which peroxide prevails) is formed after the reaction between sodium and oxygen. In the reaction between oxygen and potassium the mixture of peroxide and superoxide (in which superoxide prevails) is formed.

Superoxides of alkali metals can react with those metals to produce peroxides.

$KO_2 + K \rightarrow K_2O_2$

Peroxides of alkali metals can react with those metals to produce oxides.

$Na_2O_2 + 2Na \rightarrow 2Na_2O$

Peroxides react with water. Oxygen is produced in that kind of reactions.

$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2\uparrow$

If chemical compounds are burnt in the excess of oxygen, a mixture of oxides is produced.

$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$

$2CuS + 3O_2 \rightarrow 2CuO + 2SO_2$

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

If chemical compounds are burnt in conditions with the limited amount of oxygen, some pure chemical elements may be produced.

$2H_2S + O_2 \rightarrow 2S + 2H_2O$

$4NH_3 + 3O_2 \rightarrow 6H_2O + 2N_2$

Oxygen can be produced in laboratory in several decomposition reactions.

$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2\uparrow$

$2KClO_3 \rightarrow 2KCl + 3O_2\uparrow$

$2KNO_3 \rightarrow 2KNO_2 + O_2\uparrow$

$2H_2O_2 \rightarrow 2H_2O + O_2\uparrow$

Sulfur is a solid substance in normal conditions. Sulfur forms polyatomic molecules with different chemical formulas, with the best-known allotrope being octasulfur, cyclo-S_8. Sulfur forms over 30 solid allotropes, more than any other element.

Sulfur can be produced in industry in the reaction between hydrogen sulfide and sulfur (IV) oxide.

$2H_2S + SO_2 \rightarrow 2H_2O + 3S$

In the laboratory sulfur can be produced in several ways.

$FeS_2 \rightarrow FeS + S$

$2H_2S + O_2 \rightarrow 2S + 2H_2O$

$SO_2 + C \rightarrow CO_2 + S\downarrow$

$H_2S + Cl_2 \rightarrow 2HCl + S\downarrow$

Diatomic compounds of sulfur and metals are known as sulfides. Sulfur demonstrates oxidation state of –2 in those salts.

$2K + S \rightarrow K_2S$

$Cu + S \rightarrow CuS$

However, in pyrite (FeS_2, also known as «fool's gold») sulfur demonstrates the oxidation state of –1.

Sulfur forms SO_2 in the reaction with oxygen. Sulfuric acid anhydrate (SO_3) may be produced in the reaction between SO_2 and O_2 in the presence of a catalyst.

$S + O_2 \rightarrow SO_2$

$2SO_2 + O_2 \rightleftarrows 2SO_3$

Sulfur can directly interact with alkali and certain acids.

$3S + 6KOH \rightarrow K_2SO_3 + 2K_2S + 3H_2O$

$S + 2H_2SO_4\text{(concentrated)} \rightarrow 3SO_2\uparrow + 2H_2O$

$S + 4HNO_3\text{(concentrated)} \rightarrow 4NO_2\uparrow + SO_2\uparrow + 2H_2O$

Hydrogen sulfide in normal conditions is a colorless gas with the characteristic foul odor of rotten eggs. Water solution of H_2S demonstrates acidic properties. The best way to produce H_2S in laboratory is the reaction between a metal sulfide and acid.

$Na_2S + 2HCl \rightarrow 2NaCl + H_2S\uparrow$

$FeS + 2HCl \rightarrow FeCl_2 + H_2S\uparrow$

Some sulfides, like aluminum and magnesium sulfides, undergo complete hydrolysis and produce respective hydroxides and hydrogen sulfide.

$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2S\uparrow$

Sulfides of metals are good reducers (just like hydrogen sulfide).

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2\uparrow$

$3CuS + 8HNO_3\text{(concentrated)} \rightarrow 3CuSO_4 + 8NO\uparrow + 4H_2O$

Soluble sulfides are partially hydrolyzed in water solutions.

$K_2S + H_2O \rightleftarrows KHS + KOH$

Thiosulfate ions can be imagined as sulfate anions with one of the oxygen atoms substituted by a sulfur atom (figure 8).

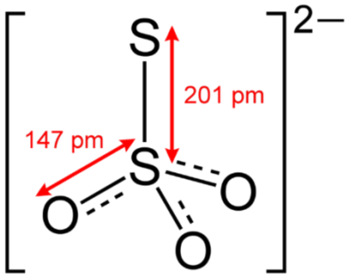


Figure 8. The structure of thiosulfate anion

Thiosulfates are prone to disproportioning reactions.

$Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + SO_2\uparrow + S\downarrow$

Strong oxidizers turn thiosulfates to sulfates, while weak oxidizers turn them to tetrathionates. Tetrathionate anion contains a chain of four sulfur atoms connected together.

