МИНИСТЕРСТВО ОБРАЗОВАНИЯ РЕСПУБЛИКИ САХА (ЯКУТИЯ)

ГАУ ДО РС (Я) «МАЛАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ САХА (ЯКУТИЯ)»

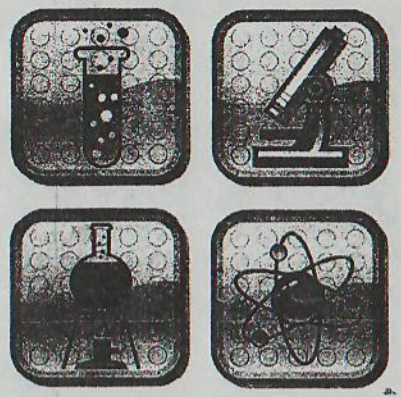
ФГАОУ ВПО «СЕВЕРО-ВОСТОЧНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ ИМ. М.К. АММОСОВА»

XXIII МЕЖДУНАРОДНАЯ ОЛИМПИАДА ШКОЛЬНИКОВ «ТУЙМААДА»

XXIII INTERNATIONAL SCHOOL OLYMPIAD «TUYMAADA»

ХИМИЯ

CHEMISTRY



I (теоретический) этап

First (theoretical) tour

Якутск, 2016

JUNIOR LEAGUE

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 A_1 and A_2 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 A_1, A_2, B – F, if 1 g of A_1 or A_2 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=25C) 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 6.71 % 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. It

caused their wide use as detonators. Compound A is able to explode itself – the blast pressure is 3514 kgf/cm^2 (1 kgf = 9.8 N) if loading density is 0.3 g/cm^3. 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:

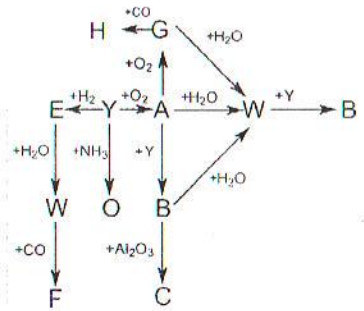
1. Name X and Y metals. Which of the ions is concentrated within the cell, and which – in the intercellular fluid?
2. Give at least two examples of the Y metal salts that are used as medicine and describe their usage.
3. Elements X and Y have been discovered by an English chemist in 1807. He separated 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 consisted 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.



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 A_1 (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 A_2 (which itself is a salt of acid A_3) with acid A_3. The second method contains the reaction of a simple gaseous substance A_4 with a compound A_5 on a copper catalyst.

It is known that A_3 can be obtained from A_4 in one stage, as well as A_5 can be turned into A_2 in one stage.

It turned out that there are several relative compounds of A_1 with similar elemental composition. One of them B_1 could result from a reaction between copper and A_1 (in fact it is exactly how it was first obtained in 1957). Today B_1 is received using another method (coefficients are correct):

$$B_2+2A_4=B_3+\ldots \text{ (70,0\% yield)}$$
$$B_3+xH_2SO_4+H_2O=B_4+\ldots \text{ (100\% yield)}$$
$$2B_4+NaOCl=B_1+\ldots \text{ (100\% yield)}$$

If you take 1.648 grams of B_2 using the above scheme you will get exactly 1 gram of B_1, and you will get 1.014 grams of intermediate B_4. B_1 turned out to be strong oxidizer, what can be shown by following reactions:

(a) $1SiH_4+2B_1=\ldots$

(b) $10Li+1B_1=\ldots$

It is also known that B_2 is an organic compound that was synthesized from its isomer B_5 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 $M(A_1) : M(B_3) = 0.740$. Write down 6 reactions related to the synthesis of A_1 and B_1.
2) What scientist implemented the reaction which disproved the vitalism theory? Write his name and surname.
3) A_1 molecule has a pyramid 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 B_1 are caused by its partial dissociation: $B_1 = 2\ B_0$. 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 ΔS and ΔG of dissociation at 298 K.
6) Is B_0 a radical?
7) Write down structures of the products of the reaction of B_0 with:
   A) NO
   B) Cl_2
   C) $CF_3–CF=CF_2$

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-J.
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 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 ^{235}U, which can sustain a fission 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:

$$^{235}_{92}U \xrightarrow{^{1}_{0}n} {}^{135}_{52}Te \xrightarrow{\beta^-} {}^{?}_{?}A \xrightarrow{\beta^-} {}^{?}_{?}B \xrightarrow{\beta^-} {}^{?}_{?}C \xrightarrow{\beta^-} {}^{?}_{?}D$$

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:

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{135}_{52}Te + {}^{?}_{?}E + 3{}^{1}_{0}n$$

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(?E) = (?-1).9128 a.m.u.;
m(n) = 1.0087 a.m.u.;

$1\ a.m.u.\cdot c^2 = 931.5\ MeV.$

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

$$C + O_2 = CO_2 + 401\ кJ$$

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 = 1W·s; 1eV = $1.6\cdot10^{-19}$ 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 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 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 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} 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.

6.

Time after reactor shutdown, h	0	2	5	7	10	15	20	30	50	60
Reactivity	0	-0,09	-0,17	-0,22	-0,25	-0,24	-0,21	-0,14	-0,08	-0,06

Reference data for calculations:

$k = \frac{ln2}{\tau_{\frac{1}{2}}}$; $k = \frac{1}{t}\cdot ln\frac{c_0}{c}$, where k – half-constant.

SENIOR LEAGUE

Problem 1

Problem 1

AUTOCATALYSIS

Substance A autocatalytically transforms into substance P. The scheme of autocatalysis can be shown as a combination of two reactions:

$$A \rightarrow P\ (k)$$
$$A + nP \rightarrow (n+1)P\ (m)$$

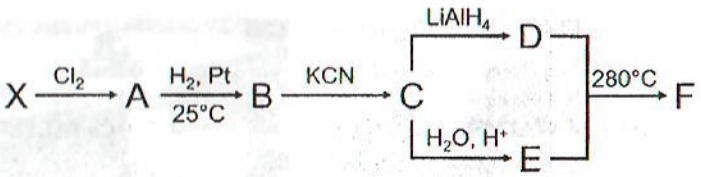
Here k and m are rate constants of these reactions. The reaction order for each substance on the corresponding stage is equal to coefficient by this substance in equation of this stage.

