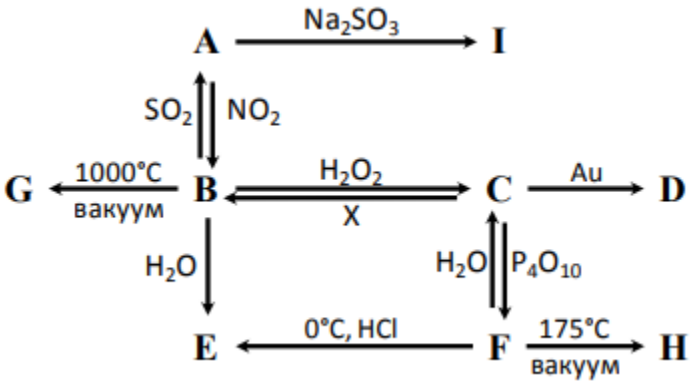
1. 2018 Regional 10-2: Inorganic Scheme

1.1	1.2	Total
10	10	10

Consider the following scheme, where all substances within the scheme contain the element **X**, which partially resembles the properties of sulfur compounds:



The following is known:

- **A** is a simple substance;
- **C** and **E** are dibasic acids;
- Titrating an 20.0 mL aliquot of a solution of 1.00 g **C** in 200 mL requires 19.7 mL of 0.07 M NaOH; In the reaction **B -> G**, the mass loss is 14.42%;
- Compound **H** can be obtained by heating a mixture of **B** and **F**, taken in the ratio 1:1.144 by weight;
- **H** is a polymer;
- The synthesis of substance **D** using a concentrated solution of **C** was carried out in an autoclave at 250 ° **C** for 10 hours. Mass fraction of **X** in **D** is equal to 29.95%; Au mass fraction - 49.81%; the substance has a yellow-orange color;
- Substance **I** consists of four elements, the mass fraction of **X** is 38.52%.

1.1 Determine the element **X.** Decipher **A-I.**

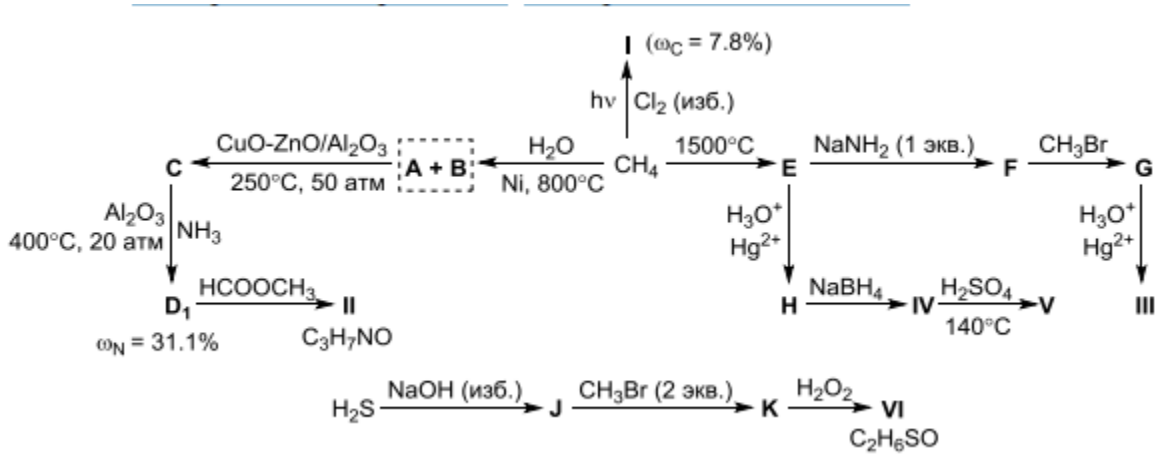
A	**B**	**C**
D	**E**	**F**
G	**H**	**I**
X		

1.2 Write balanced equations for all reactions shown. There are a total of 12 reactions.

2. 2018 Regional 10-4: Solvent Synthesis

2.1	2.2	2.3	Total
16	2	2	20

In the following scheme you will synthesize six solvents, **I-VI**:



2.1 Draw the structures of **I-VI**, **A-C**, **D1**, **E-H**, **J**, and **K**. Answer on the next page.

2.2 When **C** and NH3 react, a mixture of products **D1, D2, D3** is formed, which is then separated by distillation. Draw **D2** and **D3**. Answer on the next page.

2.3. Which two of the solvents **I – VI** can react with each other in the presence of an acid catalyst? Name the two solvents, then draw the structural formula of the product on the next page.

Solvents:

Answer Sheet

A	**B**	**C**	**D1**
E	**F**	**G**	**H**
J	**K**	**I**	**II**
III	**IV**	**V**	**VI**

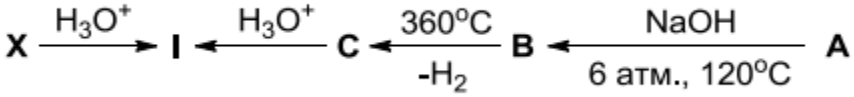
D2	**D3**	**Product of Solvent Reaction**

