

JUNIOR LEAGUE

Problem 1

ROCKET FUEL



Most space travel is carried out through the use of chemical rocket fuel. The fuel mixture must include an oxidant and reducing agent, which, as a result of the chemical reaction, releases the gaseous products that do the work and the energy that heats the released gases.

One of the most common solid oxidants used in rocket fuels is ammonium perchlorate. Organic polymers, such as polyethylene (CH₂)_n or polyisoprene (C₅H₈)_n, are usually used with it as a reducing agent.

Questions:

1. Write equations of reactions which take place in a rocket engine when ammonium perchlorate is used as an oxidant and reducing agent is: a) polyethylene; b) polyisoprene. Consider that the same products are obtained in the both reactions and 9.672 g of ammonia perchlorate is necessary for oxidation of 1 g of polyethylene. It is recommended to write polymer formulas in reaction equations as monomer units for simplifying.

It is possible to find connection between using fuel and reachable speed of flight. To simulate a space flight, one can use the Tsiolkovsky formula, according to which the initial mass of a rocket with fuel (m_0), the mass of a rocket without fuel (m), the velocity of the gases from the rocket engine (v_0) and the maximum speed reached by the rocket (v) are related by the relation:

$$\frac{m_0}{m} = e^{\frac{v}{v_0}}$$

The rate of gas outflow is directly proportional to the square root of the ratio of the gas temperature in Kelvin to the average molar mass of the gases: $v_0 \sim \sqrt{\frac{T}{M_{cp}}}$.

In other words, the success of flight (the maximum speed that a rocket is capable of developing) directly depends on the thermochemistry of the reaction between an oxidant and a reducing agent.

For example, for space travel, a mixture of ammonium perchlorate and polyethylene perchlorate in stoichiometric proportions is used as rocket fuel. Next thermochemical data are known: the heat of combustion of polyethylene in oxygen per 1 mole of CH₂ groups is equal to $Q_1 = 660$ kJ / mol, the heat of decomposition of ammonium perchlorate into simple substances and gaseous water per one mole of salt is $Q_2 = 188$ kJ / mol. The heat of the gas-phase reaction (based on 1 mole of oxygen) is also known:



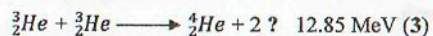
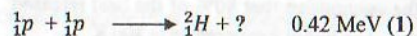
2. Calculate the value of the average molar mass of gases M_{av} formed during the chemical reaction of ammonium perchlorate with polyethylene.
3. Calculate the mass fractions of polyethylene and ammonium perchlorate in a stoichiometric mixture corresponding to the chemical reaction taking place between them.
4. Find the thermal effect of the reaction taking place in our rocket engine and express it in units of: a) kJ per 6 moles of ammonium perchlorate, b) kJ per kilogram of the mixture.
5. Assuming that the heat capacities of gaseous HCl and nitrogen are 31 J / (mol·K) (each), of gaseous water is 40 J / (mol·K), of carbon dioxide is 54 J / (mol·K), calculate the temperature T of gases, formed during the reaction. Proceed here from the assumption that 80% of the heat released during the reaction is expended to heat the gases that form. The initial temperature is 300 K.
6. Find the velocity v_0 of the gases outflow from the engine, knowing that the rate of escape of carbon dioxide at a temperature of 3000 K is 1.1 km/s.
7. Let the mass of the missile body without fuel equal 20 tons. Find the minimum mass of the fuel mixture, which is necessary for the rocket to reach the velocity $v = 5$ km/s.
8. Often, a solid metal, for example aluminum, is added to the polymer and oxidant fuel mixtures. No gases are formed in reactions involving aluminum. Explain, what is the role of metals in such mixtures?

Problem 2

SOLAR CHEMISTRY



The sun is the closest star to Earth. Solar energy is important for life on Earth. As is known, reactions of thermonuclear fusion occur on the Sun – synthesis reactions of heavy nuclei from lighter nuclei. A huge amount of energy is released in these reactions which spread on the whole Solar system. The main chain of reactions on the Sun is the synthesis of helium nuclei from protons:



Questions:

- Write the equations of nuclear reactions 1-3. Calculate the total energy released on the Sun (in MeV) per one synthesized nucleus of ${}^4_2\text{He}$.

Currently there are a large amount of solar power plants in many countries which are used for supplying cities by energy and satisfy most of the need of electrical power. In far located regions of the Republic of Sakha electric energy is generated by diesel power stations. However, the biggest solar power plant beyond the Arctic Circle «Batagai» which is located in Batagai village of the Republic of Sakha was put into operation in 2015. Power of this station is 1MW.

- Calculate how much of diesel fuel (in tonnes) in 1 year can be saved using solar power plant «Batagai». The average duration of daylight beyond the Arctic Circle is 14 hours, efficiency of diesel power station is 40%. Diesel fuel burning reaction can be shown as the reaction of cetane burning:



Reference data:

$$Q_f(\text{H}_2\text{O}(\text{gas})) = 242 \text{ kJ/mol},$$

$$Q_f(\text{CO}_2(\text{gas})) = 394 \text{ kJ/mol},$$

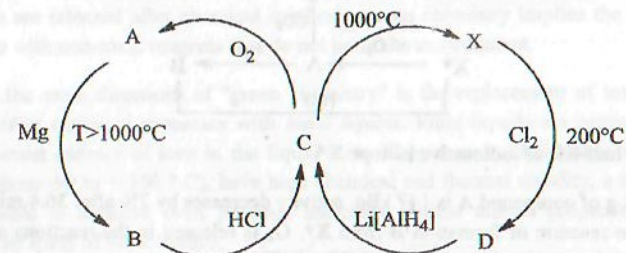
$$Q_f(\text{C}_{16}\text{H}_{34}(\text{liq})) = 375 \text{ kJ/mol},$$

$$1 \text{ W} = 1 \text{ J/s}.$$

$$1 \text{ eV (electronvolt)} = 1.6 \cdot 10^{-19} \text{ J}$$

- Using the results obtained in points 1 and 2, calculate how many nuclei (in moles) should be formed on the Sun in order to release the same amount of energy as the solar power plant "Batagai" for 1 year.

Obviously, solar panels are better for environment than gas, oil and coal, because there is no any pollution produced by solar panels. However, their production costs are much more expensive than the production cost of gas or oil, in addition, the efficiency of solar cells depends heavily on the weather conditions and the number of sunny days. Element **X** is most widely used in the production of solar panels. It is the second most abundant element in the Earth's crust. Photocells based on **X** have the highest efficiency of light transformation to electric energy. That's why clearancy of substances is important. The scheme of chemical reactions with **X** shown below:



C is the gas with the relative density of gas with respect to air 1.103, **D** – colorless fuming liquid. **X** obtaining is conducted without O_2 .

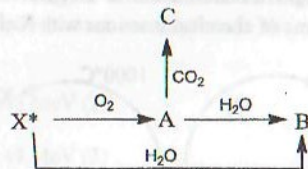
- Determine element **X** and compounds **A-D**. Write equations of chemical reactions (6 reactions).

Problem 3

RADIOACTIVE ELEMENT



The element X is very important for the vital activity of human organism. The scheme below shows the reactions of a radioactive isotope X* of this element.



1. Calculate the half-life of radioactive isotope X*.

The activity of 1 g of compound A is 147 kBq, activity decreases by 2% after 36.4 million years. H₂ is released in the reaction of formation B from X*. O₂ is released in the reactions of formation B from A as well as in reaction between A and CO₂. Difference in atomic masses between X and X* is 1.

2. Determine element X and compounds A-C. Write the equations of chemical reactions.

The radionuclide X* mainly undergoes β⁻-decay with maximal energy of beta-particles E_{β, max} = 1.31 MeV. Beta radiation is very dangerous if radionuclide is inside the body, but radioactivity of isotope X* is low and called «natural human radioactivity».

3. Write equation of X* β⁻-decay.
4. Calculate the specific energy (J/kg) absorbed by human body with weight 70 kg during 24 hours of beta radiation. The mass fraction of X in organism – 0.3%, molar fraction of X* - 0.0117%. Average energy of β-particles is 0.4 E_{β, max}, neglect removal from organism. How the calculated value is called?
5. Is the calculated quantity safe for human body if the permissible limit is 1 mSv per year.

Reference data:

1Bq (Becquerel) = 1 decay/ 1sec,
 1eV (electronvolt) = 1.6*10⁻¹⁹ J,
 1Sv (sievert) = 1J/ 1kg for β-particles

$$\text{Law of radioactive decay } A = A_0 e^{-\lambda t}, \lambda = \frac{\ln 2}{T_{1/2}},$$

Activity $A = \lambda N$

A₀ – initial activity,

λ – decay constant,

T_{1/2} – half-life,

N – number of radioactive particles.

