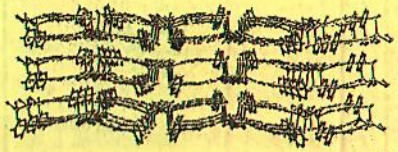
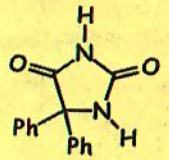
МИНИСТЕРСТВО ОБРАЗОВАНИЯ РЕСПУБЛИКИ САХА (ЯКУТИЯ)

ГОУ «ФИЗИКО-МАТЕМАТИЧЕСКИЙ ФОРУМ
«ЛЕНСКИЙ КРАЙ»

ЯКУТСКИЙ ГОСУДАРСТВЕННЫЙ
УНИВЕРСИТЕТ ИМЕНИ М.К. АММОСОВА

XIV МЕЖДУНАРОДНАЯ ОЛИМПИАДА "ТУЙМААДА" XIV INTERNATIONAL OLYMPIAD "TUYMAADA"





Задания I (теоретического) тура по химии
The first (theoretical) tour on chemistry. Problems

Якутск•Yakutsk•2007

Problem 1.

During the thermal decomposition of the unknown nitrate in an isolated vessel at 220^0C a mixture of gases with density by hydrogen of 13.3333 was obtained. During the thermal decomposition of the same nitrate in an isolated vessel at 500^0C the density of the gas mixture by hydrogen was 11.4285. All reactions have quantitive yields.

1. Determine the nitrate composition and write all the chemical reactions.
2. Where are the nitrate and its decomposition products used?

(6 points)

Problem 2.

In XVIIth century in England it was found out that willows usually grow very well near the water. So, they thought if the willow-tree grows up in moisture places it can be useful for treatment of flu and fever. English priest Stown was the first who started to use willow bark for treatment. Later from the willow a white crystalline compound, named salicyline, was obtained. After that from the salicyline an aromatic compound **A** was isolated. It consists of 60.87% weight % C, 4.38 weight % H and 34.75 weight % O. Both A and more cheaper salicyline were used for the treatment of flu. However, this compounds didn't found wide application. In 1899 company «**X**» patented medicine **B**, which was synthesized by reaction of **A** with acetic anhydride.

1. Draw the chemical structures of compounds **A** and **B**.
2. What is the name and location of company **X**?.
3. What kind of physiological activity does compound **B** have?
4. Write 4 chemical reactions for the compound **A**.

(8 points).

Problem 3.

For each of the three salts of the alkali metal with chemical formula $M_2S_2O_x$ (where **x** – is integer number from 1 to 10) one or few statements can be used.

A) anion of this salt contains O-O bond;

B) anion of this salt contains S-S bond;

C) anion of this salt contains S-O bond;

D) this salt can be obtained by the hydrosulfate decomposition;

E) this salt can be obtained by anodic oxidation of the hydrosulfate;

F) this salt can be obtained by reaction of sulfite with elemental sulfur;

G) water solution of this salt dissolves silver bromide;

H) when water solution of this salt is treated by hydroxide MOH the alkali metal sulfate M_2SO_4 is obtained;

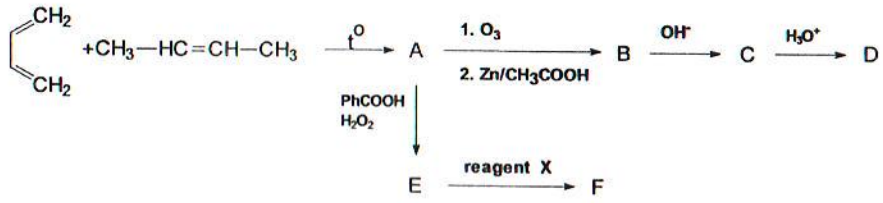
I) Mn(II) is oxidized to Mn(VII) by water solution of this salt.

For each salt write down its properties. Confirm your conclusions by chemical reactions.

(14 points)

Problem 4.

1. Write down the chemical reactions listed below. Determine structural formulas **A - F**, and structure of the reagent **X**. **F** consists of 76,67 weight % of carbon, 9.65 weight % of hydrogen, 6.39 weight % of nitrogen and oxygen.



