XXIII МЕЖДУНАРОДНАЯ ОЛИМПИАДА ШКОЛЬНИКОВ
«ТУЙМААДА»

XXIII INTERNATIONAL SCHOOL OLYMPIAD «TUYMAADA»

ХИМИЯ

CHEMISTRY

I (теоретический) этап
First (theoretical) tour

Якутск, 2016
**Problem 1**

**COMPLEX RELATIONS**

Two elements X and Y are located one after another in the periodic table and can react with each other in different ratios. Formed products A₁ and A₂ (reaction 1-2) easily hydrolyze with forming X and two gaseous products B and C (reactions 3-4). Reaction between D and Y leads to formation of D (reaction 5), which reacts with X in the presence of a catalyst with formation A₁, A₂ and B (reaction 6). The hydrolysis of substance D lead to compounds C and E (reaction 7). Chemical interaction of the hot concentrated solution of E with A₁ and A₂ again leads to B and C (reaction 8-9). X can be obtained from B through the its interaction with substance F (reaction 10). F can be used to transform A₁ to A₂ at low temperature (reaction 11). Product of the reaction between F and Y is C but X or E can be formed too depending on F and Y ratio (reaction 12-13). It is known that substances A₁ - F contain at least one of the elements X and Y.

**Questions:**
1. Determine elements X and Y and substances A₁, A₂, B - F, if 1 g of A₁ or A₂ hydrolyze with formation of 155 and 356 g of X respectively.
2. Write down equations of all reactions mentioned in the problem.
3. For what purpose is solution of X in A₂ used?
4. Calculate pH of the solution which is the result of reaction between gaseous Y (p=1 bar, t=25°C) and 100 ml of 0.01M solution of F. Change of solution volume can be neglected.

**Problem 2**

**SAFETY LAST!**

Compound A is stable at the room temperature. It contains 2 N–N bonds and 6.7% of hydrogen. It is very volatile (782 mm at 134°C), its aqueous solution is neutral. Reactions of A with salts of transition metals in water lead to black precipitates, which are explosive on impact.
caused their wide use as detonators. Compound A is able to explode itself—the blast pressure is 3514 kg/cm² (1 kgf = 9.8 N) if loading density is 0.3 g/cm³. The volume of gaseous products of explosion is 1148 ml/g (0°C, 1 atm).

**Questions:**
1. What is the compound A? Name it, and provide the structural formula of the substance A.
2. What is content of nitrogen in a product of reaction A with the excess of silver nitrate?
3. In which sphere of life these compounds are used as detonators?
4. Write the reaction of decomposition of compound A.
5. Estimate the temperature of explosion of compound A, considering a given loading density.

**Problem 3**

**CELLULAR METALS**

Metals X and Y belong to the most important bioelements. It should be noted that X is heavier than Y. In live organisms, they occur exclusively as ions. On the average, a human body contains 170 g of X and 90 g of Y. One of them is concentrated within the cell, while the other—in the intercellular fluid. X and Y ions take part in nervous impulse transmission and muscle work, promote maintain a constant volume of water in the body. Y salts are often used as medicine, as Y ions are harmless for the body even in an enhanced concentration. At the same time the excess of X ions suppresses cardiac activity, therefore one needs to exercise thorough control, when taking such medication.

**Questions:**
1. Name X and Y metals. Which of the ions is concentrated within the cell, and which—in the intercellular fluid?
2. Give at least two examples of the Y metal salts that are used as medicine and describe their usage.
3. Elements X and Y have been discovered by an English chemist in 1807. He separated metal X through electrolysis of molten hydroxide of Z. In a few days the same method was used to obtain metal Y from molten hydroxide of W. Previous experiments with their water solutions were fruitless due to the high reactivity. The names chosen by the scientist reflect the origin of these elements.
   a. What’s the name of the chemist?
   b. Write the formulas for Z and W hydroxides. What are the substances that X and Y were named after?
   c. Write the chemical equation needed to obtain one of the metals.

4. Before the discovery of electrolytic process Y was obtained through carbonate recovery in a closed crucible using element Q. Metal vapors condensed on the crucible lid. Write the chemical equation.
5. Some of the factories still obtain X using Griesheim method: its fluoride was alloyed to a binary compound, which consists of calcium and element Q, at 1000°C. Write the chemical equation.
6. Solve this figure. Give the names of substances A–H, W and write the chemical equations.

![Chemical Reaction Diagram]

**Problem 4**

**UNEXPECTED SIDES OF CHEMISTRY OF A SINGLE ELEMENT**

In 1928 research group of Otto Ruff in Germany had obtained a thermodynamically stable compound A₁ (the stability of this compound became a big surprise). It turned out that this compound could be synthesized in two ways. The essence of the first method involves the electrolysis of salt A₂ (which itself is a salt of acid A₃) with acid A₁. The second method contains the reaction of a simple gaseous substance A₄ with a compound A₃ on a copper catalyst.

It is known that A₃ can be obtained from A₁ in one stage, as well as A₂ can be turned into A₂ in one stage.

It turned out that there are several relative compounds of A₁ with similar elemental composition. One of them B₂ could result from a reaction between copper and A₃ (in fact it is exactly how it was first obtained in 1957). Today B₂ is received using another method (coefficients are correct):

\[
\begin{align*}
B₂ + 2A₁ &= B₃ + \ldots \quad (70.0\% \text{ yield})
\end{align*}
\]

\[
\begin{align*}
B₂ + xH₂SO₄ + 2H₂O &= B₄ + \ldots \quad (100.0\% \text{ yield})
\end{align*}
\]

\[
\begin{align*}
2B₄ + NaOCl &= B₃ + \ldots \quad (100.0\% \text{ yield})
\end{align*}
\]
If you take 1.648 grams of B₄ using the above scheme you will get exactly 1 gram of B₃, and you will get 1.014 grams of intermediate B₂. B₁ turned out to be strong oxidizer, what can be shown by following reactions:

(a) 1SiH₄ + 2B₄ → ...

(b) 10L₂ + 1B₄ → ...

It is also known that B₃ is an organic compound that was synthesized from its isomer B₂ by a famous chemist. This reaction disproved the vitalism theory and gave start to a new era in chemistry.

Questions:
1) Define all the unknown compounds. The molar mass ratio is M(A₁) : M(B₃) = 0.740. Write down 6 reactions related to the synthesis of A₁ and B₃.
2) What scientist implemented the reaction which disproved the vitalism theory? Write his name and surname.
3) A₁ molecule has a pyramidal shape. The angle between any two bonds in the molecule is 102.5°, and dipole moment of each bond is 0.234 D. Find a full dipole moment of this molecule. Write down all of your calculations.
4) Write down reactions (a) and (b)

Many of the chemical properties of B₁ are caused by its partial dissociation: B₁ = 2 B₃. It is of course an equilibrium with Kₑ = 0.03 at 298 K, and the enthalpy of dissociation ΔH = -3.20 kJ/mole.
5) Calculate ΔS and ΔG of dissociation at 298 K.
6) Is B₃ a radical?
7) Write down structures of the products of the reaction of B₃ with:
   A) NO
   B) Cl₂
   C) CF₂=CF₂

**Problem 5**

**THE ELEMENT OF SPACE TECHNOLOGY**

55 years ago in 1961 one great thing happened— the first man flew in the space. This was the result of years of hard work in the field of space technology. In which, because of its properties, the element M is widely used.

The beginning of the study of the element M was laid by Englishman William Gregor 225 years ago. Exploring sand from the local river he discovered black substance (compound A) from which he removed one of three elements by the reaction with HCl (reaction 1). In residue was found compound B. Both compounds can be found in nature as minerals and contain 31.57% and 59.95% of the element M by mass respectively.