Questions:

1) Write down all possible values of n in the given equation of autocatalysis.
2) Let the numerical value of m be 10000 times greater than numerical value of k. The initial concentration of A $C_0(A) = 0.010$ M, and the initial concentration of P $C_0(P) = 0$. Find, at what concentration of substance A within this reaction would give the maximum substance formation rate for substance P (only for n = 1).
3) Find the value of this maximum rate if $k = 0.001\ s^{-1}$ (only for n = 1).
4) Find the rate of formation of P at the moment when 99 % of maximum possible quantity of the compound P is formed (you may use the data from the previous tasks, n = 1).
5) Give the example of at least one autocatalytic reaction. Write down the equation of this reaction.

Problem 2

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



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:

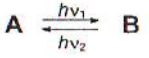
1. Write down reaction equations.
2. Give structural formulas of substances A – F and X.
3. Which polymer can be synthesized using X?

Problem 3

POLYMERS - CHAMELEONS

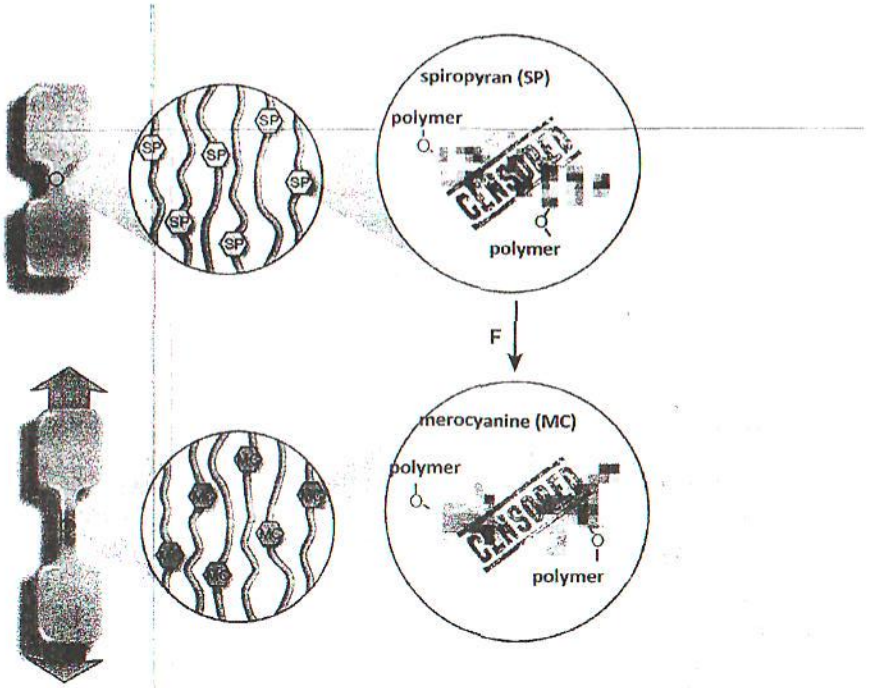
Molecules that called photochromic (photosensitive) can reversibly change its structure when exposed to light:

Scheme 1.

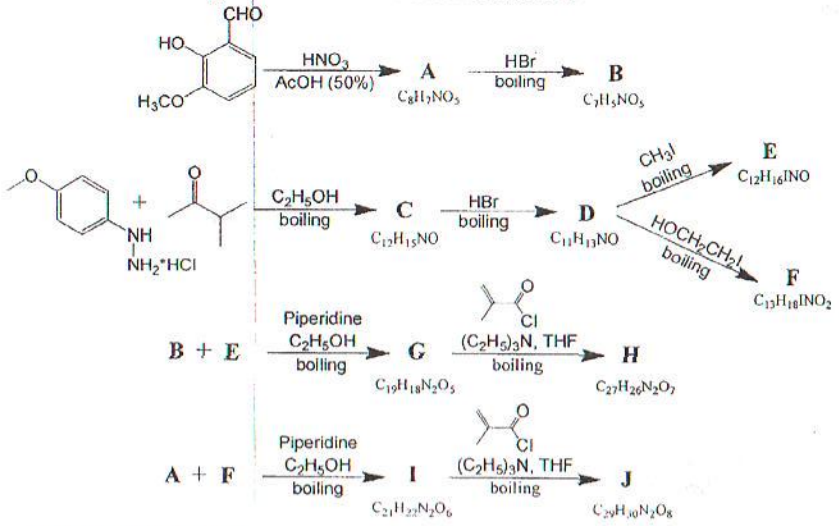


Spiropyrans are the such photochromic compounds. The spiropyrans are organic molecules consisting of two mutually perpendicular aromatic fragments. In the initial state molecules of spiropyrans are colorless, but after UV irradiation, they are able to "open" in the merocyanine form (with heterolytic 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 spiropyrans: there is an article, published in 2009 in the *Nature* journal, with the description about how the unique structure of the spiropyrans 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 similiar spiropyran **J**, which cannot change the color of polymer under mechanical stress according to the basic conclusions of researchers:



* THF: tetrahydrofuran

It is known that two singlets with equal integral intensity are observed in the aromatic region in NMR ^{1}H (25 MHz) spectra of compound **A**, whereas doublets are observed in the aromatic regions in the NMR ^{1}H spectra of the by-products in the reaction of producing compound **A**. It is also known that *NMR ^{1}H (25 MHz) spectra of compound* **C** *includes signals from protons in the* aromatic region (3 protons) and from three groups of nonequivalent protons (12 protons) in the aliphatic region of the spectrum. NMR ^{1}H (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 form for compound **G**. Explain the appearance of color in merocyanine form of compound **G** unlike the spiropyran form.

4) Explain why the inclusion of spiropyran **H** in the polymer allows changing the color of the polymer under mechanical stress, but the inclusion of spiropyran **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

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7. Write down structures of the products of the reaction of B_0 with:
   A) NO
   B) Cl_2
   C) $CF_3-CF=CF_2$

Problem 5

MEET THE SODA

$NaHCO_3$ is one of the most widely used chemical 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 Na_2CO_3. In the first step, gaseous carbon dioxide and ammonia passes through sodium chloride solution forming $NaHCO_3$ (reaction 1). Then Na_2CO_3 is obtained from $NaHCO_3$ (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 Na_2CO_3
   b) 0.01 M Na_2CO_3
   c) Buffer obtained from mixing 10 ml 0.05 M $NaHCO_3$ and 30 ml 0.20 M Na_2CO_3

Use the next values: $Ka_1(H_2CO_3) = 2.5 * 10^{-4}$, $Ka_2(H_2CO_3) = 4.7 * 10^{-11}$, $K_w = 1.0 * 10^{-14}$

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

To determine the mix of $NaHCO_3$, Na_2CO_3 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 HClwere spent in titration of obtained solution with methyl orange. It is known that litmus paper changes the color if the original solution is heated.