$Na_2S_2O_3 + 4Cl_2 + 5H_2O = Na_2SO_4 + H_2SO_4 + 8HCl$

$Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$

Sulfurous acid anhydrate (also known as sulfur (IV) oxide) demonstrates all the properties of acidic oxides. Moreover, it can behave as oxidizer or reducer. Some specific reactions are listed below.

$SO_2 + Na_2CO_3\text{(concentrated)} \rightarrow Na_2SO_3 + CO_2\uparrow$

$SO_2 + 2CO \rightarrow S + 2CO_2\uparrow$

$SO_2 + Br_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr$

$SO_2 + 2HNO_3\text{(concentrated)} \rightarrow H_2SO_4 + 2NO_2\uparrow$

Sulfurous acid produced in reactions between sulfites (salts of sulfurous acid) and other acids decomposes into SO_2 and H_2O.

$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2\uparrow + H_2O$

Sulfurous acid and its salts participate in some specific redox reactions. There are some examples.

$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$

$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$

$H_2SO_3 + Br_2 + H_2O \rightarrow H_2SO_4 + 2HBr$

$H_2SO_3 + 2H_2S \rightarrow 3S + 3H_2O$

$4K_2SO_3 \rightarrow K_2S + 3K_2SO_4$

Sulfuric acid anhydrate (sulfur (VI) oxide) demonstrates common properties of acidic oxide. SO_3 is also a strong oxidizer.

$5SO_3 + 2P \rightarrow 5SO_2\uparrow + P_2O_5$

$3SO_3 + H_2S \rightarrow 4SO_2 + H_2O$

Industrial method of sulfuric acid production includes four steps:

1. $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$ (oxidation of pyrite).
2. $2SO_2 + O_2 \rightarrow 2SO_3$ (oxidation of sulfur (IV) oxide in the presence of a catalyst).
3. $SO_3 + H_2SO_4\text{(concentrated)} \rightarrow H_2SO_4{\cdot}SO_3 = H_2S_2O_7$ (concentrated sulfuric acid interacts with sulfur (VI) oxide and produces so-called oleum also known as «fuming sulfuric acid»).
4. $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$ (oleum is then diluted by water to produce H_2SO_4 of the needed concentration).

Diluted sulfuric acid (mass percentage is lower than 20 %) demonstrates all the common features of acids. Remember that diluted (and not concentrated) sulfuric acid interacts with metals and produces hydrogen gas.

$Fe + H_2SO_4\text{(diluted)} \rightarrow FeSO_4 + H_2\uparrow$

Concentrated sulfuric acid (mass percentage is equal to 93–98 %) reacts with all metals (except aluminum, iron and chrome at low temperature, and gold and platinum at any temperature) and produces sulfur (IV) oxide. It is important to mention that concentrated sulfuric acid is a weak electrolyte and exists in form of molecules. For this reason, sulfur atoms themselves act as oxidizers when sulfuric acid is concentrated. In contrast, in diluted sulfuric acid hydrogen atoms act as oxidizers (just like in case with the most of other acids).

$Zn + 2H_2SO_4(\text{concentrated}) \rightarrow ZnSO_4 + SO_2\uparrow + 2H_2O$

Sulfuric acid of average concentrations can react with metals of an average activity and produce a variety of products.

$3Zn + 4H_2SO_4(50\ \%) \rightarrow 3ZnSO_4 + S\downarrow + 4H_2O$

$4Zn + 5H_2SO_4(30\ \%) \rightarrow 4ZnSO_4 + H_2S\uparrow + 4H_2O$

Concentrated sulfuric acid can oxidize not only metals but nonmetals as well.

$2P + 5H_2SO_4(\text{concentrated}) \rightarrow 2H_3PO_4 + 5SO_2\uparrow + 2H_2O$

$C + 2H_2SO_4(\text{concentrated}) \rightarrow CO_2\uparrow + 2SO_2\uparrow + 2H_2O$

Concentrated sulfuric acid is used to produce acids from their solid salts.

$2KNO_3(\text{solid}) + H_2SO_4(\text{concentrated}) \rightarrow K_2SO_4 + 2HNO_3\uparrow$

Sulfates (salts of sulfuric acid) can be decomposed into a metal oxide and sulfur (VI) oxide, or into a metal oxide, sulfur (IV) oxide and oxygen gas. The later reaction takes place at higher temperature than the first one: SO_3 decomposes into SO_2 and O_2.

$CuSO_4 \rightarrow CuO + SO_3\uparrow$

$2CuSO_4 \rightarrow 2CuO + 2SO_2\uparrow + O_2\uparrow$

Soluble sulfates are recognized in their solutions in the following way. Addition of barium chloride results in the formation of white precipitate of $BaSO_4$.