Problem 4

GREEN CHEMISTRY



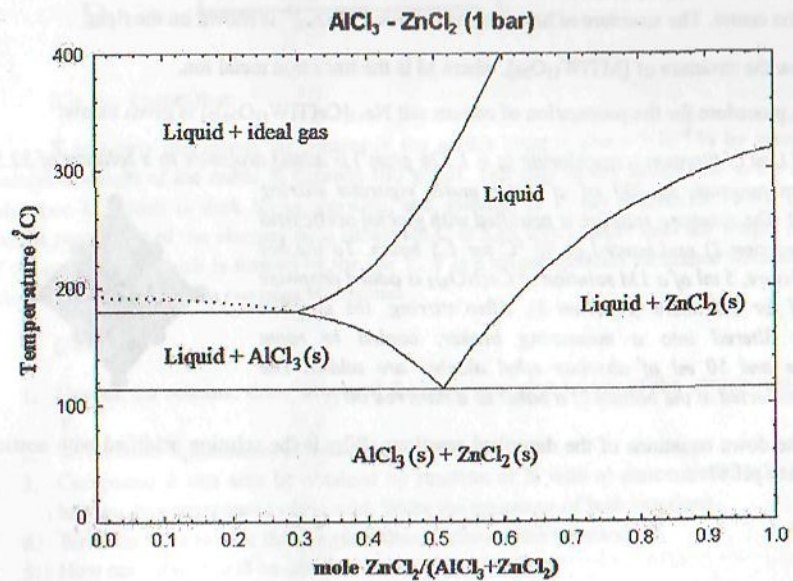
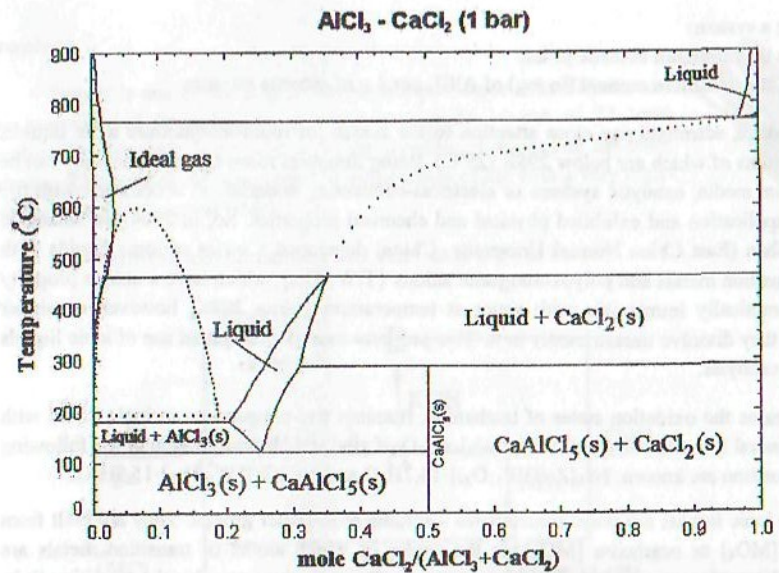
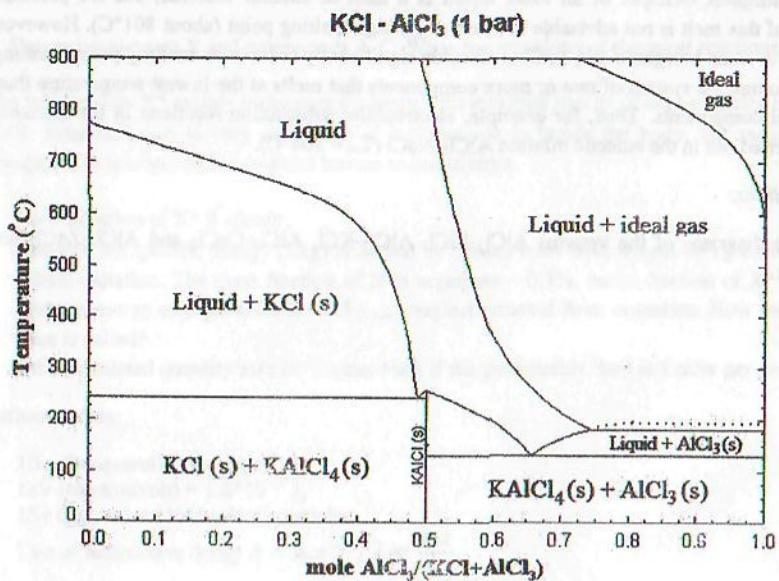
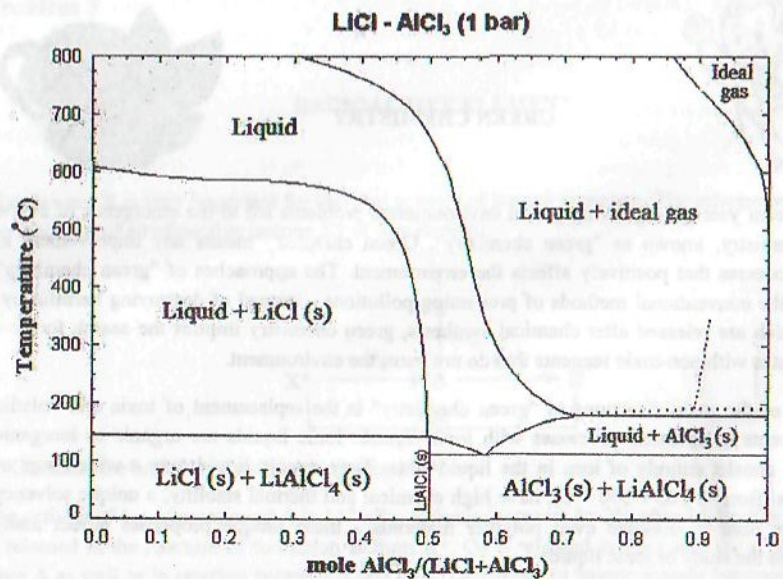
In recent years, the growing global environmental problems led to the emergence of a new trend in chemistry, known as "green chemistry". Green chemistry means any improvement in chemical processes that positively affects the environment. The approaches of "green chemistry" differ from the conventional methods of preventing pollutions - instead of destroying harmful by-products which are released after chemical synthesis, green chemistry implies the search for new synthetic routes with non-toxic reagents that do not harm the environment.

One of the main directions of "green chemistry" is the replacement of toxic and volatile organic solvents in chemical processes with *ionic liquids*. Ionic liquids are organic or inorganic salts, which consist entirely of ions in the liquid state. They remain liquid over a wide range of temperatures (from -90 to +350 °C), have high chemical and thermal stability, a unique solvency and they are able to dissolve even polymer materials - these unique properties attract many researchers to the study of ionic liquids.

The simplest example of an ionic liquid is a melt of sodium chloride, but the practical application of this melt is not advisable because of its high melting point (about 801°C). However, when added to some inorganic salt, sodium chloride significantly reduces its melting point, forming a eutectic mixture - a system of two or more components that melts at the lowest temperature than its individual components. Thus, for example, electrophilic substitution reactions in the aromatic series are carried out in the eutectic mixture AlCl₃-NaCl (T_m = 104°C).

Questions:

Phase diagrams of the systems AlCl₃-LiCl, AlCl₃-KCl, AlCl₃-CaCl₂ and AlCl₃-ZnCl₂ are given below:



1. Select a system:

- with the minimum eutectic point;
- with the minimum amount (in mg) of AlCl_3 per 1 g of eutectic mixture.

Nowadays, scientists pay close attention to the search for room-temperature ionic liquids, the melting points of which are below 298K (25°C). Being liquids at room temperature, they can be unique reaction media, catalytic systems or electrical-conducting materials in accordance with the purposes of application and exhibited physical and chemical properties. So, in 2004, the scientific group of J. Shan (East China Normal University, China) developed a series of ionic liquids with cations of transition metals and polyoxotungstate anions $\{\text{TiW}_{11}\text{O}_{39}\}$, which have a unique property – they are practically immiscible with water at temperatures below 298K, however, at higher temperatures they dissolve unrestrictedly in it. This property caused widespread use of ionic liquids in interphase catalysis.

2. Determine the oxidation states of lanthanide, titanium and tungsten in an ionic liquid with the general formula $\text{Na}_{13}[\text{Ln}(\text{TiW}_{11}\text{O}_{39})_2] \cdot x\text{H}_2\text{O}$, if zinc and chromium salts of the following composition are known: $\text{Na}_6[\text{ZnTiW}_{11}\text{O}_{39}] \cdot 14,7\text{H}_2\text{O}$ and $\text{Na}_5[\text{CrTiW}_{11}\text{O}_{39}] \cdot 15,9\text{H}_2\text{O}$.

These ionic liquids are polyoxometallates - anionic multicenter groups. They are built from tetrahedrons $[\text{MO}_4]$ or octahedra $[\text{MO}_6]$, in the center of which atoms of transition metals are located, and the vertices are occupied by oxygen atoms. Oxygen atoms are also the transition links of all tetrahedral or octahedral structural elements, and the ion of another transition metal can be located in the center. The structure of hexatungstate anion $[\text{W}_6\text{O}_{19}]^{2-}$ is shown on the right.

3. Draw the structure of $[\text{MTiW}_{11}\text{O}_{39}]$, where M is the transition metal ion.

The procedure for the preparation of cerium salt $\text{Na}_{13}[\text{Ce}(\text{TiW}_{11}\text{O}_{39})_2]$ is given below:

"1.11 ml of titanium tetrachloride ($\rho = 1.726 \text{ g/cm}^3$) is added dropwise to a solution of 32.3 g of sodium tungstate in 200 ml of water under vigorous stirring (reaction 1). The resulting solution is acidified with glacial acetic acid to pH 6 (reaction 2) and heated at 60 °C for 1.5 hours. To the hot reaction mixture, 5 ml of a 1M solution of $\text{Ce}(\text{NO}_3)_3$ is added dropwise and stirred for 2.5 hours (reaction 3). After stirring, the reaction mixture is filtered into a measuring beaker, cooled to room temperature and 50 ml of absolute ethyl alcohol are added. The product is collected at the bottom of a baker as a dark red oil ... "

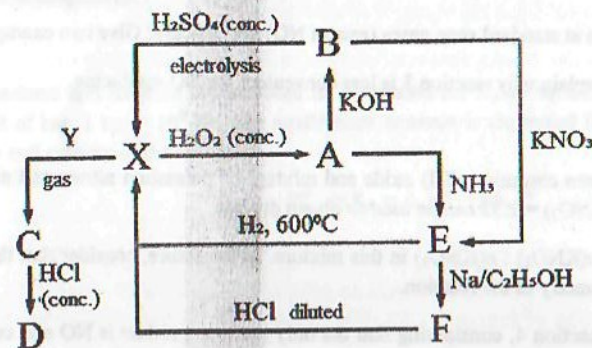


4. Write down equations of the described reactions. Why is the solution acidified with acetic acid to pH 6?

Problem 5

Tomtor is one of the largest rare earth metal deposits in Yakutia and The resources of deposits are sufficient to provide 14 out of 27 'critical' development of which is considered by the program of increasing the competitiveness of the industry. The forecast resources are 154 million tons of ore with a very high content of rare earth elements, one of which is X.