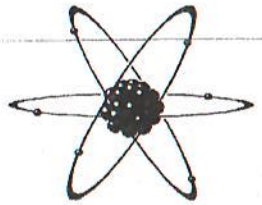
4) Determine X. Confirm your answer by calculations.

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



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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:

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{135}_{52}Te + {}^{?}_{?}E + 3{}^{1}_{0}n$$

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

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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 = 1W·s; 1eV = $1.6 \cdot 10^{-19}$ J). How much coal with carbon mass fraction of 75% is needed to get the same amount of energy?

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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 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 $J = 10^{14}$ 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.

6.

Time after reactor shutdown, h	0	2	5	7	10	15	20	30	50	60
Reactivity	0	-0,09	-0,17	-0,22	-0,25	-0,24	-0,21	-0,14	-0,08	-0,06

Reference data for calculations:

$k = \frac{ln2}{\tau_{\frac{1}{2}}}$; $k = \frac{1}{t} \cdot ln\frac{c_0}{c}$, 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 a S_nCl_2. Hydrolysis of such compounds can be described by general equation:

$$2S_xCl_2 + 2H_2O = SO_2 + (2x-1)S + 4HCl$$

Let's determine A1 formula:

$\nu(S) = 0.155/32 = 4.844 \cdot 10^{-3}$ mole

$\nu(S_xCl_2) = 1/(32x+71)$ mole

$(2x-1) \cdot 1/(32x+71) = 2 \cdot 4.844 \cdot 10^{-3}$

x=1, therefore, A_1 – sulfure dichloride (SCl_2).

Установим формулу соединения A_2:

$\nu(S) = 0.356/32 = 11.125 \cdot 10^{-3}$ моль;

$\nu(S_xCl_2) = 1/(32x+71)$ моль

$(2x-1) \cdot 1/(32x+71) = 2 \cdot 11.125 \cdot 10^{-3}$

x=2, therefore, A_2 – dithiodichloride (S_2Cl_2).

B – SO_2, C – HCl, D – SO_2Cl_2, E – H_2SO_4, F – H_2S.

2. Rection equations:

$S + Cl_2 = SCl_2$ (reaction 1)

$2S + Cl_2 = S_2Cl_2$ (reaction 2)

$2SCl_2 + 2H_2O = SO_2 + S + 4HCl$ (reaction 3)

$2S_2Cl_2 + 2H_2O = SO_2 + 3S + 4HCl$ (reaction 4)

$SO_2 + Cl_2 = SO_2Cl_2$ (reaction 5)

$2SO_2Cl_2 + 3S = SCl_2 + S_2Cl_2 + 2SO_2$ (reaction 6)

$SO_2Cl_2 + 2H_2O = H_2SO_4 + HCl$ (reaction 7)

$SCl_2 + H_2SO_4 = 2SO_2 + 2HCl$ (reaction 8)

$S_2Cl_2 + 3H_2SO_4 = 5SO_2 + 2HCl + 2H_2O$ (reaction 9)

$2H_2S + SO_2 = 3S + 2H_2O$ (reaction 10)

$SCl_2 + H_2S = S_2Cl_2 + 2HCl$ (reaction 11)

$H_2S + Cl_2 = S + 2HCl$ (reaction 12)

$H_2S + 4Cl_2 + 4H_2O = H_2SO_4 + 8HCl$ (reaction 13).

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

4. $\nu(H_2S) = V_{p-pa} \times C = 0.1 \times 0.01 = 0.001$ mole

$$(Cl_2) = \frac{PV}{RT} = \frac{101.3 \times 10^3 \times 97.8 \times 10^6}{8.31 \times 298} = 0.004 \text{ mole}$$

$\nu(H_2S) : \nu(Cl_2) = 1:4$, so, reaction 13 takes place.

$\nu(H_2SO_4)=\nu(H_2S)=0.001$ mole.

$C(H_2SO_4)=$ —— $=0.01$ mole/l

$\nu(HCl)=2\nu(Cl_2)=8\nu(H_2S)=0.008$ mole

$C(HCl)=\frac{0,008}{0,1}=0.08$ mole

HCl	=	H^+	+	Cl^-	H_2SO_4	=	$2H^+$ + SO_4^{2-}
0.08 mole/l		0.08 mole/l			0.01 mole/l		0.02 mole/l

$[H^+]=0.02+0.08=0.1$ mole/l

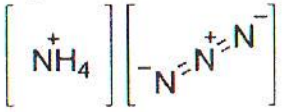
$pH=-lg[H^+]=-lg0.1=1$.

Grading

1)	Definition of elements X and Y	1 point × 2 = 2 points
2)	Definition of substances A_1-F	1 point × 7 = 7 points
3)	Reaction equations	1 point × 13 = 13 points
4)	Description of the application	1 point
5)	Calculation of pH	2 points
		Total – 25 баллов

Problem 2

1. The only compound, which meets all conditions (including stability at the room temperature), is ammonium azide – the content of hydrogen is 6.71 %, two N—N bonds in azide-anion, soluble in water with pH ~ 7.



2. The reaction of ammonium azide with silver nitrate leads to silver azide precipitate:
   $AgNO_3 + NH_4N_3 \rightarrow AgN_3\downarrow + NH_4NO_3$
   The content of nitrogen is 28.03 %.
3. Sodium azide is used in airbags. In case of road accident sodium azide decomposes very quickly with the release of big volume of nitrogen, inflating an airbag.
4. 1 g of ammonium azide is equal to 0.0167 mole. It decomposes with the release of 1.148 l / 22.4 l/mol = 0.0512 mol of gaseous mixture, so, 0.0512/0.0167=3.066 mol of gases are formed from 1 mol ammonium azide. It can be decomposed in the following ways:

   1) $NH_4N_3 \rightarrow 2N_2 + 2H_2$
   2) $NH_4N_3 \rightarrow NH_3 + 0.5N_2 + 1.5\ H_2$

   As we can see from reactions, in the first case 4 mol gases from 1 mol a.a. is formed, and 3 mol – in the second case. The value obtained experimentally shows that a.a. decomposes by the second way, in the main.