$Na_2SO_4 + BaCl_2 \rightarrow 2NaCl + BaSO_4\downarrow$

Chains of chemical reactions

$Cu(NO_3)_2 \rightarrow O_2 \rightarrow SO_3 \rightarrow Na_2SO_4 \rightarrow NaOH$

$FeS \rightarrow H_2S \rightarrow SO_2 \rightarrow H_2SO_4 \rightarrow SO_2$

$SO_2 \rightarrow S \rightarrow H_2SO_4 \rightarrow NaHSO_4 \rightarrow Na_2SO_4$

$S \rightarrow NaHSO_3 \rightarrow Na_2SO_3 \rightarrow SO_2 \rightarrow NaHSO_4$

Finish chemical reactions

$FeS_2 + O_2 \xrightarrow{t}$ ____________________

$S + NaOH \rightarrow$ ____________________

$H_2S + SO_2 \rightarrow$ ____________________

$H_2O_2 + I_2 \rightarrow$ ____________________

$Se + NaOH \rightarrow$ ____________________

Problems

1. At transmission of pure oxygen through an ozonizer, a gas density at the exit is 1.02 times higher than at the entrance. Define volume fractions of the gases at the exit of the ozonizer.

2. In a gas mixture of oxygen and carbon dioxide, the number of oxygen atoms is 5 times higher than the numbers of carbon atoms. An unknown gas with the volume equal to the volume of carbon dioxide was added to this mixture (in normal conditions). A gas mixture with average molar mass equal to 44.52 g/mol was formed. Determine the molar mass of the unknown gas.

3. The equilibrium $2SO_2(g) + O_2\ (g) \leftrightarrow 2SO_3\ (g)$ is established in the system. The equilibrium molar concentration of SO_3 is equal to 0.1 mol/L. Define equilibrium molar concentration of O_2 if it is known that by the time of the equilibrium establishment 40 % of oxygen reacted.

4. The reaction of SO_3 with water proceeds according to the following thermochemical equation:

$$SO_3\ (l) + H_2O\ (l) = H_2SO_4(l) + 130\ kJ.$$

Sulfur (VI) oxide was dissolved in 50 ml of water, and 1.95 kJ of heat was produced. Calculate a mass fraction of H_2SO_4 in the obtained solution.

5. After the reaction of combustion of hydrogen sulfide in the excess of oxygen the volume of the gas mixture decreased by 67.2 L (in normal conditions). What volume of sulfur (IV) oxide was obtained?

Multiple choice questions

1. 0.1 mole of monoclinic sulfur, which is formed by only one nuclide, contains 39.2 moles of elementary particles in the atoms. Indicate the nuclide:

a) S^{32}; b) S^{33}; c) S^{34}; d) S^{36}.

2. Indicate nonpolar molecules:

a) SF_6; b) H_2O_2; c) SO_3; d) H_2O.

3. Choose the salt of tetrationic acid:

a) $Na_2S_2O_7$; b) Na_2SO_5; c) $Na_2S_2O_8$; d) $Na_2S_4O_6$.

4. The valence of oxygen is equal to three in the compound:

a) H_2O_2; b) H_3O^+; c) HNO_3; d) O_3.

5. Choose the correct statements:

a) the bond polarity increases in the series $SO_2 – SeO_2 – TeO_2$;

b) hydrogen peroxide mixes with water at any ratio;

c) it’s more typical for hydrogen peroxide to have oxidizing properties in the acidic medium and reducing properties in the basic medium;

d) enthalpy of formation of SO_3 is equal to –432 kJ/mol, enthalpy of formation of SO_2 is equal to –297 kJ/mol, that’s why SO_3 is more stable.

6. When reducing 0.04 mole of sulfuric acid, sulfur atoms gain $1.9264 \cdot 10^{23}$ electrons. Indicate the product of sulfuric acid reduction:

a) SO_2; b) S; c) H_2S; d) SO_3.

7. The products of CuS oxidation in the excess of oxygen are:
a) CuO and S;
b) Cu_2O and SO_2;
c) Cu and SO_3;
d) Cu and S.

8. The relative density of the mixture of ozone and oxygen per hydrogen can be.
a) 40; b) 20; c) 17; d) 100.

9. Hydrosulfuric acid is a water solution of:
a) H_2S; b) H_2SO_4; c) H_2SO_3; d) $H_2S_2O_7$.

10. In which amino acids sulfur atoms can be substituted by selenium atoms?
a) isoleucine;
b) proline;
c) methionine;
d) cysteine.

EXPERIMENTAL WORK

"CHEMICAL PROPERTIES OF COMPOUNDS CONTAINING ELEMENTS FROM VIA GROUP"

The aim of the work: to study chemical properties of compounds containing elements from VIA group.

Reactants: crystals of: $KMnO_4$, MnO_2, $Na_2S_2O_3 \cdot 5H_2O$, zinc, copper. Solutions of: 3 % H_2O_2, $(NH_4)_2S$, $Pb(NO_3)_2$, Na_2SO_3, K_2S, dilute H_2SO_4 and HCl, concentrated H_2SO_4, soluble salts of Zn^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}.