2. NMR ^{1}H spectrum of **D** listed below, make the correspondence for the protons.

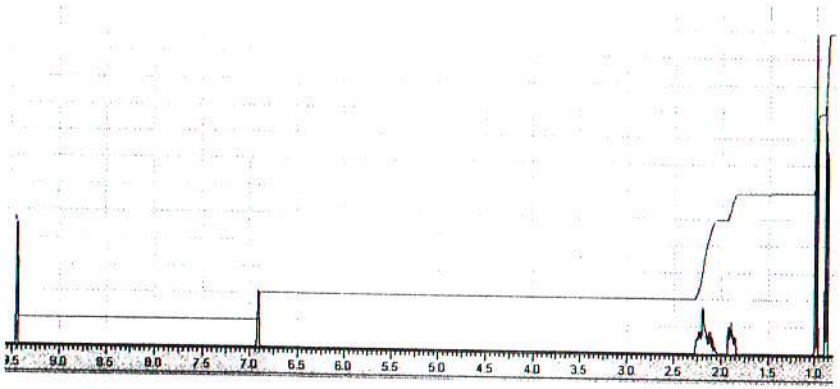


Fig. 1. NMR ^{1}H spectrum of the compound D

3. Write down the stereo-chemical result of **E** reaction with reagent **X**.

(18 points)

Problem 5.

Compound **D** is used as a flavour additive and in bakery. It has a wild strawberry flavour called "wild strawberry aldehyde". Although it does not contain aldehyde group. In the synthetic scheme listed below there are no aldehydes as well.

94,5 g of **A** fully burns with the formation of 88 g **X**, 18 g **Y**, 36,5 g **Z**.
120 g of **E** fully burns with the formation of 352 g **X**, 72 g **Y**.

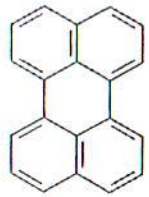
1) determine structural formulas of **X**, **Y**, **Z** and draw the structural formulas of **A-D**;
2) write down the synthetic transformations for the preparation of **D** from **A** .

(16 points)

Problem 6.

A lot of organic compounds whith π-bonds, in monocrystals and thin films have nonlinear optical properties of the third order, this properties make them useful for making tools

that transform visible light to UV-light. Such monocrystals and thin films can be used as optical switchers. One of such compounds is perylene $C_{20}H_{12}$:



Perylene $C_{20}H_{12}$, was obtained by reprecipitation from the diluted solution by addition of water under intensive sonification. After delution there are very small perylene drops in the solution, which aggregates to clusters and then nanocrystals are formed.

After nanocrystals are formed they start to disperse the light, and its intensity $I_s(t)$, divided to intensity of falling radiation I_0, can be used for the nanocrystal growth control in time. This dependence $I_s(t)/ I_0$ obeys following equation $[1 - e^{\alpha}]$, in which speed rate constant (α) depends on the temperature as shown in the table listed below:

T, *K*	α, hour $^{-1}$
310	0,415
315	0,677
325	1,553
335	3,618
345	8,166

1. Transform table data to Arrenius coordinates and draw graphic of temperature dependence.
2. Is it possible to calculate the nanocrystal growth energy of activation (E_a)? If it possible, make it.
3. Is the perylene aromatic compound? Confirm your answer with Dewar's criteria: OEDE (one electron delocalization energy) for perylene is 0,131 eV, a OENDE (one electron new delocalization energy) is 0,056 eV. Can you use for the determination of aromatic nature of perylene Huckel rule $(4n+2)$ π-electrons?
4. How can you influence on the size of the nanocrystals of perylene.

(8 points)

Solutions.

Solution to problem 1.

1. Determine the molecular weight of gas mixture at different temperatures: M_1 = 26.6666 (220^{0}C), M_2 = 22.857 (500^{0}C). It's well known that most of the nitrates decompose with formation of NO_2 and O_2. Molecular weight of this mixture will be over that 32, so the unknown nitrate was NH_4NO_3.

$$NH_4NO_3 \xrightarrow{220^oC} N_2O + 2H_2O$$

$$2NH_4NO_3 \xrightarrow{500^oC} 2N_2 + O_2 + 4H_2O$$

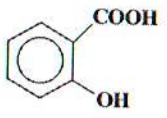
(4 points – 1 for the nitrate structure + 3 for equations)

2. NH_4NO_3 usually used as fertilizing and N_2O usually used as medicine. (2 points).

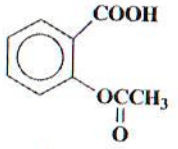
Total 6 points.

Solution to problem 2.

1. Determine the molecular formula of **A** - C:H:O = 7:6:3. Then compound **A** seems to be salicylic acid. Reaction of A with Ac_2O leads to B (acetylsalicylic acid, aspirin).



A



B

(1 point for each structure - total 2 points)

2. «Bayer AG», Germany **(1 point)**

3. Anti-fever **(1 point)**

4. For equations 1 point for each – reduction, reaction with metals, bases, metal salts, esterification. **(4 points)**.

Total 8 points.