The scheme of transformations with element X is given below:



It is also known that:

X is a very rare metal, its content in the earth's crust is about $7 \cdot 10^{-8} \%$ by mass, and the molecular weight of the metal X exceeds 100 g/mol. The only binary compound in the scheme is substance C, which is dark brown crystals, and solution of D has a greenish-brown color. The weight percentage of the element X in substance C is 5,82 times larger than the weight percentage of the counterion, which is formed by the gas Y. Y is a simple gaseous substance without color and odor. The substance F is a complex compound.

Questions:

1. Decode the scheme, draw structural formulas and give names of the compounds A-F, X and Y.
2. Write down equations of all reactions.
3. Compound A can also be obtained by reaction of X with a) concentrated sulfuric acid on heating; b) concentrated nitric acid. Write the equations of both reactions.
4. Write the equation for the complete dissociation of the substance D.
5. How can substance B be obtained from X?

Problem 6

NITROGEN MONOXIDE

YES

NO

Nitrogen monoxide (NO) is one of stable radical compound. It is usually produced from salts of nitrous acid - potassium or sodium nitrite. Reactions between potassium nitrite and acidified with sulfuric acid potassium iodide (**reaction 1**) or yellow blood salt (**reaction 2**). Reaction with dilute sulfuric acid in the absence of reducing agents is less preferable (**reaction 3**).

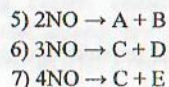
Questions:

1. Molecules of what stable at standard state gases (except NO) are radicals? Give two examples.
2. Write reactions 1 – 3. Explain why reaction 3 is less convenient for NO producing.

Solid-phase reaction between chromium (III) oxide and mixture of potassium nitrate and nitrite in mass ratio $m(\text{KNO}_2) : m(\text{KNO}_3) = 2.53$ can be used to obtain dry gas.

3. Calculate molar ration $n(\text{KNO}_2) : n(\text{KNO}_3)$ in this mixture. In the future, consider that this ratio corresponds to the stoichiometry of the reaction.
4. Write equation of the reaction 4, considering that the only gaseous product is NO and only one substance leave in the solid phase.
5. Calculate mass of chromium (III) oxide which is necessary for reaction with 10.00 g of mentioned above mixture of potassium nitrate and nitrite.

Despite its stability at standard state NO can decompose. It decomposes at 1000 – 1200 °C in accordance with the equation of **reaction 5**. **Reaction 6** occurs at high pressure and moderately high temperature. When gas is absorbed by zeolite, **reaction 7** occurs. Equations of these reactions with coefficients are presented below:



Values $\Delta_r H^\circ = -155.4 \text{ kJ/mol}$, $\Delta_r S^\circ = -172.1 \text{ J/(mol}\cdot\text{K)}$ are known for the **reaction 6**.

6. Determine products of each reaction (substances A – E), write their formulas.
7. Calculate equilibrium constant for **reaction 6** at 800 K.

NO was heated until 800 K in a vessel with 2 L volume. Initial pressure of NO at 800 K was 10 bar.

8. Calculate NO amount in the vessel after finishing of the **reaction 6** (at the onset of chemical equilibrium), if vessel volume and temperature in the vessel are constant.

If you could not solve the equation that you compiled, please write down this equation in solution.

9. In what case will final (equilibrium) partial pressure of NO be more: in the case of reaction 6 is conducted at constant pressure and temperature or in the case of reaction 6 is conducted at constant volume and temperature?

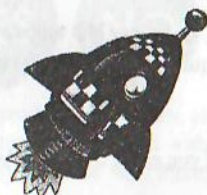
Note: products and reagents are included in expression for K_p as equilibrium pressures measured with unit of bar, $1 \text{ bar} = 10^5 \text{ Pa}$. The equilibrium constant is expressed in terms of changes in the enthalpy and entropy of the reaction:

$$-RT \cdot \ln K_p = \Delta_r H^\circ - T\Delta_r S^\circ$$

SENIOR LEAGUE

Problem 1

ROCKET FUEL



Most space travel is carried out through the use of chemical rocket fuel. The fuel mixture must include an oxidant and reducing agent, which, as a result of the chemical reaction, releases the gaseous products that do the work and the energy that heats the released gases.

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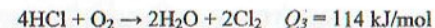
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5. Assuming that the heat capacities of gaseous HCl and nitrogen are $31 \text{ J/(mol}\cdot\text{K)}$ (each), of gaseous water is $40 \text{ J/(mol}\cdot\text{K)}$, of carbon dioxide is $54 \text{ J/(mol}\cdot\text{K)}$, calculate the temperature T of gases, formed during the reaction. Proceed here from the assumption that 80% of the heat released during the reaction is expended to heat the gases that form. The initial temperature is 300 K .
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8. Often, a solid metal, for example aluminum, is added to the polymer and oxidant fuel mixtures. No gases are formed in reactions involving aluminum. Explain, what is the role of metals in such mixtures?

Problem 2

IODINE EXTRACTION



Often, chemists are faced with the task of extracting iodine from an aqueous solution: for purification, for separation, for demonstration of impressive experiments. One of simple methods to do it is iodine extraction with organic solvents (part of solved substance transits to organic phase after addition of organic solvent to aqueous solution).

Questions:

1. What are the color of solutions of iodine in spirit and benzene?

2. How can blue solution of iodine be obtained?

Extraction process is characterized by distribution constant (equilibrium constant of transition $I_{2(aq)} \rightarrow I_{2(org)}$). Distribution constant can be expressed similarly both through equilibrium iodine concentration in water and organic phases and through solubility of

iodine in appropriate solvents:

$$K_{D(\text{org. phase-water})} = \frac{[I_{2(\text{org. phase})}]}{[I_{2(\text{aq. phase})}]} = \frac{s(I_{2(\text{org. phase})})}{s(I_{2(\text{aq. phase})})}$$

After finishing extraction process with organic solvent A from saturated aqueous solution (under crystalline iodine), iodine concentration in water was by 208 times lower than in the solvent A. Iodine solubility in pure water is 0.280 g/L. Neglecting by existence of non-molecular forms of iodine and by solubility of solvents in each other, solve next tasks:

3. Calculate iodine distribution constant between solvent A and water, and solubility of iodine in solvent A (mol/L). Consider the task data fairly accurate and give answer with an accuracy of 4 significant digits.

Iodine concentration in water phase decrease by 37.5 times in comparison with initial after extraction of iodine from 100 ml of saturated aqueous solution with organic solvent B non-mixable with water.

4. Calculate iodine distribution constant in a system solvent B/water and iodine distribution constant in a system solvent B/solvent A, considering that solvents don't mix with each other.

5. Calculate iodine solubility in the solvent B (mol/L). Consider the task data fairly accurate and give answer with an accuracy of 4 significant digits.

10.00 g of solid iodine was put into a flask in which water, solvents A and B were poured one by one. All iodine was solved and total volume of all three solutions was 677 ml. After thorough mixing of flask content and solution layering, all three phases (solution of I_2 in A, solution I_2 in B, aqueous solution of I_2) were saturated solutions. It is known, the volume of added solvent B is greater than the volume of solvent A by 10 ml.

6. Determine volumes of water, solvents A and B in obtained three-phase system.

7. Propose two principally different chemical methods to transit much part of iodine into aqueous phase in system aqueous/solvent B (in state of any substance), assuming that B is an aromatic hydrocarbon. Write appropriate reaction equations.

Problem 3

ABOUT HONEY



Many people think that honey is one of the most useful products. Currently, honey is appreciated not only because of its unique properties for cooking, but due to its antibacterial activity.

It is believed that the antibacterial activity of honey is mainly caused by presence of low-molecular substance A. Substance A in honey is formed in result of oxygen effect on substance X (one of two main monoses in honey) in presence of enzyme X-oxidase. 1 molecule of water is absorbed and 1 molecule of acid B is released in this reaction. Acid B contains 36.73 wt.% of carbon and 57.14 wt.% of oxygen and plays role of acidity regulator establishing pH in honey which also effect on antibacterial activity.

Questions:

1. Determine structural and molecular formulas of substances A, B and X if it is known, that substance A easily decomposes to more simple products in presence of catalase enzyme or manganese dioxide and substance X give sweet taste to honey. Approve your answer by calculations. Write equations of the reactions of substances A and B formation from X.

2. What monose, besides substance X, is contained in honey in large quantities? Call it. What is the most monosaccharide in honey?

As is known, not at all kinds of honey contain considerable amounts of substance A. It was found that in this case substance C is a substance with antibacterial activity. It forms in result of slow spontaneous dehydration of dihydroxyacetone or glyceraldehyde and doesn't contain cyclic fragments. These same transformations can occur enzymatically with monophosphates of dihydroxyacetone and glyceraldehyde, which in the body are in balance with one another.

3. Give structural formulas of named above dihydroxyacetone, glyceraldehyde, monophosphate of dihydroxyacetone and monophosphate of glyceraldehyde.

4. Determine the structure of substance C, if it is known that C can produce a "silver mirror".

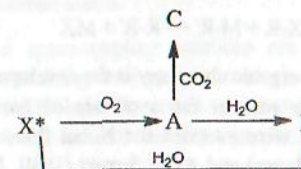
5. During what biochemical process are 1 molecule of monophosphate dihydroxyacetone and 1 molecule of glyceraldehyde phosphate formed from 1 molecule of X in a body in several stages? What substance, that has the same carbon skeleton as C, is final product of this process. Give its structural formula and name.

Problem 4

RADIOACTIVE ELEMENT



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1Bq (Becquerel) = 1 decay/ 1sec,
 1eV (electronvolt) = 1.6*10⁻¹⁹ J,
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Law of radioactive decay $A = A_0 e^{-\lambda t}$, $\lambda = \frac{\ln 2}{T_{1/2}}$,

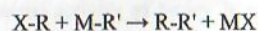
Activity $A = \lambda N$
 A₀ – initial activity,
 λ – decay constant,
 T_{1/2} – half-life,
 N – number of radioactive particles.