Experiment 1. ***Production of oxygen.***

Put 0.5 g of solid potassium permanganate in the tube and heat it. Take a smoldering match in another hand and put its end in the tube. Notice the ignition.

$2KMnO_4 \xrightarrow{t^\circ} K_2MnO_4 + MnO_2 + O_2$

Experiment 2. ***Catalytic decomposition of hydrogen peroxide.***

Pour 1–2 ml of 3 % H_2O_2 solution in the tube. Add a small portion of manganese (IV) oxide in the tube. Test the releasing gas by a smoldering match.

$2H_2O_2 \rightarrow 2H_2O + O_2$

MnO_2 played a role of a ____________________________________ in this reaction.

Experiment 3. ***Production of sulfur.***

Dissolve a crystal of $Na_2S_2O_3 \cdot 5H_2O$ in the small volume of water in the tube. Add dilute HCl or H_2SO_4 solution in that tube in a drop by drop manner. Notice the opacity happened because of colloid sulfur formation.

$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S\downarrow + H_2O$

$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + S\downarrow + H_2O$

Experiment 4. ***Production and properties of metal sulfides.***

Use five tubes for this experiment. Pour 5 drops of solutions of soluble salts of the following metals in these tubes: zinc, manganese, cadmium, lead and copper. Add 5 drops of ammonium sulfide solution in each of these tubes, mix each tube. Notice the colors of precipitates. Write the reactions.

Complete form:____

Short ionic form:____

Complete form:____

Short ionic form:____

Complete form:____

Short ionic form:____

Complete form:____

Short ionic form:____

Complete form:____

Short ionic form:____

Add 1–1.5 ml of hydrochloric acid solution in each of the tubes. Write which precipitates have been dissolved: ____________________________________.

Solubility constants of sulfides

Formula	ZnS	MnS	CdS	PbS	CuS
K_s^0	$1.6 \cdot 10^{-24}$	$2.5 \cdot 10^{-10}$	$7.9 \cdot 10^{-27}$	$1.0 \cdot 10^{-27}$	$6.3 \cdot 10^{-36}$

Experiment 5. ***Oxidative properties of concentrated sulfuric acid.***

Pour 5–10 drops of concentrated sulfuric acid solution into two tubes. Put a piece of zinc in the first solution. Put a piece of copper in the second solution. Heat both tubes. Use the blue litmus paper to test the nature of a gas releasing from the tube with copper. Use the paper with lead (II) nitrate solution to test the nature of a gas releasing from the tube with zinc. Finish the redox reactions.

$Zn + H_2SO_4 \rightarrow$

reduction: ____

oxidation: ____

water molecules:_______________________________________

$Cu + H_2SO_4 \rightarrow$

reduction: ____

oxidation: ____

water molecules:_______________________________________

Experiment 6. ***Chemical properties of sulfites.***

Add water solution of sodium sulfite in the tube with *potassium permanganate* and dilute sulfuric acid solution. Notice the change in color. Balance the redox reaction by the electron-ion method.

$Na_2SO_3 + KMnO_4 + H_2SO_4 \rightarrow Na_2SO_4 + MnSO_4 + K_2SO_4 + H_2O$
reduction: ______________________________
oxidation: ______________________________
water molecules: ______________________________

Add water solution of sodium sulfite in the tube with *potassium sulfide* and dilute sulfuric acid solution. Balance the redox reaction by the electron-ion method.

$K_2S + Na_2SO_3 + H_2SO_4 \rightarrow S + K_2SO_4 + Na_2SO_4 + H_2O$
reduction: ______________________________
oxidation: ______________________________
water molecules: ______________________________

Write the conclusion: *"Sulfite anions are ________________ in the reaction with potassium permanganate, while they are ________________ in the reaction with potassium sulfide"*

EXPERIMENTAL WORK
"CHEMICAL PROPERTIES OF SODIUM THIOSULFATE"

The aim of the work: to study chemical properties of sodium thiosulfate.

Reactants: solutions of sodium thiosulfate, sulfuric acid, bromine water, iodine water, iron (III) chloride, silver (I) nitrate.

Experiment 1. ***Reaction between acids and sodium thiosulfate.***

Pour 5–6 drops of sodium thiosulfate solution in the tube. Add 3–4 drops of sulfuric acid solution in the same tube. In this reaction thiosulfuric acid is formed. That acid breaks down soon and forms dispersed sulfur and sulfur dioxide. Balance the redox reaction using an electron-ion method.

$Na_2S_2O_3 + H_2SO_4 \rightarrow S + SO_2 + Na_2SO_4 + H_2O$
reduction: ______________________________
oxidation: ______________________________
water molecules: ______________________________

Experiment 2. ***Reaction between sodium thiosulfate and bromine water.***

Pour 5–6 drops of sodium thiosulfate solution in the tube. Add bromine water to that tube in a drop by drop manner until the appearance of precipitate (sulfur). Balance the redox reaction using an electron-ion method.