The method of obtaining M was invented by William Kroll in 1932. Method is in reduction of compound C by magnesium with high temperature. Compound C can be synthesized from compound A or from compound B by the reaction with chlorine and carbon while heated (reactions 3 and 4). In both reactions CO is released besides compound C. Also in reaction with compound A solid brown-black chlorine containing compound D is obtained.

Besides M, its binary compound E (68.91% M by mass) with element G is also widely used because of its high melting point. E can be obtained from C by reaction with hydrogen and chloride H of element G at 1300°C (reaction 5), or by reaction of M with oxide I and carbide J (78.26% G by mass) of element G at 2000°C (reaction 6), or by reaction of B with I in melted Na (reaction 7).

Questions:
1) Determine elements M and G, and also compounds A-E and H-I.
2) What is the name of the mineral B?
3) Write the equations of chemical reactions 1-7.

**Problem 6**

**PEACEFUL NUCLEAR EXPLOSIONS**

Modern civilization cannot exist without electricity. Production and use of electricity require electricity to increase every year, but humanity is faced with the problem of "energy shortage" due to the depletion of oil and gas fields and increase of environmental pollution.

Energy, which is released by nuclear reactions, is one million times higher than combustion reactions, thus caloric value of nuclear fuel is considerably greater than that of. The use of nuclear fuel for electricity generation has a promising future.

It is known that nuclear power uses isotope of uranium ²³⁵U, which can sustain a nuclear chain reaction, therefore it is used in a nuclear reactor and in a nuclear weapon. The main processes taking place in a reactor can be represented as follows:

\[
^{235}_{92}U \rightarrow ^{135}_{54}I + ^{80}_{34}Se + ^{99}_{43}Tc + ^{3}_{1}H
\]

Questions:
1) Define elements A-D and write missing designations.
   A huge quantity of heat released during the fission of uranium. Consider the first reaction in more detail:

\[
^{235}_{92}U + ^{1}_{0}n \rightarrow ^{135}_{54}I + ^{134}_{52}Se + ^{3}_{1}H + ^{3}_{1}H
\]

2) Define element E. Calculate the energy which is released by the reaction (in MeV). Use the following values of atomic weights:

\[
m(235U) = 235.0493 \text{ a.m.u.};
\]
\[
m(135Tc) = 134.9165 \text{ a.m.u.};
\]
\[
m(^{3}He) = (7-1).9128 \text{ a.m.u.};
\]
\[
m(n) = 1.0087 \text{ a.m.u.};
\]
1 a.m.u. $c^2 = 931.5$ MeV.

To imagine how enormous the energy when it is released, we can compare it with the amount of heat released during coal combustion reaction:

$$ \text{C} + \text{O}_2 = \text{CO}_2 + 401 \text{ kJ} $$

3. Taking into account the result from point 2, define amount of energy which is released (in kW/h) from 1 g of uranium. (1 J = 1 W s; 1 eV = 1.6 $10^{-19}$ J). How much coal with carbon mass fraction of 75% is needed to get the same amount of energy?

The Chernobyl disaster was a catastrophic nuclear accident that occurred on April 26, 1986. The Chernobyl disaster was the worst nuclear power plant accident in history in terms of the cost and casualties.

Today caesium-137 is one of the primary elements preventing the Chernobyl exclusion zone being re-inhabited. It easily enters the plant through the root system because it has similar chemical properties to the elements of the group 1. Caesium enters in the human body when a person breathes in or takes a meal. Caesium has the ability to accumulate in the human body and cause internal radiation exposure.

4. The half-life of the radioactive isotope $^{137}$Cs, which fell into the atmosphere as a result of the Chernobyl accident, is 29.7 years. In what year the amount of this isotope will be less than 1% of the original amount?

In the fission of uranium nuclei from their fragments the nucleus of the lighter elements and $^{135}$Xe is one of them are formed. Xenon is a reaction-inhibiting neutron absorber. If the reactor is operated at a steady state, the $^{135}$Xe atoms burn out quite quickly and do not affect the operation of the reactor. However, if the reactor power decreases rapidly, the Xenon does not have time to burn out and starts to accumulate in the reactor, significantly contributing to the reduction of reactor power. It forms the phenomenon of so-called xenon poisoning of the reactor or "iodine pit".

Because of this, the reactor becomes difficult to manage, and it can get out of control. For safety reasons, the reactor must be immediately prepared for operation and finally to stop the reactor, however, on April 26, 1986 that has not been done. On the contrary, the reactor power was increased, which has played an important role in the scenario of events leading to the accident.

Reactivity is a universal characteristic of the reactor condition, occurring in its physical processes, and the temporal behavior of the reactor. The reactivity of the reactor operating at a constant power level is zero (critical reactor). If the reactivity level is greater than zero, the reactor power increases, it accelerates. If the reactivity level is less than zero, the power decreases, the reactor stalls.

5. Using the table, draw a graph of the reactivity of the reactor from time of the shutdown of the reactor for neutron flux $J = 10^{14}$ particles per second per cm$^2$ in the conditions of iodine pit. RBMK-1000 reactors used in Chernobyl can be activated at a value of $-0.1$ reactivity. Study the graph and find how long the residents of Pripyat city would have had power outages.

<table>
<thead>
<tr>
<th>Time after reactor shutdown, h</th>
<th>0</th>
<th>2</th>
<th>5</th>
<th>7</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactivity</td>
<td>-0.09</td>
<td>-0.17</td>
<td>-0.22</td>
<td>-0.25</td>
<td>-0.24</td>
<td>-0.21</td>
<td>-0.14</td>
<td>-0.08</td>
<td>-0.06</td>
<td></td>
</tr>
</tbody>
</table>

Reference data for calculations:

$$ k = \frac{\ln 2}{\text{h}}; \quad k = \frac{1}{T} \cdot \ln 2, \quad \text{where } k \text{ – half-constant.} $$
Problem 2

High-molecular substance \( F \), that has useful properties, can be synthesized according following scheme.

\[ \begin{align*}
X & \xrightarrow{\text{Cl}_2} A \xrightarrow{\text{H}_2, \text{Pt} \atop 25^\circ C} B \xrightarrow{\text{KCN}} C \xrightarrow{\text{H}_2\text{O}, \text{H}_2} D \xrightarrow{280^\circ C} E \xrightarrow{280^\circ C} F
\end{align*} \]

113 g of \( F \) was hydrolyzed in acid media at heating until formation initial compounds D and E. Moreover, the 1 mole of NaOH is necessary and enough to react completely with formed amount of substance E.

Questions:
1. Write down reaction equations.
2. Give structural formulas of substances A, F and X.
3. Which polymer can be synthesized using X?

Problem 3

POLYMERS - CHAMELEONS

Molecules that called photochromic (photosensitive) can reversibly change its structure when exposed to light:

Scheme 1.

\[ \begin{align*}
A & \xrightarrow{\text{hv}_1} B
\end{align*} \]

Spiropyans are the such photochromic compounds. The spiropyans are organic molecules consisting of two mutually perpendicular aromatic fragments. In the initial state molecules of spiropyans are colorless, but after UV irradiation, they are able to "open" in the merocyanine form (with heterolytic breaking of the C=O bond), which has a purple color and is able to move back into spiropyran form when exposed under visible light.

However, recently, scientists have found another interesting way of application of spiropyans: there is an article, published in 2009 in the Nature journal, with the description about how the unique structure of the spiropyans molecules was used to create a polymer that is capable of changing its color under mechanical stress.