Problem 5

NOBEL REACTIONS



Cross-coupling reactions are a broad class of organic reactions that involve the interaction between two different organic substrates (most often organoelement compounds and organic halides) leading to the formation of a new carbon-carbon bond:



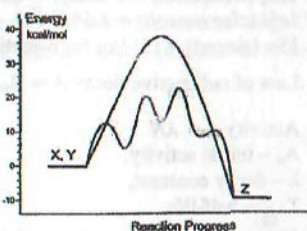
An important task of modern organic chemistry is the development of highly selective cross-coupling reactions that play a key role in the synthesis of complex functionalized organic molecules. In 2010, three scientists were awarded the Nobel Prize in Chemistry: Richard Heck (1931, USA), Eichi Negishi (1935, Japan) and Akira Suzuki (1930, Japan) for the development of cross-coupling reactions catalyzed by palladium (II) organometallic complexes. Due to the low cost of palladium complexes, their exceptional selectivity to many functional groups, high yields and mild reaction conditions, Pd-catalyzed cross-coupling reactions are currently of fundamental importance in fine organic synthesis. The general reaction schemes are given below:

| | |
|--|--|
| <p>The Heck reaction</p> $R^1X + R^2\text{CH=CH}_2 \xrightarrow{[Pd], \text{ base}} R^2\text{CH=CH}R^1$ <p>R¹ = alkenyl, (hetero)aryl, alkyl R² = alkenyl, (hetero)aryl, alkyl X = Cl, Br, I, OTf, OTs, N₂⁺</p> | <p>The Negishi reaction</p> $R^1X + R^2ZnX \xrightarrow{[Pd]} R^1-R^2 + ZnX_2$ <p>R¹ = alkenyl, (hetero)aryl, alkynyl, acyl R² = alkenyl, (hetero)aryl, alkynyl, alkyl X = Cl, Br, I, OTf, OAc</p> |
| <p>The Suzuki reaction</p> $R^1X + R^2B(Y)_2 \xrightarrow{[Pd], \text{ base}} R^1-R^2$ <p>R¹ = alkenyl, (hetero)aryl, alkyl R² = alkenyl, (hetero)aryl, alkynyl, alkyl X = Cl, Br, I, OTf Y = alkyl, OH, O-alkyl</p> | <p>The Sonogashira Reaction</p> $R^1X + R^2\text{C}\equiv\text{CH} \xrightarrow{[Pd], \text{ Cu(I)-salt, base}} R^1-R^2\text{C}\equiv\text{CH}$ <p>R¹ = alkenyl, (hetero)aryl R² = H, alkenyl, (hetero)aryl, alkyl X = Cl, Br, I, OTf</p> |

Questions:

1. What is the phenomenon of catalysis? What substances are called catalysts?

The figure below shows the energy profile of the schematic reaction $X + Y = Z$ without and in the presence of a catalyst.



2. Which of the two energy profiles correspond to the reaction in the presence of a catalyst and an uncatalyzed reaction? Estimate the value of the activation energy for each of the reaction paths. Is

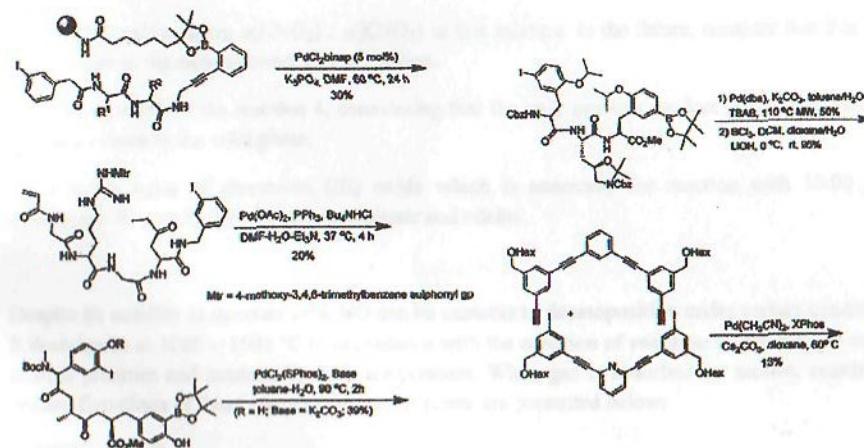
the reaction spontaneous from the thermodynamic point of view?

R. Heck, E. Negishi and A. Suzuki were the first who carried out cross-coupling reactions for sp - and sp^2 -hybridized carbon atoms, for which earlier, these reactions proceeded with low selectivity and small yields. Halogen atoms at sp - and sp^2 -hybridized carbon atoms have very low reactivity, however, catalysts based on palladium (II) complexes are extremely active to the C-Hal bond and facilitate its rupture, thereby providing practical expediency (exceptional selectivity and high yields) of cross-coupling reactions.

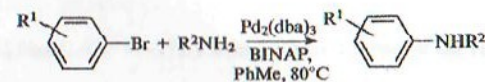
3. Draw the general structures of all possible products of cross-coupling reactions for sp - and sp^2 -hybridized carbon atoms.

Currently, Pd-catalyzed cross-coupling reactions are the dominant synthetic route of annulenes – cyclic systems containing conjugated double bonds. Benzannulenes are important components of a large number of biologically active compounds, and their synthetic analogues are developed for targeted drug delivery and anticancer therapy.

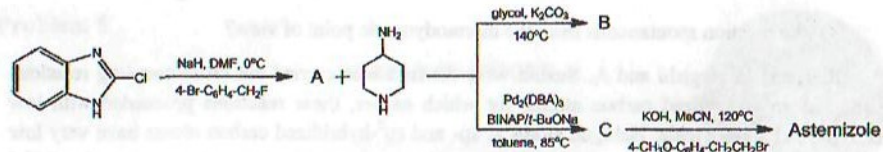
4. Give the structural formulas of products of the following Pd-catalyzed cross-coupling reactions:



In 1994, American chemists Buchwald and Hartwig described an unusual reaction for the production of *N*-substituted anilines in the presence of palladium (II) complexes:



The reaction is characterized by high regioselectivity and affects spatially more accessible nitrogen atoms, and direction and mechanism of its reaction differ from the usual nucleophilic substitution reactions. Buchwald-Hartwig amination is currently a powerful tool for creating carbon-nitrogen bonds and, in particular, is used in the synthesis of antihistamine (antiallergic) drug Astemizole, the synthesis scheme of which is given below:



5. Decode the scheme of Astemizole synthesis, draw structural formulas of the compounds A-C and Astemizole.

The organometallic palladium (II) complexes as catalysts for cross-coupling reactions were first used in the 1970s, however, the first non-catalyzed cross-coupling reactions were known back in the second half of the 19th century. In 1912 the Nobel Prize in Chemistry was awarded for one of these reactions.

6. Give at least 2 examples of non-catalyzed cross-coupling reactions. What famous scientist was awarded the Nobel Prize in 1912?

Problem 6

NITROGEN MONOXIDE



Nitrogen monoxide (NO) is one of stable radical compound. It is usually produced from salts of nitrous acid - potassium or sodium nitrite. Reactions between potassium nitrite and acidified with sulfuric acid potassium iodide (**reaction 1**) or yellow blood salt (**reaction 2**). Reaction with dilute sulfuric acid in the absence of reducing agents is less preferable (**reaction 3**).

Questions:

1. Molecules of what stable at standard state gases (except NO) are radicals? Give two examples.
2. Write reactions 1 – 3. Explain why reaction 3 is less convenient for NO producing.

Solid-phase reaction between chromium (III) oxide and mixture of potassium nitrate and nitrite in mass ratio $m(\text{KNO}_2) : m(\text{KNO}_3) = 2.53$ can be used to obtain dry gas.

3. Calculate molar ration $n(\text{KNO}_2) : n(\text{KNO}_3)$ in this mixture. In the future, consider that this ratio corresponds to the stoichiometry of the reaction.
4. Write equation of the reaction 4, considering that the only gaseous product is NO and only one substance leave in the solid phase.
5. Calculate mass of chromium (III) oxide which is necessary for reaction with 10.00 g of mentioned above mixture of potassium nitrate and nitrite.

Despite its stability at standard state NO can be unstable to decomposition under certain conditions. It decompose at 1000 – 1500 °C in accordance with the equation of **reaction 5**. **Reaction 6** occurs at high pressure and moderately high temperature. When gas is absorbed by zeolite, **reaction 7** occurs. Equations of these reaction with coefficients are presented below:

- 5) $2\text{NO} \rightarrow \text{A} + \text{B}$
- 6) $3\text{NO} \rightarrow \text{C} + \text{D}$
- 7) $4\text{NO} \rightarrow \text{C} + \text{E}$

Values $\Delta_r H^\circ = -155.4 \text{ kJ/mol}$, $\Delta_r S^\circ = -172.1 \text{ J/(mol}\cdot\text{K)}$ are known for the **reaction 6**.

6. Determine products of each reaction (substances A – E), write their formulas.
7. Calculate equilibrium constant for **reaction 6** at 800 K.

NO was heated until 800 K in a vessel with 2 L volume. Initial pressure of NO at 800 K was 10 bar.

8. Calculate NO amount in the vessel after finishing of the **reaction 6** (at the onset of chemical equilibrium), if vessel volume and temperature in the vessel are constant.

If you could not solve the equation that you compiled, please write down this equation in solution.

9. In what case will final (equilibrium) partial pressure of NO be more: in the case of reaction 6 is conducted at constant pressure and temperature or in the case of reaction 6 is conducted at constant volume and temperature?

Note: products and reagents are included in expression for K_p as equilibrium pressures measured with unit of bar, 1 bar = 10^5 Pa. The equilibrium constant is expressed in terms of changes in the enthalpy and entropy of the reaction:

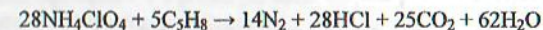
$$-RT \cdot \ln K_p = \Delta_r H^\circ - T \Delta_r S^\circ$$

SOLUTIONS

JUNIOR LEAGUE

Problem 1

The most likely products of the oxidation of hydrocarbons by ammonium perchlorate are carbon dioxide, water, nitrogen and hydrogen chloride. Let's write down the reaction with such products for polyisoprene with respect to the monomer unit C_5H_8 :



According to this equation, for oxidation of 1 g C_5H_8 :

$$m(NH_4ClO_4) = n(NH_4ClO_4) \cdot M(NH_4ClO_4) = \frac{28}{5} \cdot \frac{m(C_5H_8)}{M(C_5H_8)} \cdot M(NH_4ClO_4) = 9.672 \text{ g}$$

Because ammonium perchlorate mass is the same as mass given in the solution condition, the reaction occurs according to the written equation.