$Na_2S_2O_3 + Br_2 + H_2O \rightarrow S + Na_2SO_4 + HBr$
reduction: ______________________________
reduction: ______________________________
oxidation: ______________________________
water molecules: ______________________________

Pour 5–6 drops of bromine water in the tube. Add sodium thiosulfate solution in that tube in a drop by drop manner until the disappearance of a brown color. Balance the redox reaction using an electron-ion method. In the excess of an oxidizer thiosulfate anions turn to sulfate anions completely.

$Na_2S_2O_3 + 4Br_2 + 5H_2O \rightarrow H_2SO_4 + Na_2SO_4 + 8HBr$

reduction: ____

oxidation: ____

water molecules: ____

Experiment 3. ***Reaction between sodium thiosulfate and iodine water.***

Pour 5–6 drops of iodine water in the tube. Add sodium thiosulfate solution in that tube in a drop by drop manner until the disappearance of initial color. Iodine oxidizes thiosulfate up to the tetrathionic acid.

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

Experiment 4. ***Reaction between sodium thiosulfate and iron (III) chloride.***

Pour 5–6 drops of iron (III) chloride in the tube. Add the same amount of sodium thiosulfate solution in that tube. Notice the change in color appeared due to $Na[Fe(S_2O_3)_2]$ formation. Put the tube in the holder and notice how the color is changing. Iron (III) cations are reduced and form iron (II) cations, thiosulfate anions are oxidized and form tetrathionates.

Experiment 5. ***Reaction between sodium thiosulfate and silver (I) nitrate solution.***

Pour 4–5 drops of silver (I) nitrate solution in the tube. Add sodium thiosulfate solution to that tube in a drop by drop manner. At first white precipitate of $Ag_2S_2O_3$ will be formed. Then the color will be turning to yellow, brown and black (because of silver (I) sulfide formation).

$2AgNO_3 + Na_2S_2O_3 \rightarrow Ag_2S_2O_3\downarrow + 2NaNO_3$

$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$

If there is an excess of sodium thiosulfate a soluble complex compound will be formed.

$AgNO_3 + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaNO_3$

Write the conclusion: *“Sodium thiosulfate is a ________________________________*

____ compound”.

LESSON 16
ELEMENTS FROM GROUPS VIIA AND VIIIA AND THEIR COMPOUNDS

Main topics of the lesson:

1. *Overall description of elements from VIIA subgroup.*
2. *Chemical properties of fluorine and its inorganic compounds.*
3. *Chemical properties of chlorine, bromine, iodine and their compounds.*
4. *Chemical properties of noble gases.*
5. *Biological role, the usage in medicine and pharmaceutical analysis of compounds containing elements from VIIA and VIIIA subgroups.*

The common electronic configuration for elements from VIIA group is ns^2np^5. They lack just one electron to fulfill their outer shells. Elements from the VIIIA group have already fulfilled electron shells (ns^2np^6), so they are quite inert (noble).

The group of halogens is the only group in the periodic table that contains elements in all three familiar states of matter at standard temperature and pressure: fluorine (F_2) and chlorine (Cl_2) are gases, bromine (Br_2) is liquid, while iodine (I_2) is solid. Astatine is thought to be solid.

Fluorine can show just one oxidation state of –1, unlike other halogens which usually demonstrate oxidation states of -1, +1, +3, +5 and +7.

Fluorine has the most instable molecule because it lacks d-orbitals. That substance is able to react even with the glass.

$SiO_2 + 2F_2 \rightarrow SiF_4 + O_2\uparrow$

In that reaction, as well as in the reaction with water, fluorine simply substitutes oxygen in compounds.

$2H_2O + 2F_2 \rightarrow 4HF + O_2\uparrow$

Reactions between fluorine and strong oxidizing acids show that these acids (HNO_3 and concentrated H_2SO_4) are not that much strong oxidizers as F_2.

$2HNO_3 + 4F_2 \rightarrow 2HF + 2NF_3 + 3O_2\uparrow$

$H_2SO_4 + 4F_2 \rightarrow 2HF + SF_6\uparrow + 2O_2\uparrow$

Fluoride ions cannot act as reducers, unlike other halide anions.

Halogens react with hydrogen and form diatomic molecules which demonstrate acidic properties in water solutions.

$H_2 + Cl_2 \rightarrow 2HCl$

At room temperature halogens (except fluorine) react with water and produce two acids: hydrochloric acid (HCl) and hypochlorous acid (HClO) in case of chlorine.

$Cl_2 + H_2O \rightarrow HCl + HClO$

Resulting solution can be used as a disinfectant or bleach.

Hydrochlorous acid is instable: it spontaneously forms hydrochloric acid and atomic oxygen, which is a free radical able to oxidize many substances including proteins of pathogenic bacteria.