The scheme of synthesis of spiropyran \( H \), which was used for the polymerization in the original paper and change the color of polymer under mechanical stress, is printed below. Also, here is the scheme of synthesis of similar spiropyran \( J \), which cannot change the color of polymer under mechanical stress according to the basic conclusions of researchers:
It is known that two singlets with equal integral intensity are observed in the aromatic region in NMR $^1H$ (25 MHz) spectra of compound A, whereas doublets are observed in the aromatic regions in the NMR $^1H$ spectra of the by-products in the reaction of producing compound A. It is also known that NMR $^1H$ (25 MHz) spectra of compound C includes signals from protons in the aromatic region (3 protons) and from three groups of non-equivalent protons (12 protons) in the aliphatic region of the spectrum. NMR $^1H$ (25 MHz) spectrum of compound G includes signals from protons in the aromatic region (7 protons), from two groups of non-equivalent protons (9 protons) in the aliphatic region of the spectrum and from two protons which are corresponding to hydroxyl groups. In addition, it is known that the merocyanine forms of the compounds I and G may have a cis-or trans-configuration.

Questions:
1) Decode the scheme of spiropyrans H and J synthesis, draw structural formulas of the compounds A-J.
2) Name the types (no mechanisms) for all described reactions and give the names of reactions, if such reactions are present.
3) Draw the structural formula of merocyanine for compound G. Explain the appearance of color in merocyanine form of compound G unlike the spiropyrans form.
4) Explain why the inclusion of spiropyrans H in the polymer allows changing the color of the polymer under mechanical stress, but that inclusion of spiropyrans J in the polymer does not allow it.
5) Try to formulate fundamental purposes for which scientists have made this research with polymers modified by spiropyrans.
6) Give at least 1 example of real practical use of photochromic compounds in everyday life.

Problem 4

UNEXPECTED SIDES OF CHEMISTRY OF A SINGLE ELEMENT

In 1928 research group of Otto Ruff in Germany had obtained a thermodynamically stable compound $\text{A}_3$ (the stability of this compound became a big surprise). It turned out that this compound could be synthesized in two ways. The essence of the first method involves the electrolysis of salt $\text{A}_2$ (which itself is a salt of acid $\text{A}_3$) with acid $\text{A}_3$. The second method contains the reaction of a simple gaseous substance $\text{A}_4$ with a compound $\text{A}_3$ on a copper catalyst.

It is known that $\text{A}_3$ can be obtained from $\text{A}_4$ in one stage, as well as $\text{A}_3$ can be turned into $\text{A}_2$ in one stage.

It turned out that there are several relative compounds of $\text{A}_1$ with similar elemental composition. One of them $\text{B}_1$ could result from a reaction between copper and $\text{A}_1$ (in fact it is exactly how it was first obtained in 1957). Today $\text{B}_1$ is received using another method (coefficients are correct):

\[
\begin{align*}
\text{B}_3 \times \text{A}_1 &= \text{B}_4 + \text{B}_5 + \text{B}_6 \quad (70.00\% \text{ yield}) \\
\text{B}_7 \times \text{H}_2 \text{SO}_4 + \text{H}_2 \text{O} &= \text{B}_6 + \text{B}_9 \quad (100\% \text{ yield}) \\
2\text{B}_7 + \text{NaOCl} &= \text{B}_9 + \text{B}_1 \quad (100\% \text{ yield})
\end{align*}
\]

If you take 1.648 grams of $\text{B}_7$ using the above scheme you will get exactly 1 gram of $\text{B}_9$, and you will get 1.014 grams of intermediate $\text{B}_6$. $\text{B}_1$ turned out to be strong oxidizer, what can be shown by following reactions:

(a) $\text{ISIH}_2 + 2\text{B}_1 = \text{...}$
(b) $10\text{I} + \text{B}_1 = \text{...}$

It is also known that $\text{B}_1$ is an organic compound that was synthesized from its isomer $\text{B}_9$ by a famous chemist. This reaction disproved the vitalism theory and gave start to a new era in chemistry.

Questions:
1. Define all the unknown compounds. The molar mass ratio is $M(\text{A}_3) : M(\text{B}_9) = 0.740$. Write down 6 reactions related to the synthesis of $\text{A}_3$ and $\text{B}_9$.
2. What scientist implemented the reaction which disproved the vitalism theory? Write his name and surname.
3. $\text{A}_1$ molecule has a pyramidal shape. The angle between any two bonds in the molecule is 102.5°, and dipole moment of each bond is 0.234 D. Find a full dipole moment of this molecule. Write down all of your calculations.
4. Write down reactions (a) and (b) Many of the chemical properties of $\text{B}_1$ are caused by its partial dissociation: $\text{B}_1 = 2 \text{B}_9$. It is of course an equilibrium with $K_p = 0.03$ at 298 K, and the enthalpy of dissociation $\Delta H = 83.20$ kJ/mole.
5. Calculate $\Delta S$ and $\Delta G$ of dissociation at 298 K.
6. Is $\text{B}_1$ a radical?
7. Write down structures of the products of the reaction of $\text{B}_9$ with:
   A) $\text{NO}$
   B) $\text{Cl}_2$
   C) $\text{CF}_3$ $\text{Cl} = \text{CF}_2$.
Problem 5

MEET THE SODA

NaHCO₃ is one of the most widely used chemicals in home. Its chemical properties are known for every housewife. Some of its chemical features and characteristics are shown below.

155 years ago in 1861 Belgian chemist and industrialist Ernest Solvay patented industrial method of obtaining Na₂CO₃. In the first step, gaseous carbon dioxide and ammonia passes through sodium chloride solution forming NaHCO₃ (reaction 1). Then Na₂CO₃ is obtained from NaHCO₃ (reaction 2).

Questions:

1) Write the equations of chemical reactions and conditions under which the reactions take place.

The solutions of these chemicals are widely used in analytical chemistry for preparing buffers. Also they do not decay.

2) Calculate the pH of these solutions:
   a) 0.20 M Na₂CO₃
   b) 0.01 M Na₂CO₃
   c) Buffer obtained from mixing 10 ml 0.05 M NaHCO₃ and 30 ml 0.20 M Na₂CO₃

Use the next values: \( K_a(H_2CO₃) = 2.5 \times 10^{-4}, K_a(HCO₃^-) = 4.7 \times 10^{-11}, K_a = 1.0 \times 10^{-14} \)

3) Does the pH of the buffer depend on solution dilution?

To determine the mix of NaHCO₃, Na₂CO₃ and unknown carbonate or bicarbonate X 0.1g of this mix was completely dissolved in water. 6.5 ml of 0.10 M HCl were spent in titration of this solution with the pH indicator phenolphthalein, then 10.7 ml of 0.10 M HCl were spent in titration of obtained solution with methyl orange. It is known that litmus paper changes the color if the original solution is heated.

4) Determine X. Confirm your answer by calculations.

5) Determine the mass percentage of all components in the mix.

6) Why does litmus paper change the color? Write the explanation and equation of chemical reaction.

Problem 6

PEACEFUL NUCLEAR EXPLOSIONS

Modern civilization cannot exist without electricity. Production and use of electricity increase every year, but humanity is faced with the problem of "energy shortage" due to the depletion of oil and gas fields and increase of environmental pollution.

Energy, which is released by nuclear reactions, is one million times higher than combustion reactions, thus calorific value of nuclear fuel is considerably greater than that of. The use of nuclear fuel for electricity generation has a promising future.

