МИНИСТЕРСТВО ОБРАЗОВАНИЯ РЕСПУБЛИКИ САХА (ЯКУТИЯ)
MINISTRY OF EDUCATION OF THE REPUBLIC OF SAKHA (YAKUTIA)

ФИЗИКО-МАТЕМАТИЧЕСКИЙ ФОРУМ
«ЛЕНСКИЙ КРАЙ»

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Chemistry

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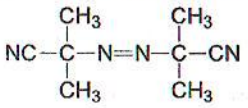
Problem 1

Slow heating of the important for industry liquid product X (T_{boil}=77°C, D_{air}=1.83) in the inert atmosphere in presence of small amount of AIBN* leads to the gradual thickening of the reaction mixture. The temperature increase higher than 130°C causes the darkening of the coagulate. After the reaction mixture is hold at 400°C for a while it is cooled down. Solid product Y is black, has cyclic structure, and metallic brilliance. In theory, its mass must be 1.039 times less than one of the initial liquid X. One of the commercial names of Y is "New Orlon".

1. Find the composition and structure of liquid X.
2. What does X undergo at slow heating? Write the equations of possible reactions. What is the reason to introduce AIBN into the reaction mixture?
3. Suppose the probable structure of the product Y. Presence of AIBN and possibility of partial evaporation of X may be neglected.
4. List the most important (in your opinion) physical-chemical characteristics, which the product Y must show due to its structure.

- AIBN is 2,2'-azobisisobutyronitril:



10 points

Problem 2

CO_2 - acidic oxide, to which there corresponds the two-basic acid. The appropriate constants pK_a acid dissociation at 0° C are equal to:
$CO_{2\ (solution)} + H_2O_{\ (liquid)} = HCO_3^-{}_{\ (solution)} + H^+_{\ (solution)}$, $pK_{a1} = 6.630$;
$HCO^-_{\ (solution)} = CO_3^{2-}{}_{\ (solution)} + H^+_{\ (solution)}$, $pK_{a2} = 10.640$

The change of volume owing to dissolution of gas in a liquid at realization of accounts is possible to neglect. The accounts carry spend for temperature 0°C.

1. The total concentration of all forms of carbon in water saturated with carbonic gas at its partial pressure 1.00 bars, is equal 0.0752 M. Calculate volume of CO_2, which can be dissolved in 1 l of water under the specified conditions.
2. Calculate equilibrium concentration of ions of hydrogen and equilibrium concentration of molecules CO_2, in water saturated with carbonic gas at its partial pressure 1.00 bars.
3. Calculate equilibrium concentration of ions of hydrogen in 0.0100 M water solution $NaHCO_3$, saturated by carbonic gas at its partial pressure 1.00 bars. Dissociation of water it is necessary to neglect.
4. Calculate equilibrium concentration of ions of hydrogen in 0.0100 M a water solution Na_2CO_3, saturated by carbonic gas at its partial pressure 1.00 bars. Dissociation of water it is necessary to neglect.
5. Solubility of $CaCO_3$ in water at 0°C is 0.0012 g in 100 ml of water. Calculate equilibrium concentration of Ca^{2+} ions (mole/l) in the saturated water solution of $CaCO_3$.

Underground waters having high rigidity are formed by contact of water with limestone rock. The process of interaction $CaCO_3$ with CO_2 dissolved in water is described by the following equation:
$CaCO_{3\ (solid)} + CO_{2\ (solution)} + H_2O_{\ (liquid)} = Ca^{2+}_{\ (solution)} + 2HCO_3^-{}_{\ (solution)}$.

The constant of balance of this process is $5.62*10^{-5}$ at 0°C.

6. Calculate concentration of Ca^{2+} ions in a solution which is taking place in balance with $CaCO_3$ in an atmosphere with partials pressure of carbonic gas 1.00 bars.
7. The solution $Ca(OH)_2$ by concentration 0.0150 M is saturated with carbonic gas at partials pressure 1.00 bars. Calculate concentration of Ca^{2+} ions in the solution in view of balance mentioned in item 6.
8. A solution of $Ca(OH)_2$ from item 7 was diluted twice by water. Then it was saturated with carbonic gas at partials pressure 1.00 bars. Calculate equilibrium concentration of Ca^{2+} ions in the received solution.
9. Calculate the product solubility of $CaCO_3$ using data available in a task.

15 points

Problem 3

The bond in molecule of H_2O_2 is reasonably strength (207 kJ/mol); therefore H_2O is dissociated either at high temperature or in presence of catalysts. Typical examples of such catalysts are iodide-ions in neutral solution. The experimental data about initial velocity of oxygen elimination at mixing of various volumes of H_2O, 3%H_2O_2, and 0.1 M KI solutions presented below:

№ exp	H_2O_2, ml	KI, ml	H_2O, ml	V, ml/min
1	50	100	150	8.8
2	100	100	100	17
3	200	100	0	35
4	100	50	150	8.5
5	100	200	0	33

1). Find out the reaction order by H_2O_2 and catalyst.

2). Write in general form the stoichiometric and the kinetic equations, i.e. the dependence of the reaction velocity vs the initial concentrations of the substances.

3). Find out the H_2O_2 concentration (in mol/l) in the start of the experiment №4 and its change during 4 min (mixture density being 1 g/ml, pressure being 1 atmosphere, t=20°C).

4). Write the mechanism of two-stage reaction with intermediate formation of IO^- ions and show the limiting (slow) reaction stage (take into account of the kinetic equation.