At higher temperature the mixture of hydrochloric acid (HCl) and chloric acid ($HClO_3$) is formed.

$3Cl_2 + 3H_2O \rightarrow 5HCl + HClO_3$

Bromine slowly reacts with water and forms hydrogen bromide (HBr) and hypobromous acid (HBrO), while iodine is minimally soluble in water and does not react with it. However, iodine will form an aqueous solution in the presence of iodide ion, such as by addition of potassium iodide (KI), because the triiodide ion ($I_2 + I^- \rightarrow I_3^-$) is formed.

Halogens oxidize metals and produce salts.

$2Na + I_2 \rightarrow 2NaI$

$2Fe + 3Cl_2 \rightarrow 2FeCl_3$

A halogen with lower atomic number is able to oxidize anions of halogens with higher atomic numbers.

$Cl_2 + 2KBr \rightarrow 2KCl + Br_2$

$Br_2 + 2KCl \neq$

$Cl_2 + 2NaI \rightarrow 2NaCl + I_2$

$I_2 + 2NaCl \neq$

$Br_2 + 2KI \rightarrow 2KBr + I_2$

$I_2 + 2KBr \neq$

Hydrogen chloride can be produced from solid chlorides of metals in the reaction with concentrated sulfuric acid, unlike hydrogen bromide and iodide. HBr and HI are easily oxidized by concentrated sulfuric acid.

$NaCl(solid) + H_2SO_4(concentrated) \rightarrow NaHSO_4 + HCl\uparrow$

$2NaBr(solid) + 2H_2SO_4(concentrated) \rightarrow Na_2SO_4 + SO_2\uparrow + Br_2 + 2H_2O$

Chlorine gas can be produced in laboratory from hydrochloric acid in the reaction with an oxidizer (for example, with manganese oxide (IV) or potassium permanganate).

$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2\uparrow + 2H_2O$

$2KMnO_4 + 16HCl \rightarrow 2MnCl_2 + 5Cl_2\uparrow + 2KCl + 8H_2O$

Potassium iodide is a strong reducer. Aged and impure samples of that salt are yellow because of aerial oxidation of iodide ions to elemental iodine.

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

Chlorine gas reacts with alkali and produces different sets of salts depending on the temperature.

$Cl_2 + 2KOH \rightarrow KCl + KClO + H_2O$ (when the temperature is low)

$3Cl_2 + 6KOH \rightarrow 5KCl + KClO_3 + 3H_2O$ (when the temperature is high)

Potassium iodate (KlO_3) which is sometimes used for iodination of table salt can be produced in a similar reaction.

$3l_2 + 6KOH \rightarrow 5Kl + KlO_3 + 3H_2O$

Hydrogen chloride in normal conditions exists as a gas. The bond between hydrogen and chlorine is covalent polar, but not ionic. When hydrogen chloride is being dissolved in water the bond between hydrogen and chlorine becomes more polar and finally hydrogen chloride molecule breaks in two ions (H^+ and Cl^-). Resulting water solution is called «hydrochloric acid». In Russian hydrochloric acid has a trivial name which can be translated into English as «salty acid». That name came from the reaction of HCl formation from the table salt (NaCl).

$NaCl(solid) + H_2SO_4(concentrated) \rightarrow NaHSO_4 + HCl\uparrow$

Hydrochloric acid demonstrates all the common properties of acids. It reacts with alkalis and basic oxides to produce salts and water.

$HCl + KOH \rightarrow KCl + H_2O$

$2HCl + K_2O \rightarrow 2KCl + H_2O$

Hydrochloric acid reacts with metals situated before hydrogen in the reactivity series.

$Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$

$Cu + HCl \neq$

Reaction between hydrochloric acid and a salt is possible in case if insoluble salt or gas is produced.

$HCl + AgNO_3 \rightarrow AgCl\downarrow + HNO_3$

$2HCl + CaSO_3 \rightarrow CaCl_2 + SO_2\uparrow + H_2O$

The presence of Cl^- ions in the solution can be checked by the addition of Ag^+ ions ($AgNO_3$ solution is used since it is one of the very few soluble salts of silver). AgCl is a white precipitate. Bromine and iodide anions also form precipitates with Ag^+, but of a different color (AgBr is light yellow, while AgI is yellow).

$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl\downarrow$

$LiBr + AgNO_3 \rightarrow LiNO_3 + AgBr\downarrow$

$KI + AgNO_3 \rightarrow KNO_3 + AgI\downarrow$

Helium and neon are the most inert noble gases. Heavier elements from the group VIIIA (argon, krypton, xenon and radon) still can be oxidized and demonstrate oxidation states of +2, +4, +6 and +8. Abovementioned elements can form different fluorides (XeF_2, XeF_4, XeF_6, KrF_2, KrF_4, RnF_4).

Xenon fluorides are hydrolyzed by water.

$XeF_4 + H_2O = XeOF_2 + 2HF$

$XeF_6 + H_2O = XeOF_4 + 2HF$

In those reactions xenon oxides can be formed as well.