5. Let's believe the volume of sleeve is equal to 1 cm^3 and charge weight is equal to 0.3 g. Then, we can use ideal gas law, pre-translating the values to more convenient for calculation:

   $PV = vRT$
   $3395*0.001 = 0.015*0.082*T$
   $T = 2760$ K.

Grading

1. The name of compound A – 2 points, structure A – 2 points
2. For the reaction equations - 1 point, the calculation – 1 point
3. *Description of the application – 2 points, everything else without of evaluation*
4. The chemical decomposition of A: for the reaction of equations: 2 x 2 = 4 points
5. For the evidence of a preferential way of decomposition – 2 points
6. Evaluation of temperature at explosion of compound A – 2 points

Total 16 points

Problem 3

1. X – K, Y – Na. Ion of K is concentrated in cells, while ion of Na – in the intercellular fluid.
2. Na_2SO_4, $NaHCO_3$, NaF, NaBr, NaI , $Na_2S_2O_3$, etc.
3. 3.1 Sir Humphry Davy
   3.2 Z - KOH, W - NaOH Potassium originated from potash (K_2CO_3), sodium – from soda (Na_2CO_3)
   3.3 $4KOH_{(fl)} = 4K_{(cathode)} + O_2\uparrow_{(anode)} + 2H_2O$ (electrolysis) or
   $4NaOH_{(fl)} = 4Na_{(cathode)} + O_2\uparrow_{(anode)} + 2H_2O$ (electrolysis)
4. $Na_2CO_3 + 2C = 2Na\uparrow + 3CO\uparrow$ at t° (element Q is C (carbon))
5. $2KF + CaC_2 = CaF_2 + 2C + 2K\uparrow$ at t°
6. 1. $2Na + O_2 = Na_2O_2$
   2. $2Na_2O_2 + 2H_2O = 4NaOH + O_2$
   3. $2NaOH + 2Na = 2Na_2O + H_2\uparrow$ at t°
   4. $Na_2O_2 + 2Na \sim 2Na_2O$
   5. $Na_2O + H_2O = 2NaOH$
   6. $Na_2O_{(к)} + Al_2O_3 = 2NaAlO_2$ alloyed at t°
   7. $Na_2O_2 + O_2 = 2NaO_2$
   8. $2NaO_2 + 2H_2O = 2NaOH + H_2O_2 + O_2$
   9. $2NaO_2 + CO = Na_2CO_3 + O_2$
   10. $2Na + 2NH_{3(fl)} = 2NaNH_2 + H_2$
   11. $2Na + H_2 = 2NaH$
   12. $NaH + H_2O = NaOH + H_2$
   13. $NaOH + CO = HCOONa$

   NaOH - W
   Na_2O_2 – A
   Na_2O - B
   $NaAlO_2$ - C
   $NaNH_2$ - D
   NaH - E
   HCOONa - F
   NaO_2 - G

Na_2CO_3 – H

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
   Determining the substances, which have given names to X and Y 0.5*2=1 point
   Chemical equation of electrolysis = 1 point
4. Chemical equation - 1 point
5. Chemical equation - 1 point
6. Each equation - 0,5 point *13=6,5 points
   Determining the substances - 0,5 point *9=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, $B_2 = (NH_2)_2CO$, $B_1 = NH_4NCO$.

According to this fact, we can assume that the second stage of B_1 synthesis is a hydrolysis of a derivative of urea, and the result of this reaction is CO_2 and ammonia's derivatives. Then it is logical to assume that B_3 contains a fragment of urea with some functional groups instead of hydrogen atoms.

So, let us assume that B_4 can be described with the formula $NH_{3-n}X_n$ (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 %, we get 1,019/M moles of B_4. Then 0,02747*0,7=1,019/M and M = 53.

If molar mass of X group in $NH_{3-n}X_n$ is x, M = 53 = 14+3-n+xn 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 A_4 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 $B_4 = NHF_2$.

Now we can calculate formula of B_1 from masses of elements. 1,019 g of B_4 contains following masses of nitrogen and fluorine:

$$m(N) = \frac{14}{14+1+38} * 1{,}019 = 0{,}269\ g$$

$$m(F) = \frac{38}{38+14+1} * 1{,}019 = 0{,}731\ g$$

$$m(N) + m(F) = 1{,}000\ g$$

We can see, that B_1 consists only from nitrogen and fluorine (because total mass of these elements is equal to the mass of B_1), and molar ratio of elements is 1:2 (as in B_4 was). Then the formula of B_1 is $(NF_2)_x$. According to the last synthesis reaction's equation, we can conclude that 2 molecules of B_4 reacts with formation of 1 molecule of B_1, and formulae of B_1 is N_2F_4 (and x = 2).

As we see from all the work we have done, a simple substance A_4 is F_2. And the single acid that can be formed from fluorine by one stage is hydrofluoric acid. Therefore A_3 = HF.

There is only one unknown compound (B_3) in A_4 synthesis scheme. As we concluded before, urea's derivative gives only one molecule of NHF_2 after hydrolysis. If both nitrogen atoms in the urea were fluorinated, we would get two molecules of NHF_2, therefore only one of nitrogen atoms in urea were oxidized by fluorine. So, $B_3 = NH_2CONF_2$. Note: other partially fluorinated urea molecules do not fit the stoichiometry of reaction of urea fluorination: 2 moles of F_2 reacts with 1 mole of urea, and it means that urea is fluorinated only twice.

As we knew from task text, $M(A_1)=0{,}740M(Б_3)=71$. A_1 consists from nitrogen and fluorine (as well as N_2F_4). Possible compounds are NF_3 and N_2F_2. But the value of molar mass fits to NF_3. So, $A_1 = NF_3$.

A_2 is fluoric acid's salt i.e. A_2 is fluoride. Its electrolysis gives a compound, that contains nitrogen, therefore a cation of A_2 also contains nitrogen. The most evident nitrogen containing cation is ammonium cation, and A_2 is NH_4F.