It is known that nuclear power uses isotope of uranium ²³⁵U, which can sustain a fission chain reaction, therefore it is used in a nuclear reactor and as a nuclear weapon. The main processes taking place in a reactor can be represented as follows:

\[ {}^{235}_{92}U + {}^1_0n \rightarrow {}^{137}_{55}P_{r} + {}^1_0n \rightarrow {}^{137}_{55}P_{r} + {}^1_0n \rightarrow {}^{129}_{53}I + {}^2_0He \]

Questions:

1. Define elements A-D and write missing designations.

A huge quantity of heat released during the fission of uranium. Consider the first reaction in more detail:

\[ {}^{235}_{92}U + {}^1_0n \rightarrow {}^{135}_{55}P_{r} + {}^1_0n + {}^1_0n \]

2. Define element E. Calculate the energy which is released by the reaction (in MeV). Use the following values of atomic weights:
   - m(235U) = 235.0493 a.m.u.;
   - m(135Te) = 134.9165 a.m.u.;
   - m(He) = 4.00260 a.m.u.;
   - m(n) = 1.00867 a.m.u.;
   - 1 a.m.u. = 931.5 MeV.

To imagine how enormous the energy when it is released, we can compare it with the amount of heat released during coal combustion reaction:

\[ \text{a. } C + O_2 = CO_2 + 401 \text{ kJ} \]

3. Taking into account the result from point No2, define amount of energy which is released (in kW·h) from 1 g of uranium. (1 J = 1 W·s; 1 eV = 1.6 \times 10^{-19} J). How much coal with carbon mass fraction of 75% is needed to get the same amount of energy?

The Chernobyl disaster was a catastrophic nuclear accident that occurred on April 26, 1986. The Chernobyl disaster was the worst nuclear power plant accident in history in terms of the cost and casualties.

Today cesium-137 is one of the primary elements preventing the Chernobyl exclusion zone being re-inhabited. It easily enters the plant through the root system because it has similar chemical
properties of the elements of the group I. Caesium enters in the human body when a person breathes in or takes a meal. Caesium has the ability to accumulate in the human body and cause internal radiation exposure.

4. The half-life of the radioactive isotope $^{137}Cs$, which fell into the atmosphere as a result of the Chernobyl accident, is 29.7 years. In what year the amount of this isotope will be less than 1% of the original amount?

In the fusion of uranium nuclei from their fragments the nucleus of the lighter elements and $^{135}Xe$ is one of them are formed. Xenon is a reaction-inhibiting neutron absorber. If the reactor is operated at a steady state, the $^{135}Xe$ atoms burn out quite quickly and do not affect the operation of the reactor. However, if the reactor power decreases rapidly, the Xenon does not have time to burn out and starts to accumulate in the reactor, significantly contributing to the reduction of reactor power. It forms the phenomenon of the so-called xenon poisoning of the reactor or "iodine pit". Because of this, the reactor becomes difficult to manage, and it can get out of control. For safety reasons, the operator must put down the control rods and finally to stop the reactor, however, on April 26, 1986 that has not been done. On the contrary, the reactor power was increased, which has played an important role in the scenario of events leading to the accident.

Reactivity is a universal characteristic of the reactor condition, occurring in its physical processes, and the temporal behavior of the reactor. The reactivity of the reactor operating at a constant power level is zero (critical reactor). If the reactivity level is greater than zero, the reactor power increases, it accelerates. If the reactivity level is less than zero, the power decreases, the reactor stalls.

5. Using the table, draw a graph of the reactivity of the reactor from time of the shutdown of the reactor for neutron flux $J = 10^{14} \text{ particles per second per cm}^2$ in the conditions of iodine pit. RBMK-1000 reactors used in Chernobyl can be activated at a value of $-0.1$ reactivity. Study the graph and find how long time the residents of Pripyat city would have had power outages.

<table>
<thead>
<tr>
<th>Time after reactor shutdown, h</th>
<th>0</th>
<th>2</th>
<th>5</th>
<th>7</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactivity</td>
<td>0.0089</td>
<td>0.0017</td>
<td>0.0022</td>
<td>0.0025</td>
<td>0.0024</td>
<td>0.0021</td>
<td>0.0014</td>
<td>0.0008</td>
<td>0.0006</td>
<td></td>
</tr>
</tbody>
</table>

Reference data for calculations:

$k = \frac{\ln 2}{t_{1/2}}$; $k = \frac{1}{t} \ln \frac{C_0}{C}$, where $k$ - half-constant.

SOLUTIONS

JUNIOR LEAGUE

Problem 1

1. Only $S$ (sulfur) and $Cl$ (chlorine) can satisfy the problem conditions. $X = S; Y = Cl$.

Reaction between $S$ and $Cl$ leads to formation of compounds as $S_x Cl_y$. Hydrolysis of such compounds can be described by general equation:

$2S_x Cl_y + 3H_2O \rightarrow SO_3 + (2x-1)S + 4HCl$

Let's determine $A_1$ formula:

$v(S) = 0.155/32 = 4.844 \times 10^{-3} \text{ mole}$

$v(S Cl_2) = 1/(32x+71) \text{ mole}$

$(2x-1)/1/(32x+71) = 2.4 \times 10^{-3}$

$x=1$, therefore, $A_1 = Sulfur dichloride (S Cl_2)$.

Удостоверяя формулу соединения $A_1$:

$v(S) = 0.356/32 = 11.125 \times 10^{-3} \text{ моль}$

$v(S Cl_2) = 1/(32x+71) \text{ моль}$

$(2x-1)/1/(32x+71) = 2.1125 \times 10^{-3}$

$x=2$, therefore, $A_2 = Dithiodichloride (S_2 Cl_2)$.

$B = SO_3, C = HCl, D = SO_2 Cl_2, E = H_2SO_4, F = H_2S$.

2. Reaction equations:

$S + Cl_2 \rightarrow S Cl_2$ (reaction 1)

$2S + Cl_2 \rightarrow S_2 Cl_2$ (reaction 2)

$2SOCl_2 + 3H_2O \rightarrow SO_2 + S + 4HCl$ (reaction 3)

$2S Cl_2 + 3H_2O \rightarrow SO_3 + S Cl_2 + 3HCl$ (reaction 4)

$SO_3 + Cl_2 \rightarrow SO_2 Cl_2$ (reaction 5)

$2S_2 Cl_2 + 3S \rightarrow 3S Cl_2 + S Cl_2 + 2SO_2$ (reaction 6)

$SO_2 Cl_2 + 3H_2O \rightarrow 1/3 SO_4 + 2HCl$ (reaction 7)

$Cl_2 + H_2SO_4 \rightarrow 2SO_2 + 2HCl$ (reaction 8)

$SO_2 Cl_2 + 2H_2O \rightarrow 1/3 SO_4 + 2HCl$ (reaction 9)

$H_2S + SO_3 \rightarrow 3S + 2HCl$ (reaction 10)

$Cl_2 + H_2S \rightarrow S Cl_2 + 2HCl$ (reaction 11)

$H_2S + Cl_2 \rightarrow 2HCl$ (reaction 12)

$H_2S + 4Cl_2 + 4H_2O \rightarrow H_2SO_4 + 8HCl$ (reaction 13)

3. Solution of sulfur in dithiodichloride is used in the vulcanization of rubber at low temperatures (cold vulcanization).