$XeF_6 + 3H_2O = XeO_3 + 6HF$

Interestingly, xenon cannot react directly with oxygen to produce oxides.

Such compounds are prone for disproportioning reactions.

$2XeF_2 = Xe\uparrow + XeF_4$

$3XeF_4 = Xe\uparrow + 2XeF_6$

It is predictable that atoms of xenon in such compounds are strong oxidizers.

$4KI + XeF_4 \rightarrow Xe + 2I_2 + 4KF$

$Pt + XeF_4 + 2HF \rightarrow Xe + H_2[PtF_6]$

Even platinum can be oxidized by the xenon (IV) fluoride in the presence of hydrogen fluoride.

Fluorine is known as a necessary element for tooth tissue. Chloride anions are the most common anions both inside and outside the cells. Iodine is accumulated in thyroid gland where it becomes a building block of such hormone as triiodothyronine (T_3) that is produced from thyroxine (T_4). Bromine has no definite function in the organism, while it is known to demonstrate sedative effects. Noble gases are used as narcoleptic agents in anesthesiology because they can bind different receptors in the nervous system. Radon is used in radiation therapy.

Chains of chemical reactions

$Cl_2 \rightarrow Ca(ClO)_2 \rightarrow HClO \rightarrow HCl \rightarrow Cl_2$

$HCl \rightarrow NaCl \rightarrow Cl_2 \rightarrow KClO_3 \rightarrow KCl$

$KClO \rightarrow HClO \rightarrow HCl \rightarrow FeCl_2 \rightarrow FeCl_3$

$HBr \rightarrow Br_2 \rightarrow KBrO_3 \rightarrow HBrO_3 \rightarrow FeBr_3$

Finish chemical equations

$K_2Cr_2O_7 + HCl \text{ (conc.) } \xrightarrow{t}$ ____________________

$KI + H_2SO_4 \rightarrow$ ____________________

$HBrO_3 + I_2 \rightarrow$ ____________________

$I_2 + HNO_3 \text{ (conc.) } \rightarrow$ ____________________

$HClO_3 + P + H_2O \rightarrow$ ____

$HClO_4 + P_2O_5 \rightarrow$ ____

Problems

1. An excess of chlorine was passed through 200 g of hot potassium hydroxide solution. At decomposition of one of the produced salts, 4.00 L of oxygen (in normal conditions) was obtained. What was a mass fraction of potassium hydroxide in the solution?

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2. What mass of hydrogen iodide is required to add to 30 g of a solution with a mass fraction of HI equal to 3 % to obtain a solution with a mass fraction of the acid equal to 15 %?

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3. What mass of potassium permanganate and volume of hydrochloric acid solution with a mass fraction of HCl equal to 26.9 % (ρ = 1.235 g/ml) are required to produce chlorine which can completely force out bromine from potassium bromide containing in 250 g of solution with a mass fraction of KBr equal to 14.8 %.

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Multiple choice questions

1. Choose the series in which all the substances react with hydrochloric acid:
a) $Cu(OH)_2$, $ZnSO_4$, $AgNO_3$;
b) $NaHCO_3$, NaBr, Hg;
c) MnO_2, $CaCO_3$, SiO_2;
d) $Cr(OH)_3$, $Na_3[Al(OH)_6]$, Fe.

2. Choose the statements about halogens as pure elements (simple substances):
a) halogens have a characteristic strong smell;
b) the normal development of bones is impossible without fluorine;
c) the lack of iodine in the water and food reduces the production of thyroid hormones;
d) halogens are readily soluble in organic solvents, and less soluble in water.

3. The pH value in 0.001M hydrobromic acid solution is equal to:

a) 3; b) 11; c) 12; d) 2.

4. Define the correspondence between the reactants and the visible effects of their interactions:

1) $AgNO_3 + Cl_2 \rightarrow$
2) $AgNO_3 + KCl \rightarrow$
3) $AgNO_3 + KBr \rightarrow$
4) $AgNO_3 + NaI \rightarrow$

a) gas;
b) brown precipitate;
c) green color;
d) white precipitate;
e) light-yellow precipitate;
f) yellow precipitate.

5. Which substances are produced if calcium chlorate is heated up in the presence of MnO_2 catalyst:

a) potassium chloride and oxygen;
b) potassium hypochlorite and oxygen;
c) potassium chloride and perchlorate;
d) potassium perchlorate and ozone.

6. Because of fluorine high reactivity, it may be produced only by the reaction(s):

a) the oxidation of fluoride ions with molecular chlorine;
b) the electrolysis of the solutions containing fluoride ions;
c) the electrolysis of liquid salts (at high temperature) containing fluoride ions;
d) the electrolysis of fluorine salts containing oxygen.