Solution to problem 3.

1. One of the solution is following salts:

$K_2S_2O_7$ – **C, D, H**

$K_2S_2O_3$ – **B, C, F, G**

$K_2S_2O_8$ – **A, C, E, I**

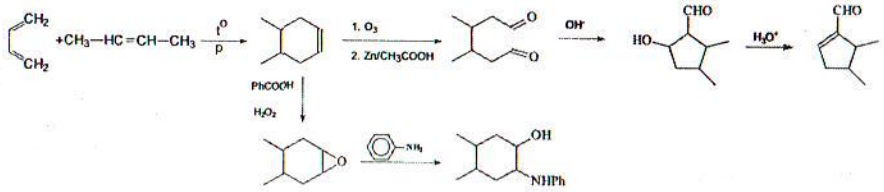
For the determination of structures 1 point each = 3 points

For the correct correlation of properties with structures without reactions 0.5 points each, with reactions 1 point each = 11 points.

Total = 14 points.

Solution to problem 4.

1.



6 stages – 2 point for each

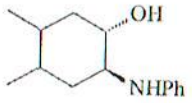
Reagent X structure – 2 points

2.

9.4 – s – CHO, 6.9 – s – CH=, 2.3 – 1.8 – m-protons of the ring, 1.0 and 0.8 – s $2CH_3$ groups

2 points

3.



2 points

Total 18 points.

Solution to problem 5.

X and **Y** are carbon dioxide and water, **Z** is HCl (M_r=36.5)

Molecular formula of **A**:

ν (CO_2)=88g/ 44g/mol=2 mol

ν (H_2O)=18g /18g/ mol=1моль

ν (HCl) = 36.5g /36.5 g/mol=1mol

ν(C)=2 mol ν (H)=3 mol ν(Cl)=1mol

m(C) = 24g m(H)= 3g m(Cl) = 35.5 g

m (C + H + Cl) = 62,5

m (A) = 94.5 g

So, **A** contains oxygen.

m(O) = 94.5 g – 62.5 g = 32 g

ν(O)=32g/16 g/mol = 2 mol

C : H : O : Cl = 2 : 3 : 2 : 1

$C_2H_3O_2Cl$ – the only one molecular formula

A - is $ClCH_2COOH$

Molecular formula of **E**:

ν (CO_2)=352g / 44g/mol= 8 mol

ν (H_2O)=72g /18g/mol= 4mol

ν(C)=8 mol ν (H)=8 mol

m(C) = 96g m(H)= 8g

m (C + H) = 104 g

m (E) = 120 g

So, **E** contains oxygen too.

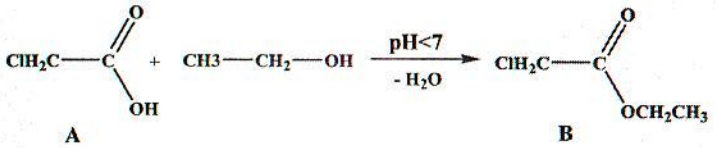
m(O) = 120 g – 104 g = 16 g

ν(O)=16g/16 g/mol = 1 mol

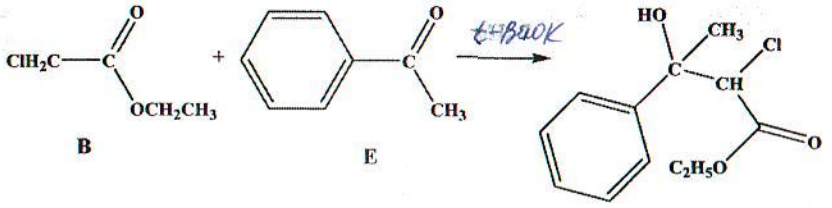
C : H : O = 8 : 8 :1

C_8H_8O – is the only one molecular formula.

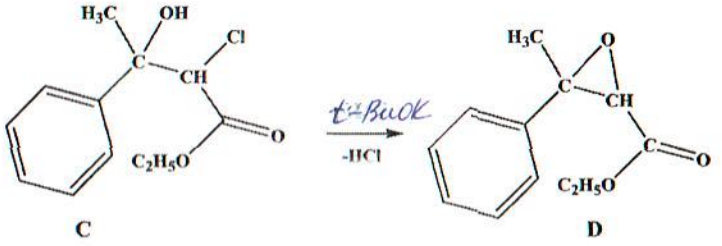
E - is acetophenone other compounds is not suitable



A **B**



B **E**



C **D**

For the determination of X, Y, Z – 1 point

A and E 2·1point = 2 points