$4. v(H_2S) = \frac{VPr}{R} = \frac{101.3 \times 10^3 \times 97.8 \times 10^3}{8.31 \times 298} = 0.004 \text{ mole}$

$v(H_2S) \times v(Cl_2) = 1:4$, so reaction 13 takes place.
\[ v(H_2SO_4) = v(H_2S) = 0.001 \text{ mole.} \]
\[ C(H_2SO_4) = 0.01 \text{ mole/l} \]
\[ v(HCl) = 2v(Cl_2) = 8v(H_2S) = 0.008 \text{ mole} \]
\[ C(HCl) = 0.008 \text{ mole/l} \]
\[ HCl = H^+ + Cl^- \]
\[ H_2SO_4 = 2H^+ + SO_4^{2-} \]
\[ [H^+] = 0.02 + 0.08 = 0.1 \text{ mole/l} \]
\[ pH = -\log[H^+] = -\log 0.1 = 1 \]
Grading:
1. Determining X, Y 1*+2=2 points
   Right proportion of metal ions in the cell 0.5*2=1 point
2. Slats of Na 0.5*2=1 point max
3. Chemist's surname 1 point
   Determining Z, W 0.5*2=1 point
4. Determining the substances, which have given names to X and Y 0.5*2=1 point
   Chemical equation of electrolysis = 1 point
5. Chemical equation - 1 point
6. Each equation - 0.5 point 13-6,5 points
   Determining the substances 0.5 point *8=4,5 points

Total = 21 points

Problem 4

1) Reaction that refuted the vitalism theory is a reaction of isomerization of ammonium cyanate into urea. So, B₁ = (NH₄)₂CO₃, B₂ = NH₄CO(NCO).

According to this fact, we can assume that the second stage of B₁ synthesis is a hydrolysis of a derivative of urea, and the result of this reaction is CO₂ and ammonia's derivatives. Then it is logical to assume that B₁ contains a fragment of urea with some functional groups instead of hydrogen atoms.

So, let us assume that B₁ can be described with the formula NH₃ₓXₘ (ammonia's derivative) and let its molar mass be M. If we take 1.648 grams of urea (or 0.02747 moles) and if reaction's yield is 70.6%, we get 1.019M moles of B₁. Then 0.02747*0.7=1.019M and M = 53.

If molar mass of X group in NH₃ₓXₘ is x, M = 53 = 14+3-n+2x and x=36/n+1. For n = 1, x = 37; for n = 2, x = 19 and for n = 3, x = 13. We should note that X must be an atom single element because A₁ is a simple substance. We can surely choose a pair n = 2 and x = 19 from different probable values of x. X is fluorine then, and B₁ = NH₄F₃.

Now we can calculate formula of B₁ from masses of elements, 1.019 g of B₁ contains following masses of nitrogen and fluorine:

\[ m(N) = \frac{14}{14 + 3 + 18} \times 1.019 = 0.269 \text{ g} \]
\[ m(F) = \frac{38}{38 + 14 + 1} \times 1.019 = 0.731 \text{ g} \]
\[ m(N) + m(F) = 1.000 \text{ g} \]

We can see, that B₁ consists only from nitrogen and fluorine (because total mass of these elements is equal to the mass of B₁) and molar ratio of elements is 1:2 (as in B₁ was). Then the formula of B₁ is (NF₂)₂. According to the last synthesis reaction's equation, we can conclude that 2 molecules of B₁ reacts with formation of 1 molecule of B₁, and formula of B₁ is NF₂ and (x = 2).

As we see from all the work we have done, a simple substance A₁ is F₂. And the single acid that can be formed from fluorine by one stage is hydrofluoric acid. Therefore A₂ = HF.

There's only one unknown compound (B₃) in A₄ synthesis scheme. As we concluded before, urea's derivative gives only one molecule of NH₄F after hydrolysis. If both nitrogen atoms in the urea were fluorinated, we would get two molecules of NH₄F, therefore only one of nitrogen atoms in urea were oxidized by fluorine. So, B₃ = NH₄CONF₂. Note: other partially fluorinated urea molecules do not fit the stoichiometry of reaction of urea fluorination: 2 moles of F₂ reacts with 1 mole of urea, and it means that urea is fluorinated only twice.

As we knew from text task, M(A₁) = 0.740M(B₁) = 71. A₁ consists from nitrogen and fluorine (as well as F₂). Possible compounds are NF₃ and NF₂. But the value of molar mass fits to NF₃. So, A₁ = NF₃.

A₃ is fluoracid's salt i.e. A₃ is fluoride. Its electrolysis gives a compound, that contains nitrogen, therefore a cation of A₂ also contains nitrogen. The most evident nitrogen containing cation is ammonium cation, and A₂ is NH₄F.

A₄ gives ammonium fluoride by one stage, therefore A₄ can be either ammonia, or hydrogen fluoride. However, HF is coded as A₄, so, A₃ is NH₃.

Reaction equations:

\[ 3\text{NH}_3\text{F}=\text{NH}_4\text{F}_2+6\text{HF} \]
\[ \text{NH}_4\text{F}_3+3\text{HF} \]
\[ \text{CuCl}_2+2\text{NF}_3=\text{CuF}_2+2\text{NF}_4 \]
\[ \text{NH}_3\text{CONH}_2+2\text{F}_2=\text{NH}_4\text{CONF}_2+2\text{HF} \]
\[ 2\text{NH}_4\text{CONF}_2+4\text{H}_2\text{O}(\text{NH}_4)\text{SO}_4+2\text{CO}_2+2\text{NH}_4\text{F}_2 \]
\[ 2\text{HF}+\text{NaOCl}=\text{NaF}_2+\text{H}_2\text{O}+\text{NaCl} \]

2) The name of that chemist is Friedrich Wöhler.

3) Let \( \alpha \) be a module of vector of dipole moment of N-\( F \) bond, \( \alpha T \) is a distance between two vectors' endings (number of vectors is three, but it is not too important here), \( \alpha \cos \theta \) is a projection of each vector on the vertical axis, \( \alpha \sin \theta \) is a projection on horizontal plane. We also know the angle \( \phi \) between two vectors, \( \phi = 102.5^\circ \).

We can calculate \( \alpha \) from cosine theorem: \( \alpha^2=2a^2-2a^2\cos\phi \). After using values if \( a \) and \( \phi \), \( \alpha = 0.794 \) (for \( a = 0.234 \) D).

Obtuse angle in the triangle with sides \( x, x, T \) is equal to 120° because sum of three equal angles is a full circle or 360° (it would be clear if we shall construct a full pyramid NF₃). Therefore, both remaining angles in this triangle are 30°. We can find \( x \) from sine theorem for this triangle now: \( x = T \times \sin 30° \times \sin 120° = 0.210 \text{ D} \). Furthermore, we can find \( c \) from Pythagorean theorem: \( c^2=a^2-x^2=0.234^2-0.210^2, c = 0.1032 \text{ D} \).

It remains to note, that sum of three dipole moments vectors is sum of three horizontal and three vertical projections. Sum of horizontal projections is zero (they are laying on \( x \)) and sum of
vertical projections is $3 \times 0.1032 = 0.3096 \approx 0.310 D$. So, the total dipole moment of molecule is 0.310 D.

4) (a) $\text{SiH}_4 + 2\text{NF}_3 = \text{SiF}_4 + 2\text{NH}_3$ and $\text{SiH}_4 + 2\text{NF}_3 = \text{H}_2\text{SiF}_4 + 2\text{NH}_3 + 2\text{HF}$

(b) $10\text{Li} + \text{N}_2\text{F}_4 = 2\text{Li}_2\text{N} + 4\text{HF}$

5) $\Delta G_c = -\text{RT} \ln K = 8687 \text{ J/mole}$

$\Delta S_c = (\Delta H_c - \Delta G_c) / T = 2500 \text{ J/(mole*K)}$

6) Yes, it is a radical.