A_5 gives ammonium fluoride by one stage, therefore A_5 can be either ammonia, or hydrogen fluoride. However, HF is coded as A_3, so, A_5 is NH_3.

Reaction aquations:

$3NH_4F=N_2+NF_3+6H_2$

$NH_3+3F_2=NF_3+3HF$

$Cu+2NF_3=CuF_2+N_2F_4$

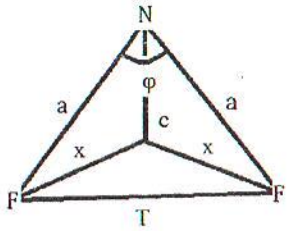
$NH_2CONH_2+2F_2= NH_2CONF_2+2HF$

$2NH_2CONF_2+H_2SO_4+2H_2O=(NH_4)_2SO_4+2CO_2+2NHF_2$

$2NHF_2+NaOCl=N_2F_4+H_2O+NaCl$

2) The name of that chemist is Friedrich Wöhler.

3)



Let «a» be a module of vector of dipole moment of N-F bond, «Г» is a distance between two vectors' endings (number of vectors is three, but it is not too important here). «c» is a projection of each vector on the vertical axis, «x» is a projection on horizontal plane. We also know the angle φ between two vectors, φ = 102,5°.

We can calculate T from cosine theorem: $T^2=2a^2-2a^2\cos\varphi$. After using values if a and φ, T = 0,364 B (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 NF_3). Therefore, both remaining angles in this triangle are 30°. We can find x from sine theorem for this triangle now: $x = T*\sin30°/\sin120° = 0{,}210$ D. Furthermore we can find c from Pythagorean theorem: $c^2=a^2-x^2=0{,}234^2-0{,}210^2$. c = 0,1032 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*0,1032 = 0,3096 ≈ 0,310D. So, the total dipole moment of molecule is 0,310 D.

4) (a) $SiH_4+2N_2F_4=SiF_4+2N_2+4HF$ или $SiH_4+2N_2F_4=H_2SiF_6+2N_2+2HF$
(b) $10Li+N_2F_4=2Li_3N+4LiF$

5) $\Delta G = -RTlnK = 8687$ J/mole
$\Delta S = (\Delta H - \Delta G)/T = 250,0$ J/(mole*K)

6) Yes, it is a radical.

7) A) $NONF_2$
B) $NClF_2$
C) $CF_3–CF(NF_2)–CF_2(NF_2)$

Grading:

1	Right formulas of compounds A_1-A_5, B_1-B_5	0,5 point * 10 = 5 points
	Right equations of 6 reactions	0,5 points * 6 = 3 points
2	Right name and surname of the chemist	1 point
3	Right calculation of dipole moment	3 points
4	Right equations of (a) and (b) reactions	1 point * 2 = 2 points
5	Right calculation of ΔG and ΔS of reaction	1 point * 2 = 2 points
6	A fact that B_0 is a radical	1 point
7	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 $FeCl_3$. From mass fraction **A - $FeTiO_3$.**

1) $FeTiO_3+2HCl=FeCl_2+H_2O+TiO_2$;

2) $TiCl_4+2Mg=Ti+2MgCl_2$;

3) $2FeTiO_3+7Cl_2+6C=2TiCl_4+2FeCl_3+6CO$;

4) $TiO_2+2Cl_2+2C=TiCl_4+2CO$;

Compound **C** - $TiCl_4$.From mass fraction we can find that compound **E-TiB_2.** Thereby **G-B, H-BCl_3, I-B_2O_3, J-B_4C.**

5) $2TiCl_4+4BCl_3+10H_2=2TiB_2+20HCl$;

6) $7Ti+B_2O_3+3B_4C=7TiB_2+3CO$

7) $TiO_2+B_2O_3+10Na=5Na_2O+TiB_2$;

Solution: **M-Ti; A-$FeTiO_3$; B-TiO_2; C-$TiCl_4$; D-$FeCl_3$; E-TiB_2; G-B; H-BCl_3; I-B_2O_3; J-B_4C.**

2.The main name of the mineral TiO_2 is **rutile**. Also it can be named as **anatase** or **brookite**.

Grading

1) Defining element M – 2 points
2) Defining compounds A-E – 1 point each (total 5 points)
3) Defining element G – 1 point
4) Defining compounds H-J – 0.5 points each (total 1,5 points)
5) Reactions – 1 point each (total 7 points)
6) The name of the mineral B (one of three) – 1.5points

Total - 18 points.

Problem 6

1. $^{235}_{92}U \xrightarrow{^1_0n} {}^{135}_{52}Te \xrightarrow{\beta^-} {}^{135}_{53}I \xrightarrow{\beta^-} {}^{135}_{54}Xe \xrightarrow{\beta^-} {}^{135}_{55}Cs \xrightarrow{\beta^-} {}^{135}_{56}Ba$

2. $^{235}_{92}U + {}^1_0n \rightarrow {}^{135}_{52}Te + {}^{98}_{40}Zr + 3{}^1_0n$

$\Delta m = 235.0493+1.0087 – (134.9165+97.9128+3·1.0087) = 0.2026$ amu.

$Q = 0.2026 \cdot 931.5$ МэВ = 188.7219 МэВ ≈ 188.7 MeV.

3. 1 g = $6.02 \cdot 10^{23}$ a.m.u.

If 235 a.u.m. is released 188.7 MeV, then 1 g will give $4.83 \cdot 10^{23}$ MeV. 1 MeV = $1.6 \cdot 10^{-13}$ J, then

$4.83 \cdot 10^{23}$ MeV = $7.73 \cdot 10^{10}$ J = $2.15 \cdot 10^4$ kW·h.

m(C) = $7.73 \cdot 10^{10}$ J · 12/ 401000 J = $2.31 \cdot 10^6$ g = 2.31 t.

m(coal) = 2.31·100/75 = 3.08 t.