Thus, the same products are obtained in the reaction with polyethylene (monomeric unit is CH_2) and equation of the reaction with polyethylene looks like:



2. The reaction between 6 mol of NH_4ClO_4 equivalent amount of polyethylene releases n moles of gases:

$$n = 3 + 5 + 6 + 14 = 28 \text{ mol}$$

$$\text{Their mass is equal to: } m = 3 \cdot 28 + 5 \cdot 44 + 6 \cdot 36.5 + 14 \cdot 18 = 775 \text{ g}$$

Therefore, average molar mass M_{av} of released gaseous mixture is equal to: $M_{av} = \frac{m}{n} = 27.7 \text{ g/mol}$

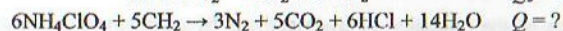
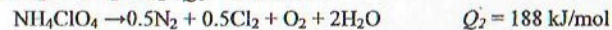
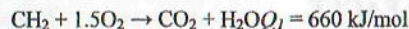
3. Let's consider a mixture of 6 moles of ammonium perchlorate and 5 moles of polyethylene (based on CH_2 monomer) to calculate the mass fractions in the stoichiometric mixture. Mass fractions of substances in the mixture are:

$$w(NH_4ClO_4) = \frac{n(NH_4ClO_4) \cdot M(NH_4ClO_4)}{n(NH_4ClO_4) \cdot M(NH_4ClO_4) + n(CH_2) \cdot M(CH_2)} = \frac{6 \cdot 117.5}{6 \cdot 117.5 + 5 \cdot 14} = 0.910$$

$$w(CH_2) = 1 - w(NH_4ClO_4) = 1 - 0.910 = 0.090$$

So, mass percentages are: 91.0% of NH_4ClO_4 , and 9.0% of polyethylene.

4. Let's write down the reactions for which thermal effects are known and the reaction of polyethylene with 6 mols of ammonium perchlorate, the heat effect of which must be calculated:



As it seen, the last reaction is obtained by adding 5 first reactions, 6 second and subtracting 1.5 third reactions. Hence, according to the law of Hess:

$$Q = 5Q_1 + 6Q_2 - 1.5Q_3 = 4257 \text{ kJ}$$

The obtained heat value corresponds to the reaction of 6 moles of NH_4ClO_4 with 5 moles of CH_2 groups of polyethylene, that is, 4257 kJ of heat is released from the mass of the mixture m_0 equal to:

$$m_0 = 6 \cdot M(\text{NH}_4\text{ClO}_4) + 5 \cdot M(\text{CH}_2) = 775 \text{ g} = 0.775 \text{ kg}$$

Then the thermal effect, expressed in kJ per 1 kg of the mixture (item (b)), will be:

$$Q' = \frac{4257 \text{ kJ}}{0.775 \text{ kg}} = 5493 \text{ kJ per 1 kg of mixture}$$

5. With the formation of 3 moles of N_2 , 5 moles of CO_2 , 6 moles of HCl and 14 moles of H_2O , 4257 kJ of heat is released, 80% of which is used to heat the released gases. Let's calculate the temperature T of gases:

$$3C_{\text{N}_2} \cdot (T - 300) + 5C_{\text{CO}_2} \cdot (T - 300) + 6C_{\text{HCl}} \cdot (T - 300) + 14C_{\text{H}_2\text{O}} \cdot (T - 300) = 4257000 \cdot 0.8$$

$$T = 300 + \frac{4257000 \cdot 0.8}{3C_{\text{N}_2} + 5C_{\text{CO}_2} + 6C_{\text{HCl}} + 14C_{\text{H}_2\text{O}}} = 3371 \text{ K}$$

6. Because outflow velocity is $v_0 \sim \sqrt{\frac{T}{M_{av}}}$, ratio between outflow velocity of CO_2 , given in the condition, and unknown velocity for our gaseous mixture can be found:

$$\frac{v_0}{v_{\text{CO}_2}} = \sqrt{\frac{T M_{\text{CO}_2}}{T_{\text{CO}_2} M_{av}}} = \sqrt{\frac{3371 \cdot 44}{3000 \cdot 27.7}} = 1.336;$$

$$v_0 = 1.336 v_{\text{CO}_2} = 1.47 \text{ km/s}$$

7. If fuel mass is equal to x , then the initial rocket mass is equal to $x+20$. Therefore, according to Tsiolkovsky formula:

$$\frac{x+20}{x} = e^{1.47}$$

Solving this equation, we obtain $x = 580$ tons. That is, in order to accelerate to similar speeds, the mass of fuel should exceed the mass of the ship by almost thirty times!

8. Metal (aluminum, magnesium) strongly exothermically reacts with oxidants, so the use of metals raises the temperature of the gases, and, consequently, their outflow velocity from the engine. This increases the acceleration and speed of the rocket.

Another explanation and consequence of the exothermicity of the reactions is that due to the reactions of metals with the oxidants, the reaction mixture warms up and the oxidation reactions of the polymer go faster, which allows more efficient release of gases and heat.

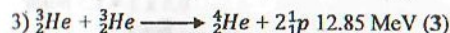
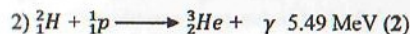
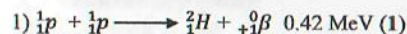
Evaluation system:

- | | | |
|---|--|----------|
| 1 | Correct 2 reaction equations – 1.5 points per each | 3 points |
| 2 | Correct calculation of the average molar mass | 2 points |
| 3 | Correct calculation of the molar fractions of components in the mixture – 1.5 points per each | 3 points |
| 4 | Correct calculation of the thermal effect expressed in units of kJ per 6 mol of ammonium perchlorate and of kJ per kg of the mixture – 2 points per each | 4 points |
| 5 | Correct calculation of the gaseous mixture temperature | 2 points |
| 6 | Correct calculation of outflow velocity | 2 points |
| 7 | Correct calculation of the minimum required mass of fuel | 2 points |
| 8 | Any correct explanation (one factor of two is enough) | 2 points |

TOTAL 20 points

Problem 2

1. Equations of nuclear reactions:



Two nuclei $\frac{3}{2}He$ take part in last step. Thus, first and second steps occur twice. Amount of energy released per helium-4 nucleus is:

$$E(\frac{4}{2}He) = 2E_1 + 2E_2 + E_3 = 2 \cdot 0.42 + 2 \cdot 5.49 + 12.85 = 24.67 \text{ MeV}$$

2. Let's calculate the amount of energy produced during 1 year by solar plant:

$$E = Pt = 1 \cdot 10^6 \cdot 365 \cdot 14 \cdot 60 \cdot 60 = 1.84 \cdot 10^{13} \text{ J}$$

Calculation of the heat released on burning of 1 mole cetane:



$$Q = 17Q_f(\text{H}_2\text{O}(\text{gas})) + 16Q_f(\text{CO}_2(\text{gas})) - Q_f(\text{C}_{16}\text{H}_{34}(\text{liq})) = 17 \cdot 242 + 16 \cdot 394 - 375 = 10043 \text{ kJ} - \text{per 1 mole of cetane.}$$

Let's find the mass of cetane:

$$E = \eta Qn$$

$$n = \frac{E}{\eta Q} = \frac{1.84 \cdot 10^{13}}{0.4 \cdot 10043 \cdot 10^3} = 4.6 \cdot 10^6 \text{ mol}$$

$$m = n \cdot M = 4.6 \cdot 10^6 \cdot 226 = 1.04 \cdot 10^9 \text{ g} = 1040 \text{ t}$$

3. Convert MeV to J:

$$E({}_2^4\text{He}) = 24.67 \cdot 1.6 \cdot 10^{-19} \cdot 10^6 = 3.95 \cdot 10^{-12} \text{ J}$$

The number of nuclei and amount of helium-4:

$$N = \frac{E}{E({}_2^4\text{He})} = \frac{1.84 \cdot 10^{13}}{3.95 \cdot 10^{-12}} = 4.66 \cdot 10^{24}$$

$$n = \frac{N}{N_A} = \frac{4.66 \cdot 10^{24}}{6.02 \cdot 10^{23}} = 7.74 \text{ mol}$$

4. X - Si, A - SiO₂, B - Mg₂Si, C - SiH₄, D - SiCl₄

Equations of chemical reactions:

- 1) SiO₂ + 4Mg = Mg₂Si + 2MgO
- 2) Mg₂Si + 4HCl = 2MgCl₂ + SiH₄
- 3) SiH₄ + 2O₂ = SiO₂ + 2H₂O
- 4) SiH₄ = Si + 2H₂
- 5) Si + 2Cl₂ = SiCl₄
- 6) SiCl₄ + LiAlH₄ = SiH₄ + LiCl + AlCl₃

Evaluation system:

- | | |
|---|----------------------|
| 1. Nuclear reactions | 0,5 x 3 = 1,5 point |
| Calculation of energy | 1 point |
| 2. Calculation of energy for 1 year | 1 point |
| Equation of chemical reaction | 1 point |
| Q calculation | 1 point |
| Mass calculation | 1 point |
| 3. Nuclei amount calculation | 1 point |
| 4. Determination of compounds A-D and element X | 0,5 x 5 = 2,5 points |
| Equations of chemical reactions | 0,5 x 6 = 3 points |

TOTAL 13 points

Problem 3

1. The reaction of X with water gives H₂. It can tell that X is alkaline or alkaline-earth metal. O₂ is released in reaction A with H₂O and CO₂. Thus, A can be peroxide or superoxide. After that calculation of half-life and molar mass of A is necessary to clearly determine compounds.