5). Suppose that hydrogen peroxide degradation velocity is followed of Arrenius' equation, estimate the relative velocity in presence of the various catalysts. Present the catalysts in the table:

The kinetic parameters of H_2O_2 degradation in presence of various catalysts

Catalyst	E_a, kJ/mol	Relative velocity at 22°C
Surface of reaction vessel	≈73	1
I^-	≈56	?
Fe^{2+}/Fe^{3+}	≈42	?
Catalaze (enzyme)	≈1.7	?

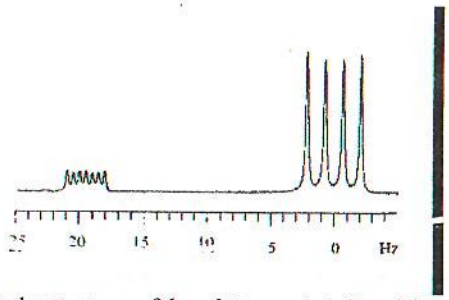
6). In the middle of the 19th century English chemists A.Garcurt and U.Esson had performed the precise measurement of the reaction kinetic between H2O2 and HI at temperature range from 0 to 50°C (every 5°C) So, if the velocity at 0.0°C accept to 1, then at 25°C velocity will be 8.27, while at 50°C velocity will be equal 49.3. From such kind of measurements, not knowing exact value of zero, chemists could calculate "the kinetic" value of zero. They have

interpreted this value as temperature by which any reaction does not occur (at that time Arrenius' equation was not known). Calculate from these data the value of the absolute zero, using Arrenius' equation.

15 point

Problem 4

Black-gray crystalline simple substance **A** is oxidized by air at 700°C forming white crystals of substance **B** containing 68.94% of oxygen. Heating of the mixture of **B** with fluorite in concentrated sulfuric acid produces colorless gas **C**, which is then absorbed by cold water to give two acids **D** and **E**. **D** is a weak acid and its solubility in cold water is quite low. In contrary **E** is a strong and well soluble in water acid. Its neutralization with sodium hydroxide leads to a solution, which ^{19}F NMR spectrum consists of two separated multiplets as shown in a Figure:



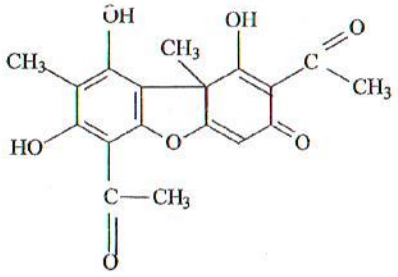
3. Write the structures of the substances **A**, to **E** and the equations of the reactions involved. Explain the ^{19}F NMR pattern of the salt of the acid **E**.

10 points

Problem 5

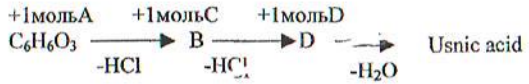
Usinic acid is natural antibiotic isolated from wide spread lichen Usnea in Yakutia. In medicine usinic acid is used in the form of sodium solt for wounds and burns treatment.

Usnic acid



1. How many stereoisomers has usnic acid?
2. Do all the usnic acid stereoisomers have the same melting point?

The scheme of the synthesis of usnic acid is presented below:

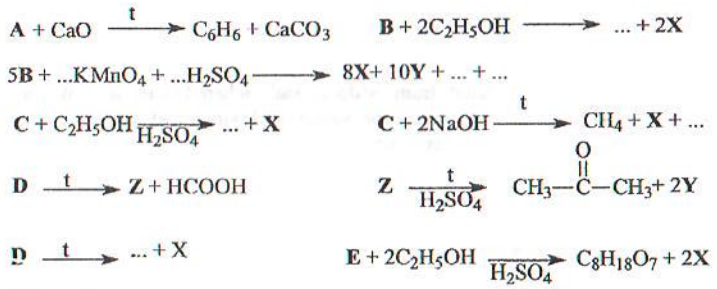


3. Draw structural formula of following substances: **A, B, C,** and **D**. Show the conditions of the reactions.
4. Term the substance **D** according IUPAC nomenclature.
5. Show the reaction centers in the molecule of usnic acid. For each reaction center one example should be demonstrated.
6. New usnic acid derivatives were synthesized for the creation more powerful drugs. One of the example is 5, 7 –bis(diethylaminorthoxy)usnic acid ditartrate with anticancer propetics. Draw its structural formula.
7. In 1930s 2.4-dinitrophenole has used as drug for body weight reduction. The method was based on the ability of 2.4-dinitrophenole to come into mitochondrial membrane and uncouple oxidative phosphorylation. As result, warm production is increased due to fat oxydation but ATP synthesis does not go. May usnic acid have the same propetics as 2.4-dinitrophenol? Argue your answer.
8. Usnic acid has mutagenic effect therefore it is used only for external treatment. Explain this case.

10 points

Problem 6

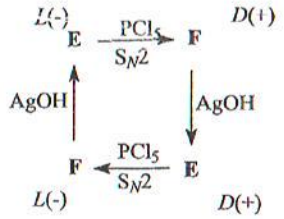
Sugar, vitamin C, organic acids **A, B, C, D, E (A - E)** are giving characteristic acid-sweet taste of berries vaccinium vitis-idea (lat.). Antiseptic property and causes an opportunity of a long storage of berries in a fresh kind is caused by presence of the acid **A**.
Only **X** and **Y** are formed then acids **A – E** are burning. Some reactions of acids are shown on the scheme.



Scheme 1

Only acid **E** (of given acids **A -E**) contains the chiral atom of carbon atom. P. Valden (1896) has shown transformation of enanthiomers on the example of reversible isomerisation of E L(-) into E D(+). He used PCl_5 and AgOH.

Scheme 2



The task:

1) determine **A - F, X, Y, Z**. Draw the structural formulas;
2) write all reactions on the schemes 1 and 2;
3) list acids A - E by way of the decrease of acidity (pK_{a1} in H_2O).

13 points