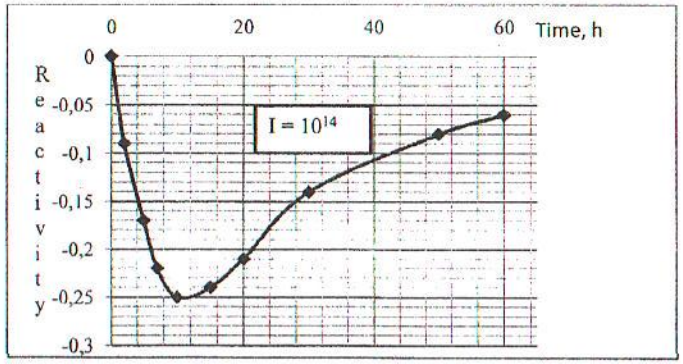
1 g of uranium releases an equal amount of energy 3.08 t of coal.

4. $t = \frac{T_{1/2}}{ln2} ln\frac{1}{0.01}$ =197 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:



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.

Grading:

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

2. Writing the element E ..... 1 points
   Calculation of the released energy ..... 4 points
3. *Writing the energy which is released from 1 g of uranium* ..... 3 points
   Calculation of amount of coal ..... 2 points
4. Calculation of year ..... 4 points
5. Drawing of the graph ..... 2 points
   Determination the time by graph ..... 2 points

Total 20 points

SOLUTIONS

SENIOR LEAGUE

Problem 1

1) It is known that 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 $n > 2$, 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.

$$\frac{dP}{dt} = r = kC(A) + m(n+1)C(A)C(P)^n - mnC(A)C(P)^n = kC(A) + mC(A)C(P)^n$$
$$= kC(A) + mC(A)(C_0(A) - C(A))^n$$

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.

$$\frac{dr}{dC(A)} = k + m(C_0(A) - C(A))^n - nmC(A)(C_0(A) - C(A))^{n-1} = 0$$
$$k + 10000k(C_0(A) - C(A))^n - 10000knC(A)(C_0(A) - C(A))^{n-1} = 0$$
$$1 + 10000(C_0(A) - C(A))^n - 10000nC(A)(C_0(A) - C(A))^{n-1} = 0$$

Then we can use given values of $C_0(A) = 0{,}01M$ and n = 1.

$$1 + 10000 \times (0{,}01 - C(A))^1 - 10000 \times C(A)(0{,}01 - C(A))^0 = 0$$
$$1 + 100 - 10000C(A) - 10000C(A) = 0,$$
$$C(A) = 101 : 20000 = 0{,}00505\ M = 5{,}05\ mmole/l$$

Note: the calculated value of C(A) is a maximum because $r'(C(A)) < 0$ if C(A) > 0,00505 M and $r'(C(A)) > 0$ if C(A) < 0,00505 M.

3) $r = kC(A) + 10000kC(A)(C_0(A) - C(A))^n = 5{,}05 \times 10^{-6} + 10 \times 5{,}05 \times 10^{-3} \times 4{,}95 \times 10^{-3} = 2{,}550 \times 10^{-4}\ \frac{mole}{l \times s}$

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

$$r = kC(A) + 10000kC(A)(C_0(A) - C(A))^n = 10^{-5}\frac{mole}{l \times s}$$

5) One of well-known examples of autocatalytic reactions is oxidation of some compounds by $KMnO_4$ in acidic conditions: 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:

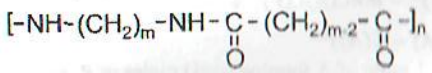
$$2KMnO_4 + 5K_2SO_3 + 3H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 3H_2O$$

Grading:

1	Right possible values of n (1 point for each n)	1 point * 2 =2 points
2	Right calculation of value of C(A)	6 points
3	Right calculation of value of maximum rate	2 points
4	Right calculation of value of rate	2 points
5	Any right example of autocatalytic reaction with its equation	3 points
		Total: 15 points

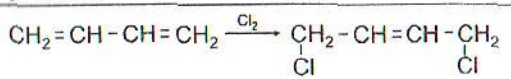
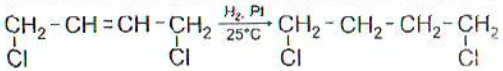
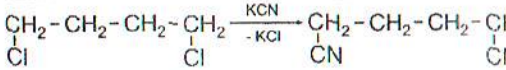
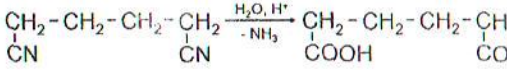
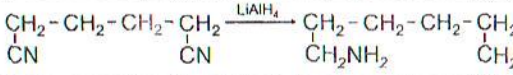
Problem 2

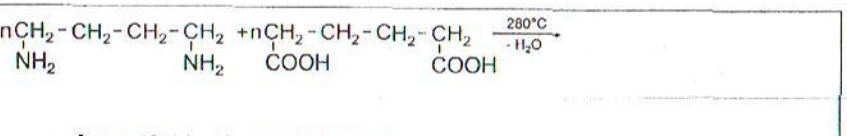
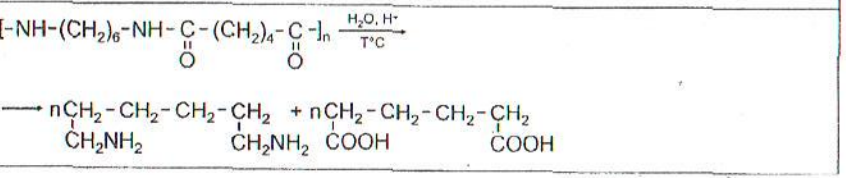
1. It is obvious from scheme that F is a polyamide. Also it is known that D and E have the equal number of carbon atoms. Because F is a polyamide, E is a diacid. So, 1 mole of NaOH reacts with 0.5 moles of acid E. If 0.5 moles of acid E are formed, then 113 g of F is 0.5 moles of repeating chains of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



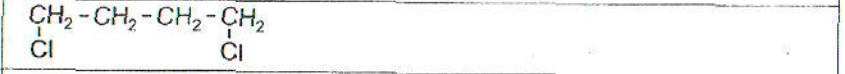
Where m – amount of carbon atoms between amino groups.
We form the equation:

Therefore, substance X is butadien-1,3.

№	Уравнение
1	
2	
3	
4	
5	

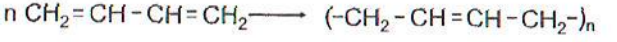
6	
7	

2.

X	
A	
B	
C	
D	
E	
F	

3.

Any correct answer could be accepted. For example: butadiene rubber. Free radical polymerization or using metallocene catalysts.