Half-life can be found with law of the radioactive decay:

$$A = A_0 e^{-\lambda t}$$

Putting $A = 0.98A_0$ and taking logarithm:

$$\ln(0.98) = -\lambda \cdot t$$

$$\lambda = \frac{-\ln(0.98)}{t} = \frac{-\ln(0.98)}{36.4 \cdot 10^6} = 5.55 \cdot 10^{-10} \text{ year}^{-1} = 1.76 \cdot 10^{-17} \text{ s}^{-1}$$

$$T_{1/2} = \frac{\ln 2}{\lambda} = \frac{\ln 2}{5.55 \cdot 10^{-10}} = 1.25 \cdot 10^9 \text{ year} = 1.25 \cdot 10^9 \cdot 365 \cdot 24 \cdot 60 \cdot 60 = 3.94 \cdot 10^{16} \text{ s}$$

Then we find the molar mass A.

$$A = \lambda N$$

$$N = n \cdot N_A = \frac{m}{M} N_A$$

$$A = \lambda \frac{m}{M} N_A$$

$$M = \frac{\lambda m N_A}{A} = \frac{\ln 2 \cdot m N_A}{T_{1/2} \cdot A} = \frac{\ln 2 \cdot 1 \cdot 6,02 \cdot 10^{23}}{3,94 \cdot 10^{16} \cdot 147 \cdot 10^3} = 72 \frac{\text{g}}{\text{mol}}$$

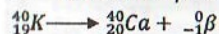
A can be only ⁴⁰KO₂.

2. X - K, A - KO₂, B - KOH, C - K₂CO₃

Equations of chemical reactions:

- 1) K + O₂ = KO₂
- 2) 4KO₂ + 2H₂O = 4KOH + 3O₂
- 3) 2K + 2H₂O = 2KOH + H₂
- 4) 4KO₂ + 2CO₂ = 2K₂CO₃ + 3O₂

3. Reaction of β⁻-decay:



4. Specific energy absorbed by body is called absorbed dose. It is expressed as follows:

$$D = \frac{E}{m}$$

E - total average energy of particles for a period of time, m - mass of the body.

$$E = 0.4 E_{\beta, \max} \cdot N(\beta - \text{particles for 24 hours}) = 0.4 E_{\beta, \max} \cdot A t$$

$$A = \lambda N = \lambda n N_A = \lambda \frac{m \omega(K)}{M(K)} \chi N_A$$

$\omega(K)$ - mass fraction of potassium, χ - molar fraction of potassium-40

$$A = 1.76 \cdot 10^{-17} \frac{70 \cdot 10^3 \cdot 0.003}{39} \cdot 0.0117 \cdot 10^{-2} \cdot 6.02 \cdot 10^{23} = 6675 \text{ Bq}$$

$$E = 0.4 E_{\beta, \max} \cdot A \cdot t = 0.4 \cdot 1.31 \cdot 10^6 \cdot 1.6 \cdot 10^{-19} \cdot 6675 \cdot 24 \cdot 60 \cdot 60 = 4.8 \cdot 10^{-5} \text{ J}$$

$$D = \frac{4.8 \cdot 10^{-5}}{70} = 6.9 \cdot 10^{-7} \frac{\text{J}}{\text{kg}}$$

5. 1 year absorbed dose is:

$$6.9 \cdot 10^{-7} \cdot 365 = 2.5 \cdot 10^{-4} Sv = 0.25 mSv$$

This value is less 4 times than limit.

Evaluation system:

- | | |
|---------------------------------------|--------------------|
| 1. Calculation of half-life | 2 points |
| 2. Determination of unknown compounds | 1 x 4 = 4 points |
| Equations of chemical reactions | 0,5 x 4 = 2 points |
| 3. Reaction of decay | 1 point |
| 4. Calculation of absorbed dose | 3 points |
| The right name of quantity | 1 point |
| 5. Calculation of 1 year dose | 1 point |
| TOTAL | 14 points |

Problem 4

Solution:

1. The system with the minimum eutectic point is the system $AlCl_3$ - $LiCl$ ($T_m = 110^\circ C$). Since all the eutectic points lie in a narrow range from 100 to 120 $^\circ C$, any choice can be counted as correct if the eutectic points are correctly indicated on the phase diagrams.

Compositions of eutectic systems:

| Molar ratio, % | m_{AlCl_3} , g | m_{CaCl_2} , g | m_{AlCl_3} per 1g of mixture, mg |
|---|------------------|------------------|------------------------------------|
| 58 mol. % $AlCl_3$ / 42 mol. % $LiCl$ | 77,43 | 95,28 | 813 |
| 66 mol. % $AlCl_3$ / 34 mol. % KCl | 88,11 | 113,44 | 777 |
| 75 mol. % $AlCl_3$ / 25 mol. % $CaCl_2$ | 100,13 | 127,88 | 783 |
| 49 mol. % $AlCl_3$ / 51 mol. % $ZnCl_2$ | 65,42 | 134,78 | 485 |

The system with the minimum amount of $AlCl_3$ is the system $AlCl_3$ - $ZnCl_2$. An error in measuring the molar content of the components should be no more than 2 mol. %.

2. Based on the zinc and chromium salt formulas, it can be established that the $\{TiW_{11}O_{39}\}$ fragment has an oxidation state of -8. Consequently, the oxidation state of lanthanide is:

$$Na_{13}[Ln(TiW_{11}O_{39})_2] + 1 \cdot 13 + x + (-8) \cdot 2 = 0. \quad \text{Hence, } x = +3.$$

Let's find out the oxidation states of titanium and tungsten. Tungsten exhibits different oxidation states from +2 to +6, however, the oxidation state of W^{+6} is most satisfactory. Then, the oxidation state of titanium is:

$$\{TiW_{11}O_{39}\}^{-8} y + 6 \cdot 11 + (-2) \cdot 39 = -8. \quad \text{Hence, } y = +4.$$

3. The central metal ion M^{n+} is surrounded by 11 octahedra $[WO_6]$ and 1 tetrahedron $[TiO_4]$. They are aligned as shown in the proposed structure $[W_6O_{19}]$: 6 octahedra $[WO_6]$ are coordinated around the transition metal ion, from below it is surrounded by 3 octahedra $[WO_6]$ and on top by 2 octahedra $[WO_6]$ and 1 tetrahedron $[TiO_4]$.



4. First, let's calculate moles of reagents for the reaction 1:

$$M(Na_2WO_4) = 23 \cdot 2 + 184 + 16 \cdot 4 = 294 \text{ g/mol}$$

$$n(Na_2WO_4) = 32,3/294 = 0,11 \text{ mol}$$

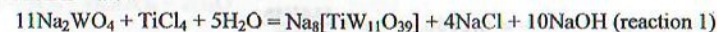
$$m(TiCl_4) = 1,11 \cdot 1,726 = 1,916 \text{ g}$$

$$M(TiCl_4) = 48 + 35,5 \cdot 4 = 190 \text{ g/mol}$$

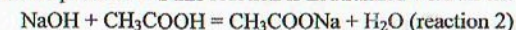
$$n(TiCl_4) = 1,916/190 = 0,01 \text{ mol}$$

$$n(Na_2WO_4) : n(TiCl_4) = 11:1$$

Because of the non-equimolar ratio of sodium ions and chloride ions, the third participant of the reaction is water:



The sodium hydroxide produced in this reaction is neutralized with an excess of acetic acid:



Let's calculate moles of reagents for the reaction 3:

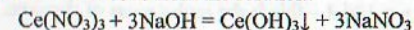
$$n(Na_8[TiW_{11}O_{39}]) = 0,01 \text{ mol}$$

$$n(Ce(NO_3)_3) = 0,005 \cdot 1 = 0,005 \text{ mol}$$

$$n(Na_8[TiW_{11}O_{39}]) : n(Ce(NO_3)_3) = 2:1$$



The solution is acidified with acetic acid to pH 6 to remove sodium hydroxide for preventing precipitation of cerium ions from the solution:



Evaluation system:

- | | |
|--|------------------|
| 1. For the system with minimum eutectic point | 1 point |
| For the calculation of amount of $AlCl_3$ in each system | 1 x 4 = 4 points |
| 2. For the determination of oxidation states | 1 x 3 = 3 points |
| 3. For the structure $[MTiW_{11}O_{39}]$ | 4 points |
| 4. For the calculation of moles of reagents | 1 x 3 = 3 points |
| For the reaction equations | 1 x 3 = 3 points |
| For the explanation of acidifying solution | 1 point |
| TOTAL | 19 points |

Problem 5

1-2. Based on the fact that the gas Y consists of only one element, it is not difficult to guess that this is oxygen. Let's suppose that the oxide has the formula Me_xO_y :

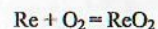
Let's calculate the molar mass of element X from oxide C. Weight percentage of oxygen:

$$100/6,82=14,66\%. \quad \frac{16n}{2x+16n} = 0,1466. \quad x = \frac{13,6544n}{0,2932}$$

| n | M | Element |
|---|-------|---------|
| 1 | 46,6 | - |
| 2 | 93,1 | - |
| 3 | 139,7 | - |
| 4 | 186,3 | Re |
| 5 | 232,9 | - |

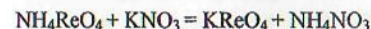
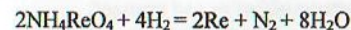
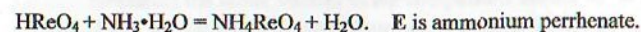
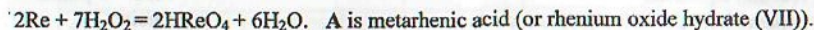
For $n = 4$, we calculated $x = 186,3$ – this is the molar mass of rhenium.

X is rhenium. Therefore, C is rhenium (IV) oxide:



$\text{ReO}_2 + 6\text{HCl} = \text{H}_2[\text{ReCl}_6] + 2\text{H}_2\text{O}$. D is hydrogen hexachlorhenate (IV) or hexachlorhenic (IV) acid.

Rhenium is oxidized to Re^{+7} by strong oxidizing agents:



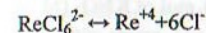
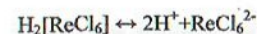
F is sodium nonahydridorhenate (VII).