7) A) NONF$_2$
   B) NCF$_2$
   C) CF$_2 \cdot \text{CF(NF}_2 \cdot \text{CF(NF}_2$

**Grading:**

1. Right formula of compounds A1-A3, B1-B3: 0.5 point * 10 = 5 points
2. Right equations of 6 reactions: 0.5 points * 6 = 3 points
3. Right name and surname of the chemist: 1 point
4. Right calculation of dipole moment: 3 points
5. Right equations of (a) and (b) reactions: 1 point * 2 = 2 points
6. Right calculation of $\Delta G$ and $\Delta S$ of reaction: 1 point * 2 = 2 points
7. A fact that B3 is a radical: 1 point
8. Right products of reactions: 1 * 3 = 3 points

**Total - 20 points**

**Problem 5**

1. Compound A contains three elements, then B is binary. As in reaction with chlorine and carbon CO is obtaining, therefore, B is an oxide. B-MO$_n$, where $n = 0.5, 1, 3/2, 2, 5/2, 3, 7/2$, by trial-and-error method we can find that M-Ti, B-TiO$_2$.

   Brown-black compound D, which is obtained from reaction of compound A with chlorine is rather FeCl$_2$. From mass fraction A = FeTiO$_3$.

   1) FeTiO$_3 + 2\text{HI} = \text{FeCl}_2 + \text{H}_2\text{O} + \text{TiO}_2$
   2) TiCl$_4 + 2\text{MgCl}_2 = 2\text{MgCl}_3 + \text{TiCl}_4$
   3) $2\text{FeTiO}_3 + 7\text{Cl}_2 + 3\text{CO} = 2\text{FeCl}_3 + 2\text{TiCl}_4 + 6\text{CO}$
   4) $\text{TiO}_2 + 2\text{Cl}_2 + 2\text{C} = \text{TiCl}_4 + 2\text{CO}$

   Compound C = TiCl$_4$. From mass fraction, we can find that compound E-TiB$_2$. Thereby G-B, H-BCl$_3$, I-B$_2$O$_3$, J-B$_3$C.

5) $2\text{TiCl}_4 + 4\text{BCl}_3 + 10\text{HCl} = 2\text{TiB}_2\text{O}_3 + 2\text{H}_2\text{Cl}_2$
6) $7\text{Ti} + 2\text{B}_2\text{O}_3 + 3\text{B}_3\text{C} = 7\text{TiB}_2\text{O}_3 + 3\text{CO}$
7) $\text{TiO}_2 + 3\text{B}_2\text{O}_3 + \text{Na}_2\text{O} = 5\text{Na}_2\text{O} + 2\text{TiB}_2\text{O}_3$

**Solution:** M-TiA=FeTiO$_3$; B-TiO$_2$; C-TiCl$_4$; D-FeCl$_3$; E-TiB$_2$; G-B; H-BCl$_3$; I-B$_2$O$_3$; J-B$_3$C.

2. The main name of the mineral TiO$_2$ is rutile. Also it can be named as anatase or brookite.

**Grading:**

1. Writing the elements A-D............................................. 2 points

---

**Problem 6**

1. $\frac{3}{2} \ddot{\text{H}}_2 \ddot{\text{O}} \ddot{\text{O}} + \frac{1}{2} \ddot{\text{H}}_2 \ddot{\text{S}} \ddot{\text{O}} \ddot{\text{O}} + \frac{1}{2} \ddot{\text{H}}_2 \ddot{\text{O}} \ddot{\text{I}} \ddot{\text{O}} \ddot{\text{O}} + \frac{1}{2} \ddot{\text{H}}_2 \ddot{\text{S}} \ddot{\text{O}} \ddot{\text{O}} \ddot{\text{C}} \ddot{\text{S}} \ddot{\text{O}} \ddot{\text{O}} + \frac{1}{2} \ddot{\text{H}}_2 \ddot{\text{O}} \ddot{\text{I}} \ddot{\text{O}} \ddot{\text{O}} \ddot{\text{C}} \ddot{\text{S}} \ddot{\text{O}} \ddot{\text{O}} \ddot{\text{I}} \ddot{\text{O}} \ddot{\text{O}}$

Am = 235.0493 + 1.0087 = (134.9165 + 97.9128 + 13.0087) = 0.2026 amu.
Q = 0.2026 - 931.5 MsB = 188.7219 MsB = 188.7 MeV.
3. $t = 6.02 \times 10^{27}$ amu.

If 235 amu is released 188.7 MeV, then 1 g will give 4.83 \times 10^{27} MeV. 1 MeV = 1.6 \times 10^{12} J, then

$4.83 \times 10^{27} \text{ MeV} = 7.73 \times 10^{19} J = 2.13 \times 10^6 \text{ kWh}$.

$m(C) = 7.73 \times 10^{19} J / 12 / 4010000 \text{ J} = 2.31 \times 10^6 \text{ g} = 2.31 \text{ t}$.

$m(\text{coal}) = 2.31 \times 10^6 / 7000 = 3.28 \text{ t}$.

1 kg of uranium releases an equal amount of energy 3.08 t of coal.

4. $t = \frac{1}{2} ln \frac{1}{0.01} = 197 \text{ years}$.

1986 + 197 = 2183 year

In the year 2183.99% of caesium isotope will be released.

5. The graph of the reactivity of the reactor from time to time, since the shutdown of the reactor:

**Grading:**

1. Writing the elements A-D............................................. 2 points

---

Find the intersection of the curve with the value -0.1 reactivity, therefore, approximate waiting time for the start-up of reactor is about 40 hours.
SOLUTIONS

SENIOR LEAGUE

Problem 1

1) It is known that the number of molecules that take part in a simple reaction can be equal to 1, 2, or 3. So, it means that n can be equal to 1 or 2. If n > 2, the number of molecules of reagents in the second stage would be more than 3.

2) Let C(A) and C(P) be current concentrations of A and P and let \( C_0(A) \) be initial concentration of A. Since from 1 mole of A we get 1 mole of P in both stages, we can conclude that total concentration \( C(A) + C(P) \) is constant in time. So \( C(A) + C(P) = C_0(A) \) and \( C(P) = C_0(A) - C(A) \).

Let \( r \) be rate of forming of product P.

\[
\frac{dP}{dt} = r = kC(A) + m(n + 1)C(A)C(P)^n - mncA(A)C(P)^n = kC(A) + mC(A)C(P)^n
\]

\[
= kC(A) + mC(A)(C_0(A) - C(A))^n
\]

On the second stage n moles of P reacts with 1 mole of A forming \((n+1)\) moles of P, and the summary result of second reaction is equal to the formation 1 mole P from 1 mole A. The stoichiometry of second stage is equal to first stage's stoichiometry.

We should solve an equation \( r(C(A)) = 0 \) where \( r(C(A)) \) is derivative of \( r(C(A)) \) to find maximum of \( r \).

\[
\frac{dr}{dC(A)} = k + m(C_0(A) - C(A))^n - mnc(A)(C_0(A) - C(A))^{n-1} = 0
\]

\[
k + 10000k(C_0(A) - C(A))^n - 10000mC(A)(C_0(A) - C(A))^{n-1} = 0
\]

\[
1 + 10000(C_0(A) - C(A))^n - 10000mC(A)(C_0(A) - C(A))^{n-1} = 0
\]

Then we can use given values of \( C_0(A) = 0.01 \text{M} \) and \( n = 1 \).

\[
l + 10000 \times (0.01 - C(A))^n - 10000 \times C(A)(0.01 - C(A))^{n-1} = 0
\]

\[
1 + 10000C_0(A) - 10000C(A) = 0,
\]

\[
C(A) = 0.01 \times 10000 = 0.00005 \text{M} = 5.05 \text{mmole/l}
\]

Note: the calculated value of \( C(A) \) is a maximum because \( r(C(A)) < 0 \) if \( C(A) > 0.00005 \text{M} \) and \( r(C(A)) > 0 \) if \( C(A) < 0.00005 \text{M} \).