7. Chlorine dissolves in cold water. The resulting solution contains the particles:

a) ClO_3^-, Cl^-, H^+, H_2O;
b) ClO^-, Cl^-, Cl_2, H^+, H_2O;
c) ClO_3^-, Cl^-, OH^-, H_2O;
d) ClO_2^-, Cl^-, Cl_2, H_2O.

8. Which reactions are impossible in water solution:

a) $KBr + I_2 \rightarrow$
b) $KBr + Cl_2 \rightarrow$
c) $KCl + I_2 \rightarrow$
d) $KCl + Br_2 \rightarrow$

9. Hydrochloric acid reacts with each substance in the series:

a) sodium carbonate, calcium hydrogen carbonate, zinc, aluminum oxide;
b) potassium chlorate, copper (II) oxide, lead (IV) oxide, iron (III) hydroxide;
c) potassium hydrogen sulfite, potassium bromide, concentrated sulfuric acid, calcium nitrate;
d) manganese (II) oxide, calcium carbonate, sodium silicate, ammonia;
e) malachite, dolomite, potassium chlorate, hydrofluoric acid.

10. Chlorine atoms act as both oxidizers and reducers in the reactions:

a) $Cl_2 + NH_3 \rightarrow$

b) $Cl_2 + NaBr \rightarrow$

c) $Cl_2 + NaOH \rightarrow$

d) $Cl_2 + H_2O \rightarrow$

EXPERIMENTAL WORK
"PROPERTIES OF ELEMENTS FROM VIIA GROUP"

The aim of the work: to study chemical properties of elements from VIIA group.

Reactants: iron (II) sulfate; chrome sulfate; sodium chloride; potassium bromide; potassium iodide; potassium dichromate; solutions of: ammonia; chlorine water; sodium hydroxide (0.1 M); silver nitrate; sulfuric acid.

Experiment 1. ***Oxidation of iron (II) cations by chlorine.***

Pour iron (II) solution into two tubes. Add distilled water in the first tube. Add chlorine water in the second tube. Then add ammonia solution to the both tubes. Notice the colors of precipitates in each of the two tubes.

$FeSO_4 + 2NH_3 \cdot H_2O \rightarrow Fe(OH)_2\downarrow + (NH_4)_2SO_4$

$2FeSO_4 + 6NH_3 \cdot H_2O + Cl_2 \rightarrow 2Fe(OH)_3\downarrow + 2NH_4Cl + 2(NH_4)_2SO_4$

Experiment 2. ***Oxidation of chrome (III) cation into the chromate anion by chlorine water in the basic medium.***

Pour 1–2 drops of chrome (III) sulfate in the tube. Add concentrated solution of an alkali to that tube until the dissolving of a precipitate. Then add an excess of chlorine water to the same tube. Heat the tube. Notice the shift of color from green to yellow. Write complete reactions knowing their short ionic forms.

Short ionic form: $Cr^{3+} + 6OH^{-} \rightarrow [Cr(OH)_6]^{3-}$

Complete form:____

Short form: $2[Cr(OH)_6]^{3-} + 3Cl_2 + 4OH^{-} \rightarrow 2CrO_4^{2-} + 6Cl^{-} + 8H_2O$

Complete form:____

Experiment 3. Test reactions for halide ions.

Pour 3–5 drops of NaCl in the first tube, pour 3–5 drops of KBr in the second tube, pour 3–5 drops of KI in the third tube. Add 1–3 drops of silver nitrate in each of those three tubes. Notice the colors of precipitates. Write reactions in complete and short ionic forms.

Complete form:____

Short ionic form:______________________________________

Complete form:____

Short ionic form:______________________________________

Complete form:____

Short ionic form:______________________________________

Experiment 4. ***Reduction of potassium dichromate by halides.***

Pour 2–4 drops of potassium dichromate (in the acidic medium) in each of three tubes. Add 2–3 drops of potassium iodide in the first tube, add 2–3 drops of sodium bromide in the second tube, add 2–3 drops of sodium chloride in the third tube.

Write redox reactions (in case if they are possible) and balance them by an electron-ion method.

Complete reaction: ____________________
reduction: ____________________
oxidation: ____________________
water molecules: ____________________
Complete reaction: ____________________
reduction: ____________________
oxidation: ____________________
water molecules: ____________________
Complete reaction: ____________________
reduction: ____________________
oxidation: ____________________
water molecules: ____________________

Write the conclusion: *“The oxidizing properties are ____________________ in the following line:* $Cl_2 – Br_2 – I_2$*”.*

LESSON 17

COLLOQUIUM ON THE CHEMICAL PROPERTIES OF ELEMENTS FROM p-BLOCKS OF THE PERIODIC SYSTEM

Main types of tasks:

1. *Chains of chemical reactions.*
2. *Reactions with complex compounds.*
3. *Hydrolysis reactions.*
4. *Redox reactions.*
5. *Short ionic equations.*
6. *Problems.*
7. *Theoretical questions.*

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CONTENTS