3. Reactions of producing A from X:



4. The reaction of dissociation of substance D:



5. To produce potassium perrhenate from rhenium, it is necessary to add a concentrated alkali solution to the metallic rhenium:



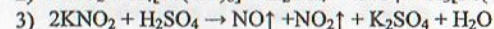
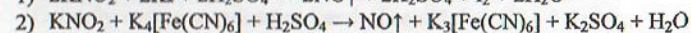
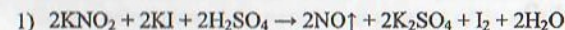
Evaluation system:

- | | |
|---|---------------------------|
| 1. For formulas of compounds A-F, X and Y | 0,5 points x 8 = 4 points |
| 2. For reactions | 1 point x 10 = 10 points |
| 3. For obtainment of A from X | 1 point x 2 = 2 point |
| 4. For dissociation reaction | 1 point |
| 5. For obtainment of B from X | 1 point |
| TOTAL | 18 points |

Problem 6

1. Except NO, the molecules of such gases as NO_2 , ClO_2 also are radicals.

2. Equations of reactions 1 – 3



Reaction 3 is inconvenient for production of NO because it leads to obtaining of gas mixture (NO and NO_2). It is not good to produce pure NO or it need additional purification of the product.

3. Let's calculate molar ratio of substances in the mixture knowing molar masses:

$$M(\text{KNO}_2) = 85.1 \text{ g/mol} \quad \text{и} \quad M(\text{KNO}_3) = 101.1 \text{ g/mol:}$$

$$n(\text{KNO}_2) : n(\text{KNO}_3) = \frac{m(\text{KNO}_2)}{M(\text{KNO}_2)} : \frac{m(\text{KNO}_3)}{M(\text{KNO}_3)} = \frac{m(\text{KNO}_2)}{m(\text{KNO}_3)} \cdot \frac{M(\text{KNO}_3)}{M(\text{KNO}_2)} = 2.53 \cdot \frac{101.1}{85.1} = 3$$

4. KNO_2 , KNO_3 and Cr_2O_3 take part in in the reaction 4. Solid product of Cr_2O_3 oxidation must be potassium chromate K_2CrO_4 (potassium dichromate is thermally unstable and for him it is impossible to equalize the reaction in accordance with condition) and the only gas in accordance with condition is NO.



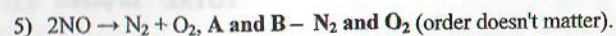
Stoichiometry of this reaction corresponds to ratio $n(\text{KNO}_2) : n(\text{KNO}_3) = 3:1$. Therefore, reaction equation is correct.

5. 1 mol of Cr_2O_3 ($M = 152.0 \text{ g/mol}$) reacts in accordance with **reaction 4** with 1 mol of KNO_3 ($M = 101.1 \text{ g/mol}$) and 3 mol of KNO_2 ($M = 85.1 \text{ g/mol}$). It means that 152.0 g of Cr_2O_3 reacts with $101.1 + 3 \cdot 85.1 = 356.4 \text{ g}$ of the mixture of KNO_2 and KNO_3 . Then next ratio can be written:

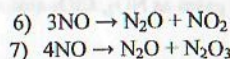
$$\frac{152.0}{356.4} = \frac{m}{10.0}$$

Where m – mass of chromium oxide which is necessary for reaction with 10 g of the mixture. From this equation we obtain $m = 4.26 \text{ g}$.

6. Nitrogen oxide decomposes to simple substances in the **reaction 5**, which occurs at $1000 - 1200 \text{ }^\circ\text{C}$. It is approved by coefficients:



In reactions 6 and 7, there is a disproportionation to other nitrogen oxides. The choice of oxides is understandable from the reaction coefficients:



As it seen, **C – N_2O ; D – NO_2 ; E – N_2O_3** .

7. Equilibrium constant of the reaction is calculated from the formula:

$$K_p = e^{\frac{T\Delta_r S^\circ - \Delta_r H^\circ}{RT}} = e^{\frac{800(-172.1) + 155400}{8.314 \cdot 800}} = 14.36$$

8. The pressure is directly proportional to the amount of substance at the constant volume and temperature, therefore final pressures of NO_2 and N_2O can be designated as x . In this case final (equilibrium) pressure of NO is equal to $10 - 3x$. Let's write down expression for equilibrium constant:

$$K_p = \frac{x^2}{(10 - 3x)^3} = 14.36 \quad (*)$$

Solution of this equation is the value of $x = 3.045 \text{ bar}$. Then final (equilibrium) pressure of NO will be: $p(\text{NO}) = 10 - 3 \cdot 3.045 = 0.865 \text{ bar} = 86500 \text{ Pa}$.

Amount of substance NO in the equilibrium:

$$n(\text{NO}) = \frac{pV}{RT} = \frac{86500 \cdot 0.002}{8.314 \cdot 800} = 0.0260 \text{ mol}$$

9. In the case of conducting **reaction 6** at the constant pressure, final (equilibrium) pressure of system will be equal to 10 bar and final volume will be less than 2 L because number of gas molecules decrease during reaction. Therefore, it is needed to decrease system volume (and, accordingly, increase total pressure) to obtain equilibrium state formed in isobaric process, from equilibrium state described in item 8. In the same time, according to the Le Chatelier principle, equilibrium will move to decrease of molecule number in gaseous phase i.e. to the NO decomposition.

It means equilibrium partial pressure of NO at the constant pressure is less than equilibrium partial pressure of NO formed in isobaric process. In other words, greater partial pressure of NO is reached at conducting reaction 6 in the constant volume.

Evaluation system:

| | | |
|---|---|------------|
| 1 | Two correct examples of gases – 1 point for each | 1 point |
| 2 | Correct equations of reactions 1 – 3 – 0.5 point for each Correct explanation about reaction 3 – 0.5 point | 2 points |
| 3 | Correct calculation of the molar ratio of substances in mixture | 1 point |
| 4 | Correct equation of the reaction 4 | 1 point |
| 5 | Correct calculation of chromium (III) oxide mass | 1.5 points |
| 6 | Correct determination of substances A – E – 0.5 point for each formula | 2.5 points |
| 7 | Correct calculation of the equilibrium constant of the reaction 6 | 1 point |
| 8 | Correctly written equation for chemical equilibrium (*) – 1 point Correct calculation of NO amount – 2 points | 3 points |
| 9 | Correct answer – 0.5 point Competent explanation – 1.5 points | 2 points |

TOTAL 16 points

SENIOR LEAGUE

Problem 1

Solution of Problem 1 JUNIOR LEAGUE

TOTAL: 20 points

Problem 2

Spirituous solutions of iodine are colored in brown color (variants are acceptor: fulvous, red-brown). Benzene solutions have a violet color.

2. Blue iodine solution can be obtained by dissolution of iodine in aqueous (or spirituous) solution of starch. The resulting blue complex will color the solution in blue.

3. Let concentration in aqueous phase was c in the result of extraction. Thus, concentration in the solvent A phase was $208c$. Therefore, distribution constant is equal to:

$$K_{D(A\text{-aqueous})} = \frac{208c}{c} = 208$$

To find iodine solubility in solvent A (mol/L), iodine solubility in the task must be convert to need to us measurement units:

$$s(I_2 \text{ aqueous}) = \frac{0.280 \text{ g/L}}{253.8 \text{ g/mol}} = 1.103 \cdot 10^{-3} \text{ mol/L}$$

According to conditions, distribution constant is expressed by the same method both through equilibrium concentration and through iodine solubility in appropriate solvents (denote solubility as s):

$$K_{D(A\text{-aqueous})} = \frac{s(I_2 \text{ in } A)}{s(I_2 \text{ aqueous})} = 208,$$

$$s(I_2 \text{ in } A) = s(I_2 \text{ aqueous}) \times K = 208 \cdot 1.103 \cdot 10^{-3} = 0.2294 \text{ mol/L}$$

(Error ± 1 is allowed in the last digit)

4. Let concentration in aqueous phase was c in the result of extraction. Thus iodine concentration in water was $37.5c$ before extraction. Total amount of iodine, taking in account that aqueous solution volume is 0.1 L, is equal to: $n_{\text{total}} = 37.5c \times 0.1 = 3.75c$.

Iodine amount in aqueous phase after extraction: $n_{\text{aqueous}} = c \times 0.1 = 0.1c$.

Iodine amount in B: $n_B = n_{\text{total}} - n_{\text{aqueous}} = 3.75c - 0.1c = 3.65c$

Iodine concentration in B, taking in account that its volume is 0.01 L: $c_B = 3.65c / 0.01 = 365c$.

Iodine distribution constant in system B/water is equal to: $K_{D(B\text{-aqueous})} = 365c/c = 365$.

Let's write iodine distribution constant expression through solubility to find it for system solvent B/solvent A:

$$K_{D(B-A)} = \frac{s(I_2 \text{ in } B)}{s(I_2 \text{ in } A)} = \frac{s(I_2 \text{ in } B) / s(I_2 \text{ aqueous})}{s(I_2 \text{ in } A) / s(I_2 \text{ aqueous})} = \frac{K_{D(B\text{-aqueous})}}{K_{D(A\text{-aqueous})}} = \frac{365}{208} = 1.755$$

5. Iodine solubility in solvent B is equal to:

$$s(I_2 \text{ in } B) = K_{D(B\text{-aqueous})} \cdot s(I_2 \text{ aqueous}) = 365 \cdot 1.103 \cdot 10^{-3} = 0.4026 \text{ mol/L}$$

(Error ± 2 is allowed in the last digit)

6. 10 g of iodine is $10 / 253.8 = 0.0394$ mol. This amount fully dissolved with formation of saturated solutions in three phases, therefore:

$$s(I_2 \text{ in } B)V_B + s(I_2 \text{ in } A)V_A + s(I_2 \text{ aqueous})V_{\text{water}} = 0.0394$$

$$0.4026V_B + 0.2294V_A + 1.103 \cdot 10^{-3}V_{\text{water}} = 0.0394 \quad (1)$$

Next, we take into account that the total volume is 0.677 liters, and the volume of solvent B is greater than the volume of solvent A by 0.010 liters:

$$V_B + V_A + V_{\text{water}} = 0.677 \quad (2)$$

$$V_B - V_A = 0.010 \quad (3)$$

It remains to solve a system of three equations (1) - (3) with three unknowns. After, we receive the answer:

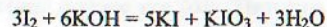
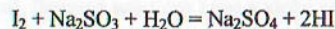
$$V_B = 0.0650 \text{ L} = 65.0 \text{ ml,}$$

$$V_A = 0.0550 \text{ L} = 55.0 \text{ ml,}$$

$$V_{\text{water}} = 0.5570 \text{ L} = 557 \text{ ml.}$$

7. To transfer iodine to the aqueous phase, its ionic forms can be obtained: either in a negative oxidation level (reduction) or in a positive oxidation level (reactions with alkalis leading to iodates).