3) \( r = kC(A) + 10000kC(A)(C_0(A) - C(A))^n = 5.05 \times 10^{-6} + 10 \times 5.05 \times 10^{-3} \times 4.95 \times 10^{-3} = 2.55 \times 10^{-4} \text{ mole L}^{-1} \text{ s}^{-1} \)

4) As was given in the body of a task, at that moment \( C(A)=10^{-4} \text{ mole/L} \). So

\[
r = kC(A) + 10000kC(A)(C_0(A) - C(A))^n = 10^{-4} \text{ mole L}^{-1} \text{ s}^{-1}
\]

5) One of well-known examples of autocatalytic reactions is oxidation of some compounds by \( \text{KMnO}_4 \) in acidic conditions: \( \text{Mn}^{2+} \) ions catalyze the oxidation and they are one of products at the same time. Any autocatalytic reaction is a right answer to this task, for example:

\[
2\text{KMnO}_4 + 5\text{K}_2\text{SO}_3 + 3\text{I}_2 = 6\text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O}
\]
Grading:
1. Right possible values of n (1 point for each)
2. Right calculation of value of C(A)
3. Right calculation of value of maximum rate
4. Right calculation of value of rate
5. Any right example of autocatalytic reaction with its equation

Total: 15 points

Problem 2
1. It is obvious from scheme that F is a polyamide. Also it is known that D and E have the equal number of carbon atoms. Because F is a polyamide, E is a diacid. So, 1 mole of NaOH reacts with 0.5 moles of acid E. If 0.5 moles of acid E are formed, then 113 g of F is 0.5 moles of repeating chains of polyamide:

\[ [-\text{NH-}-(\text{CH}_2)_m-\text{NH-}^+ - \text{C-}^--(\text{CH}_2)_n-2^\circ - \text{C-}]_n \]

Where \( m \) – amount of carbon atoms between amino groups.
We form the equation:

Therefore, substance X is butadien-1,3.

<table>
<thead>
<tr>
<th>№</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₂=CH-CH=CH₂ Cl Cl</td>
</tr>
<tr>
<td>2</td>
<td>CH₂=CH-CH=CH₂ 1/2 ( \text{KOH} ) Cl Cl</td>
</tr>
<tr>
<td>3</td>
<td>CH₂-CH₂-CH₂-CH₂ KOH CH₂-CH₂-CH₂-CH₂</td>
</tr>
<tr>
<td>4</td>
<td>CH₂-CH₂-CH₂-CH₂ H₂O, H₂SO₄ CH₂-CH₂-CH₂-CH₂ CN</td>
</tr>
<tr>
<td>5</td>
<td>CH₂-CH₂-CH₂-CH₂ H₂O, H₂SO₄ CH₂-CH₂-CH₂-CH₂ CN</td>
</tr>
</tbody>
</table>

Problem 3
1. For each reaction equation 1 point
2. For each structural formula of substance 1 point
3. Polymer name – 1 point.

Total: 15 points
I) In view of the problem conditions about the presence of the two singlets with equal integral intensity in the aromatic region in the NMR $^1$H (25 MHz) spectrum of compound A, we can make an unambiguous conclusion that the nitro group is in para position to the hydroxy group in compound A. In a given molecular formula of compound B, boiling of A in HBr leads to hydrolysis of the methoxy group in A.

The reaction of producing C - a classic example of a Fischer indole synthesis reaction. The structure of the molecule of compound C can be reliably confirmed by the data about the number of protons and their equivalence in the NMR $^1$H (25 MHz) spectrum of compound C. The reaction of preparation D from C is analogous to the reaction of preparation B from A, that also can be understood from the molecular formula of compound D. Reactions of preparation E and F from D - classical reactions of alkylation the nitrogen atom in the indole D, which gave the corresponding salts.

Reaction of producing G and I spiropyrans are the condensations of ortho-hydroxy aromatic aldehydes with heterolytic cations having an active methylene group, with forming spiro junction. Conditions of the problem can also help to determine the structures of G and I spiropyrans:

A) "spiropyrans are organic molecules consisting of two mutually perpendicular aromatic fragments", "they are able to "open" in the mercocyanine form (with heterolytic breaking of the C-O bond); it helps to determine the shape and atoms in spiro junction

B) "merocyanine forms of the compounds I and G may have a cis or trans-configuration", "NMR $^1$H (25 MHz) spectrum for compound G includes signals from protons in the aromatic region (7 protons), from two groups of non-equivalent protons (9 protons) in the aliphatic region of the spectrum, and from two protons which are corresponding to hydroxy groups: it helps to determine the presence of the double bond and its conjugation with the aromatic system in one of the fragments of spiropyran.

Reactions of H and J producing are classical reactions of hydroxyl groups acylation.

2) Denote the types of reactions:
- Reaction of compound A synthesis: nitration of aromatic compound
- Reaction of compound B synthesis: hydrolysis of ether
- Reaction of compound C synthesis: formation of aryl hydrazone and its cyclocondensation (Fischer reaction)
- Reaction of compound D synthesis: hydrolysis of ether
- Reaction of compound E (F) synthesis: alkylation of the nitrogen atom with an alkyl halide
- Reaction of compound G (I) synthesis: condensation of an ortho-hydroxy aromatic aldehyde with heterolytic cation with an active methylene group
- Reaction of compound H (J) synthesis: acylation of the hydroxyl groups

3) When UV irradiation or mechanical stretching (from different sides) of molecules of spiropyran there is an opening of spiro-junction with heterolytic breaking C-O bond and the formation of merocyanine form.

4) When stretched the polymer with spiropyran H included in structure, stretching comes from different sides of spiropyran molecules and creates a load on the spiro-junction, which is relatively easily opened and formed colored merocyanine form within the polymer.

If stretched the polymer with spiropyran J incorporated with its structure, then the stretching forces affects only on the indole side of spiropyran molecules and don't bear the load on spiro-junction. Consequently, in this case stretching does not lead to produce of merocyanine form of spiropyran in the polymer.
5) The most obvious fundamental problem, which is solved by the scientists by the creation of composition of spiropyran-polymer, is to demonstrate the ability of creation materials that visually responsive to the application of mechanical effects to them. Further it could allow to study the effects of mechanical stress and damage to various polymer materials, it may also could enable the visualization of their integrity evaluation and determination of necessary modifications to improve their qualities.

6) Materials based on photochromic compounds are currently used as a variable optical density filters in eye protection devices and optical instruments, in the optical information recording and processing devices and laser technology. The closest example of real practical use of photochromic compounds in life - the so-called "chameleon" glasses that darken in sunny weather on the street, and in the absence of UV irradiation lighter back. Another practical example - glass helmets of military aircraft pilots, which in a split second darken from UV radiation from a nuclear explosion and protecting the pilots from the light wave.