Grading

1)	For each reaction equation 1 point	7 points
2)	For each structural formula of substance 1 point	7 points
3)	Polymer name – 1 point.	1 points
		Total: 15 points

Problem 3

1) 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 hydroxyl 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**.

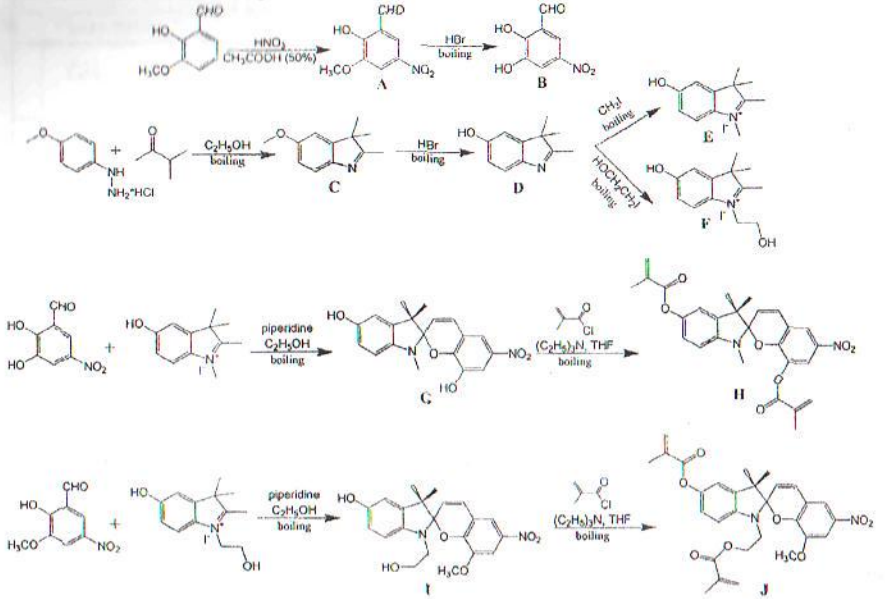
The reaction of producing **C** - a classic example of a Fischer indole synthesis reaction. The structure of the molecule of compound **C** can be reliably confirmed by the data about the number of protons and their equivalence in the NMR ^{1}H (25 MHz) spectrum of compound **C**. The reaction of preparation **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 merocyanine 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 hydroxyl 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 it's cyclocondensation (Fischer reaction)

Reaction of compound **D** synthesis: hydrolysis of ether

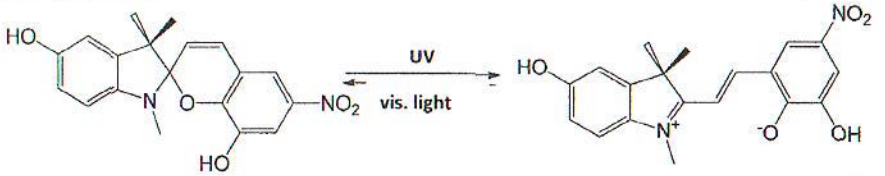
Reaction of compound **E** (**F**) synthesis: alkylation of the nitrogen atom with an alkyl halide

Reaction of compound **G** (**I**) synthesis: condensation of an ortho-hydroxy aromatic aldehyde with heterolytic cation with an active methylene group

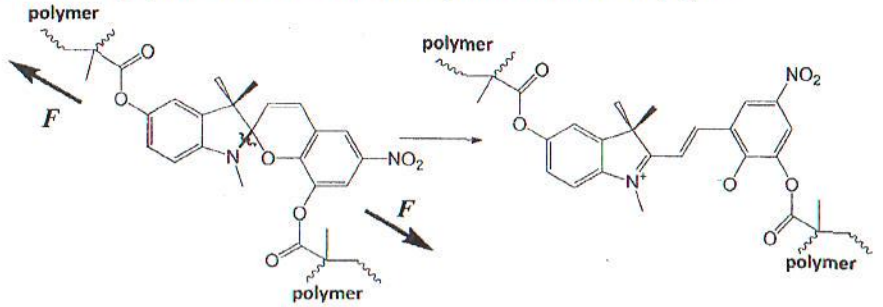
Reaction of compound **H** (**J**) synthesis: acylation of the hydroxyl groups

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.

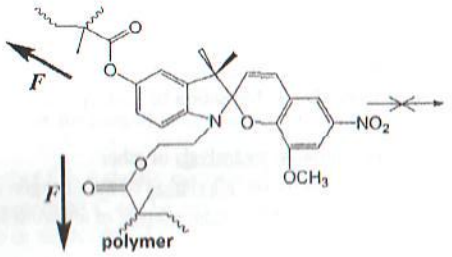
Merocyanine form has completely conjugated π-system with electron releasing and withdrawing groups unlike spiropyran form. In this point of view it is able to absorb a greater extent electromagnetic radiation in the visible region of spectrum, that causes the appearance of color for merocyanine form.



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**, **E (F)**, **G (I)**, **H (J)**	0,5 points * 7 = 3,5 points
	Correct name of reaction of producing **C** (Fischer reaction)	0,5 points
3	Correct structural formula of merocyanine form of compound **G**	2 points
	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 for polymers with inclusion of spiropyrans **H** and **J**	1 point
5	Logical formulation of possible fundamental purposes	2 points
6	Correct example of real practical use of photochromic compounds in everyday life	1 point

Total: ***25 points***

Problem 4

Solution of Problem 4 JUNIOR LEAGUE

Total: ***20 points***

Problem 5

1. Solvay process chemical reactions:

1) $NaCl + NH_3 + CO_2 + H_2O \approx NH_4Cl + NaHCO_3$

2) $2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$ (t°C)

2. In solution of Na_2CO_3 the next reaction occurs:

$CO_3^{2-} + H_2O = HCO_3^- + OH^-$

So that's why the pH will be more than 7. X moles of OH^- is formed in solution:

$(C_0\text{-}x)$ x x

$CO_3^{2-} + H_2O = HCO_3^- + OH^-$

The constant of equilibrium:

$K = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{x^2}{C_0 - x}$; if the value x is very small comparing to C_0, we can assume $[CO_3^{2-}] = C_0$

$x = \sqrt{KC_0}$. Next we obtain K:

$Ka_1 = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$; $Ka_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$; $Kw = [OH][H^+]$