Appropriate reaction equations:



Using of reaction equations in ionic form is allowed. Also, the other variants of chemical bonding of iodine into soluble forms should be considered as a correct answer.

Evaluation system:

- | | | |
|---|--|----------|
| 1 | Correct color of spirituous and benzene solutions of iodine. 1 point for each solution. | 2 points |
| 2 | Correct description of the method of blue solution preparation | 1 point |
| 3 | Correct calculation of iodine distribution constant in system solvent A/aqueous (1 point) and iodine solubility in solvent A (1 point) | 2 points |
| 4 | Correct calculation of iodine distribution constant in system B/aqueous | 2 points |
| | Correct calculation of iodine distribution constant in system B/A | 1 point |
| 5 | Correct calculation of iodine solubility in solvent B | 1 point |
| 6 | Correct calculation of the volumes of water, solvents A and B. 1 point for each volume. | 3 points |
| 7 | 2 principally different methods of iodine transferring in aqueous phase. 0.5 point for each method. | 2 points |
| | 0.5 point for each reaction equation. | |

TOTAL 14 points

Problem 3

1. Substance decomposed in presence of catalase and manganese dioxide is hydrogen peroxide, i.e. A – H₂O₂.

2. In acid B are 36.73 wt% of carbon, 57.14 wt% of oxygen and hydrogen with mass fraction:

$$w(\text{H}) = 100 - 36.73 - 57.14 = 6.13 \text{ wt.}\%$$

Let's determine the molar ratio of elements in acid B:

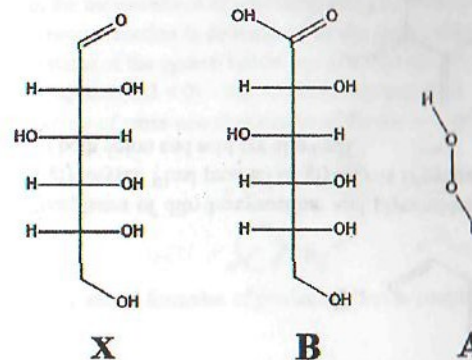
$$C:H:O = \frac{w(C)}{12} : \frac{w(H)}{1} : \frac{w(O)}{16} = 3.06:6.13:3.57 = 6:12:7$$

Therefore, acid B has molecular formula C₆H₁₂O₇. Since it is formed at the oxidation of monosaccharide, B is gluconic acid and X – glucose.

Equation of A and B formation reaction from X:

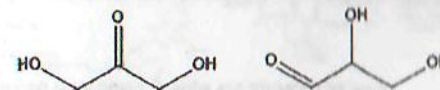


Structural formulas A, B and X:



2. Two of the most monosaccharides are fructose and glucose. Accordingly, we are talking about fructose. And it is fructose in honey most.

3. Structural formulas of dihydroxyacetone and glyceraldehyde:

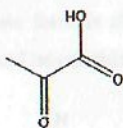


Structural formulas of the phosphates of dihydroxyacetone and glyceraldehyde (last one should be phosphated through the terminal hydroxyl group because only such isomer can be obtained from phosphate of dihydroxyacetone and be in equilibrium with it):

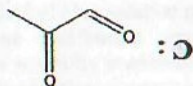
TOTAL 13 points

- 1 Correct determination of gross formulas of substances A, B and X (0.5 point for each substance) 1.5 points
- 2 Correct structural formulas of substances A, B and X (1 point for each formula) 3 points
- 3 Correct reactions equations of the formation of A and B from X (0.5 point) 0.5 points
- 4 Correct name of monosaccharide (fructose) – 1 point 1.5 points
- 5 An indication that fructose is contained the most in honey – 0.5 point 2 points
- 6 Structural formulas of dihydroxyacetone, glyceraldehyde, phosphates of dihydroxyacetone and glyceraldehyde – 0.5 point for each formula 1.5 points
- 7 Correct name of the process (glycolysis) 1 point
- 8 Correct structure and correct name of the final product of glycolysis – 1 2 points

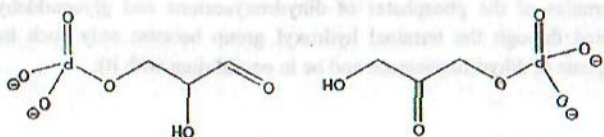
Evaluation system:



5. Phosphates of dihydroxyacetone and glyceraldehyde are produced in the process of glycolysis. Final product of glycolysis is pyruvate or pyruvic acid and structural formulas of both anion and acid are allowed)



4. Phosphates of dihydroxyacetone and glyceraldehyde are in equilibrium in living organisms, thus substance C can be corresponded to the product of elimination of phosphoric acid from both of these substances. Because substance C produces "silver mirror", it is logical that it is produced directly from glyceraldehyde phosphate which is aldehyde. When it eliminates, enol is obtained from it, which rapidly regroups into methylglyoxal. So, methylglyoxal is the substance C.



Structures with protonated phosphate groups are allowed as well.

Problem 4

Solution of Problem 3 JUNIOR LEAGUE

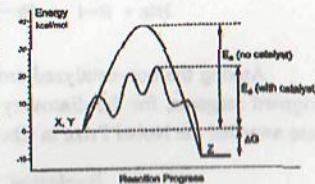
TOTAL:14 points

Problem 5

1. **Catalysis is the acceleration or excitation** of chemical reactions in the presence of catalysts – substances that repeatedly enter into an intermediate chemical reaction with the participants of the reaction and restore their original chemical composition after each cycle.

Catalyst is a substance that, when added to the reaction mixture, facilitates the transfer of one or both of the reaction components to the active particles and *returns to the initial state after the reaction.*

Any answers with indicating the main features of the phenomenon of catalysis and catalyst are accepted.



2. Activation energy is the value of the energy barrier:

$$E_a \text{ (no catalyst)} = 38 \text{ kcal/mol}$$

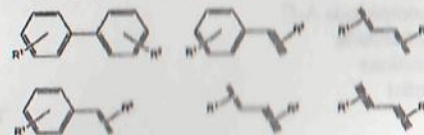
$$E_a \text{ (with catalyst)} = 22 \text{ kcal/mol}$$

An error in the measurement of activation energies should be no more than 2 kcal/mol.

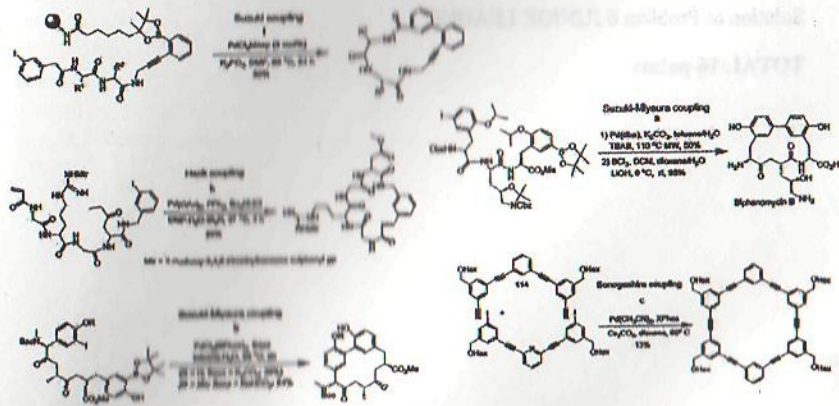
The spontaneous reaction is determined by the Gibbs energy, which is expressed as a difference in the energy states of the system before and after the reaction:

$$\Delta G = -10 \text{ kcal/mol } (\Delta G < 0) \text{ – the reaction is spontaneous.}$$

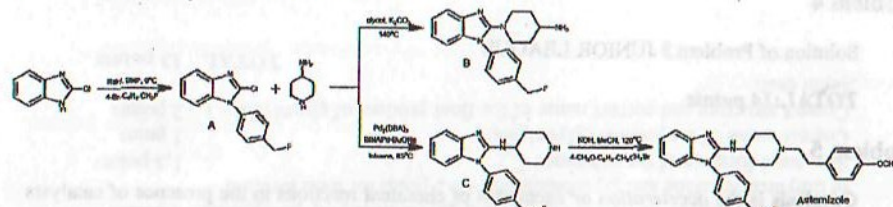
3. Products of cross-coupling reactions for sp - and sp^2 -hybridized carbon atoms:



4. The structural formulas of products of cross-coupling reactions:



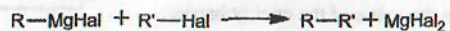
5. Scheme of synthesis of Astemizole:



6. The Wurz-Fittig reaction is one of the first non-catalyzed cross-coupling reactions:



Among the non-catalyzed cross-coupling reactions is also the reaction of alkyl halides with Grignard reagents, for the discovery of which French chemists Victor Grignard and Paul Sabatier were awarded the Nobel Prize in Chemistry in 1912:



Evaluation system:

- | | |
|--|--------------------|
| 1. For the definitions of catalysis and catalyst | 0,5 x 2 = 1 point |
| 2. For the calculation of activation energy | 1 x 2 = 2 points |
| For the calculation of Gibbs energy | 1 point |
| 3. For general structures of products | 0,5 x 6 = 3 points |
| 4. For structures of products | 2 x 5 = 10 points |
| 5. For the formulas of compounds A-C | 1 x 3 = 3 points |
| For the formula of Astemizole | 1 point |
| 6. For 2 examples of reactions | 1 x 2 = 2 points |
| For the name of scientist | 1 point |
| TOTAL | 24 points |

Problem 6

Solution of Problem 6 JUNIOR LEAGUE

TOTAL:16 points