Grading:

1 Correct structure formulas of A-F 1 point * 6 = 6 points
Correct structure formulas of G-J 2 points * 4 = 8 points
2 Correct names of types for reactions of producing A, B, C, D. 0.5 points * 7 = 3.5 points
E (F), G (I), H (J) Correct name of reaction of producing C (Fischer reaction) 0.5 points
3 Correct structural formula of merocyanine form of 2 points compound G
Correct explanation of the appearance of color in merocyanine form of compound G unlike the spiropyran form 1 point
4 Correct explanation of the peculiarities of mechanical stress 1 point
for polymers with inclusion of spiropyrans H and J
5 Logical formulation of possible fundamental purposes 2 points
6 Correct example of real practical use of photochromic 1 point compounds in everyday life

Total: 25 points

Problem 4
Solution of Problem 4 JUNIOR LEAGUE

Total: 20 points

Problem 5

1. Solvay process chemical reactions:
   1) NaCl + NH₃ + CO₂ + H₂O = NH₄Cl + NaHCO₃
   2) 2NaHCO₃ = Na₂CO₃ + CO₂ + H₂O (6°C)

2. In solution of Na₂CO₃ the next reaction occurs:
   CO₃²⁻ + H₂O = HCO₃⁻ + OH⁻
   So that's why the pH will be more than 7. X moles of OH⁻ is formed in solution:
   (CO₃²⁻) x x
   CO₃²⁻ + H₂O = HCO₃⁻ + OH⁻
   The constant of equilibrium:
   K = [HCO₃⁻][OH⁻] / [CO₃²⁻]
   x² = Kx²C₀
   The value of constant:
   x = C₀ / K
   [HCO₃⁻] = [OH⁻] = [CO₃²⁻] = [H⁺]
   K = [HCO₃⁻][OH⁻] / [CO₃²⁻]
   K = [HCO₃⁻][H⁺] / [CO₃²⁻]

   a) C₀ = 0.20 M. Putting the values we will obtain x:
   x = 0.20 / 0.20 = 1
   pH = 14 - 1 = 13

    (in this case the solution of quadratic equation is identical. The using of simple formula gives right answer because the summand Kx in the quadratic equation is very small comparing to C₀. So we can assume Kx ∼ 0)

   b) C₀ = 0.01 M. In this case we should solve quadratic equation:
   K = x² / C₀
   x² + Kx - C₀ = 0
   D = K² - 4C₀K
   x₁ = (-K + √D) / 2C₀
   x₂ = (-K - √D) / 2C₀
   obviously this answer is not correct, the x is:
\[
x = 1.3 \times 10^{-3}
p\text{OH} = -\log(1.3 \times 10^{-3}) = 2.9.
pH = 14 - 2.9 = 11.1.
\]

*(in this case we cannot assume $K_x = 0$, so that's why using simple formula gives wrong answer)*

c) Find the concentrations after mixing:

\[
[HCO_3^-] = \frac{c_0v_0}{v_1} = 0.0125 \text{ M}
\]

\[
[CO_3^{2-}] = \frac{c_0(v_1 - v_2)}{v_1} = 0.1500 \text{ M}
\]

Next reactions take place in solution:

\[
CO_3^{2-} + H_2O = HCO_3^- + OH^-
\]

\[
HCO_3^- + H_2O = CO_3^{2-} + H_3O^+
\]

\[
K_a = \frac{[HCO_3^-][H^+]}{[CO_3^{2-}]},
\]

\[
[H^+] = K_a\frac{[CO_3^{2-}]}{[HCO_3^-]}, \quad \text{pH} = -\log[H^+] = -\log K_a + \log\left[\frac{[CO_3^{2-}]}{[HCO_3^-]}\right],
\]

\[
\text{pH} = \log(4.7 \times 10^{11}) + \log \left(\frac{0.1250}{0.0125}\right) = 11.4
\]

3. The pH of the buffer does not depend on dilution, because in

\[
\text{pH} = -\log K_a + \log\left[\frac{[CO_3^{2-}]}{[HCO_3^-]}\right],
\]

there is only ratio between the components of buffer.

4. Changing of color of litmus paper may tell us about that X is carbonate/bicarbonate of ammonium, because of releasing ammonia while heated. Reaction of forming the hydrocarbonate-ion from carbonate-ion takes place with phenolphthalein

\[
CO_3^{2-} + H^+ = HCO_3^-
\]

\[
n(CO_3^{2-}) = C_{HCO_3} V_1 = 0.10 \times 6.5 \times 10^{-3} = 6.5 \times 10^{-4} \text{ mol}
\]

In titration with methyl orange goes next reaction:

\[
HCO_3^- + H^+ = H_2O + CO_2
\]

In this reaction also takes part the HCO_3^- which was obtained from previous reaction. The amount of HCO_3^- in original solution:

\[
n(HCO_3^-) = C_{HCO_3}(V_2 - V_1) - 0.10(10.7 - 6.5) \times 10^{-3} = 4.2 \times 10^{-3} \text{ mol}
\]

There are two cases:

i) NaHCO_3 Na_2CO_3 NH_3HCO_3

ii) NaHCO_3 Na_2CO_3 (NH_3HCO_3)

In the first case

\[
n(HCO_3^-) = n(NaHCO_3) + n(NH_3HCO_3) = a + b
\]

The mass of the mix is

\[
m = n(NaHCO_3) M(NaHCO_3) + n(Na_2CO_3) M(Na_2CO_3) + n(NH_3HCO_3) M(NH_3HCO_3) =
\]

\[
84a + 79b + 0.0689 = 0.1
\]

We have two equations:

\[
84a + 79b + 0.0689 = 0.1
\]

\[
a + b = 4.2 \times 10^{-3}
\]

Writing the b from the second equation and putting it in the first we obtain:

\[
84a + 79(4.2 \times 10^{-3} - a) = 0.0311
\]

\[
a = -4.2 \times 10^{-3} - \text{obviously this answer is not correct. So X should be (NH_3HCO_3)
\]

In second case

\[
n(CO_3^{2-}) = n(Na_2CO_3) + n(NH_3HCO_3) = c + d
\]

The mass of the mix is

\[
m = n(NaHCO_3) M(NaHCO_3) + n(Na_2CO_3) M(Na_2CO_3) + n(NH_3HCO_3) M(NH_3HCO_3) =
\]

\[
0.0353 + 106c + 96d
\]

We have two equations:

\[
0.0353 + 106c + 96d = 0.1
\]

\[
c + d = 6.5 \times 10^{-2}
\]

Writing the d from the second equation and putting it in the first we obtain:

\[
106c + 96(6.5 \times 10^{-2} - c) = 0.0647
\]

\[
c = 2.3 \times 10^{-3} \text{ mol}
\]

\[
d = 4.2 \times 10^{-3} \text{ mol}
\]

Putting it in m will give 0.11.

5.\[
\text{w}(NaHCO_3) = \frac{84a + 79b}{0.1} \times 100\% = 35.3\%
\]

\[
\text{w}(Na_2CO_3) = \frac{106c + 96d}{0.1} \times 100\% = 24.4\%
\]

\[
\text{w}(NH_3HCO_3) = \frac{84a + 79(4.2 \times 10^{-3} - a)}{0.1} \times 100\% = 40.3\%
\]

6. Solution has pH more than 7, so next reaction, which explains the color change, can take place:

\[
NH_3 + OH^- = NH_2 + H_2O
\]

**Grading:**

1) Reaction 1 – 1 point

2) Reaction 2 – 1 point (0.5 points without conditions)

a) 3 points

b) 3 points

c) 3 points

3) Right explanation - 2 points

4) Correctly determined X – 2 points

5) Calculations to confirm (NH_3HCO_3) – 1 point

6) Conclusion and calculation that NH_3HCO_3 is wrong – 3 points

7) Three right answers 1 point for each

8) Right answer and equation

9) Three right answers

**Total: 25 points**