$K = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{[HCO_3^-]\,Kw}{[CO_3^{2-}][H^+]} = \frac{Kw}{Ka_2}$

The x is:

$x = \sqrt{\frac{Kw}{Ka_2} C_0}$

a) $C_0 = 0.20$ M. Putting the values we will obtain x:

$x = \sqrt{\frac{Kw}{Ka_2} C_0} = \sqrt{\frac{10^{-14}}{4.7 * 10^{-11}} * 0.20} = 6.5 * 10^{-3}$

$pOH = -\lg[OH^-] = -\lg(6.5 * 10^{-3}) = 2.2.$

$pH = 14 - pOH = 14 - 2.2 = 11.8.$

(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 KC_0. So we can assume $Kx \sim 0$)

b) $C_0 = 0.01$ M. In this case we should solve quadratic equation:

$K = \frac{x^2}{C_0 - x}$; $x^2 + Kx - KC_0 = 0$

$D = K^2 + 4KC_0$; $K = \frac{Kw}{Ka_2} = \frac{1 * 10^{-14}}{4.7 * 10^{-11}} = 2.1 * 10^{-4}$

$D = (2.1 * 10^{-4})^2 + 4 * 2.1 * 10^{-4} * 0.01 = 8.4 * 10^{-6}$

$\sqrt{D} = 2.9 * 10^{-3}$

$x_1 = \frac{-K + \sqrt{D}}{2} = \frac{-2.1 * 10^{-4} + 2.9 * 10^{-3}}{2} = 1.3 * 10^{-3}$;

$x_2 = \frac{-K - \sqrt{D}}{2} = \frac{-2.1 * 10^{-4} - 2.9 * 10^{-3}}{2} = -1.6 * 10^{-3}$, obviously this answer is not correct, the x is:

$x = 1.3 * 10^{-3}$

pOH = - lg(1.3 * 10^{-3}) = 2.9.

pH = 14 – 2.9 = 11.1.

(in this case we can not assume Kx ~0, so that's why using of simple formula gives wrong answer)

c) Find the concentrations after mixing:

$[HCO_3^{2-}] = \frac{C(NaHCO3)*V_1}{V_1+V_2} = 0.0125$ M

$[CO_3^{2-}] = \frac{C(Na2CO3)*V_2}{V_1+V_2} = 0.1500$ M

Next reactions take place in solution:

$CO_3^{2-} + H_2O = HCO_3^- + OH^-$

$HCO_3^- + H_2O = CO_3^{2-} + H_3O^+$

$Ka_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$;

$[H^+] = Ka_2\frac{[HCO_3^-]}{[CO_3^{2-}]}$; pH = -lg$[H^+]$ = -lg Ka_2+lg$\frac{[CO_3^{2-}]}{[HCO_3^-]}$;

pH = -lg (4.7 * 10^{-11}) + lg $\frac{0.1500}{0.0125}$ = 11.4

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

pH = -lgKa_2+lg$\frac{[CO_3^{2-}]}{[HCO_3^-]}$; 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

$CO_3^{2-} + H^+ = HCO_3^-$

Find the amount of CO_3^{2-}

$n(CO_3^{2-}) = C_{HCl}\ V_1 = 0{,}10 * 6{,}5 * 10^{-3} = 6{,}5 * 10^{-4}$ 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:

$n(HCO_3^-) = C_{HCl}(V_2 - V_1) = 0.10\ (10{,}7 - 6{,}5) * 10^{-3} = 4.2 * 10^{-4}$ mol

There are two cases

I) $NaHCO_3$ Na_2CO_3 NH_4HCO_3

II) $NaHCO_3$ Na_2CO_3 $(NH_4)_2CO_3$

In the first case $n(HCO_3^-) = n(NaHCO_3) + n(NH_4HCO_3) = a + b$

The mass of the mix is

$m = n(NaHCO_3)\ M(NaHCO_3) + n(Na_2CO_3)\ M(Na_2CO_3) + n(NH_4HCO_3)\ M(NH_4HCO_3) =$
$84a + 79b + 0.0689 = 0.1$

We have two equations

$84a + 79b + 0.0689 = 0.1$

$a+b = 4.2 * 10^{-4}$

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

$84a + 79(4.2 * 10^{-4} - a) = 0.0311$

$5a + 0.0332 = 0.0311$

$a = -4.2 * 10^{-4}$ – obviously this answer is not correct. So X should be $(NH_4)_2CO_3$

In second case $n(CO_3^{2-}) = n(Na_2CO_3) + n((NH_4)_2CO_3) = c + d$

The mass of the mix is

$m = n(NaHCO_3)\ M(NaHCO_3) + n(Na_2CO_3)\ M(Na_2CO_3) + n((NH_4)_2CO_3)\ M((NH_4)_2CO_3) =$
$0.0353 + 106c + 96d$

We have two equations

$0.0353 + 106c + 96d = 0.1$

$c + d = 6.5 * 10^{-4}$

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

$106c + 96(6.5 * 10^{-4} - c) = 0.0647$

$10c + 0.0624 = 0.0647$

$c = 2.3 * 10^{-4}$ mol

$d = 4.2 * 10^{-4}$ mol

Putting it in m will give 0.1g.

5. $w(NaHCO_3) = \frac{84*4.2*10^{-4}}{0.1}100\% = 35.3\%$

$w(Na_2CO_3) = \frac{106*2.3*10^{-4}}{0.1}100\% = 24.4\%$

$w((NH_4)_2CO_3) = \frac{96*4.2*10^{-4}}{0.1}100\% = 40.3\%$

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

$NH_4^+ + OH^- = NH_3 + H_2O$

Grading:

1)	Reaction 1 – 1 point Reaction 2 – 1 point (0.5 points without conditions)	2 points
2)	a) 3 points b) 3 points c) 3 points	9 points
3)	Right explanation - 2 point	2 points
4)	Correctly determined X – 2 points Calculations to confirm $(NH_4)_2CO_3$ – 1 point Conclusion and calculation that NH_4HCO_3 is wrong – 3 points (if there is only conclusion without calculation – 1 point)	7 points
5)	Three right answers 1 point for each	3 points
6)	Right answer and equation	2 point
		Total 25 points

Problem 6

Solution of Problem 6 JUNIOR LEAGUE

Total: 20 points