3. 2018 Regional 11-3: Organic Scheme

3.1	Total
20	20

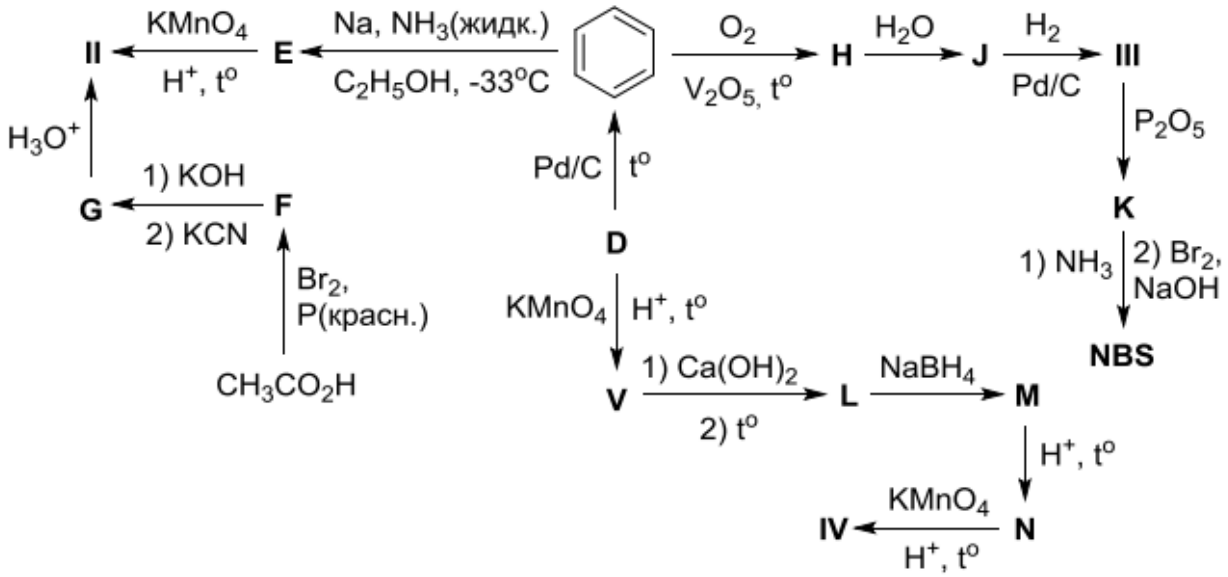
In this problem we will discuss five substances **I – V**, representatives of the same class of organic compounds. Substance **I**, contained in sorrel, rhubarb and cannon, was first obtained by the German chemist Friedrich Wohler in 1824 from binary gas **X**, in which the mass fraction of carbon is 46.15%.

Currently, in industry, **I** can be obtained from the following scheme from **A,** which is an oxide that does not form salts with either acids or bases (i.e. is not an acidic, basic, or amphoteric oxide):



Compound **II** is widely found in nature and is used to synthesize various amino acids. Substance **III** plays a huge role in the life cycles; besides this, it is possible to synthesize the very organic synthesis reagent NBS from it. The α-keto derivative of substance **IV** plays an extremely important role in the Krebs cycle. Finally, substance **V** is used as a food additive, as well as in the production of nylon.

Substances **II – V** can be obtained from monocyclic substance **D** (C6H10), as well as some other paths:



Some known information:

- ωC (**X**) - ωC (**I**) = 0.1948 (ωC is the mass fraction of carbon in substances);
- Compound **C** does not contain hydrogen;
- **II** is the only oxidation product of **E** containing carbon;
- **V** is the only organic product of oxidation **D**;
- Compound **F** has one bromine atom in its composition;
- **NBS** molecule is a five-membered cycle with one heteroatom and contains an N – Br bond.

3.1. Give the structural formulas of substances **I – V, A – N, X** and **NBS**. Give the trivial names of substances **I – V** as well. Use integer masses of elements.

A	**B**	**C**	**D**
E	**F**	**G**	**H**
J	**K**	**L**	**M**
N	**I**	**II**	**III**
IV	**V**	**X**	**NBS**

4. 2018 Regional 11-5: Inorganic Kinetics

4.1	4.2	4.3	4.4	4.5	Total
4	6	2	6	4	20

Unusual binary substance **X**, containing 74.07% oxygen by mass, has many unusual properties. In the gas phase, it consists of molecules, and in solid form - from ions. The substance **X** decomposes by a first order reaction, and in all decomposition reactions, both in the gas phase and in many organic solvents, the activation energy is almost the same.

4.1. Establish the formula of substance **X**. Name at least one binary substance in which the mass fraction of oxygen is greater than in **X**. Confirm the answer by calculation.

4.2. Write the structural formulas of the **X** molecule and the ions that make up the solid **X**, taking into account that in all these particles one of the elements has valency (oxidation state? steric number? coordination number?) IV, and the octet rule is fulfilled for all atoms. Predict the geometric shape of each ion.

4.3. With full decomposition of **X** in the gas phase at a constant temperature, the pressure increases 2.5 times. Write the reaction equation of decomposition.

4.4 In the gas phase, at a temperature of 318 K, substance **X** decomposes at a rate of 5% per minute, and at 328 K - at a rate of 15% per minute. Determine the half-life of **X** at 318 K and calculate the activation energy.

4.5. In chloroform, the decomposition reaction X proceeds slightly faster than in the gas phase: the half-life at 318 K is 10 min. At what temperature will the half-life be 2 times longer?

5. 2018 National Tour 2 Biochemistry P1: NMR is bad ☹

5.1	5.2	5.3	5.4	Total
15	2	1	2	20

Four characters of one literary work donated blood for analysis. Each blood sample was studied with modern instrumental methods, highlighting various chemical compounds (**1, 2, 3, 4**, each character has only one substance). The results of studies of these substances, as well as compound **2'**- product of the catalytic dehydrogenation of compound **2** - is given in the table.

(In the lists of NMR signals с - singlet, д - doublet, т - triplet, м - multiplet, гм – group of multiplets, * - two overlapping signals).

Вещество	Один из стерео-изомеров **1**	**2**	**2'**	**3**	**4**
Масс-спектрометрия: молекулярный ион (m/z)	90	136	132	130	156, 154
^{1}H ЯМР (δ, м. д.)	8.17 (1H, т), 2.76 (2H, м), 1.15 (3H, т)	5.40 (1H, м), 4.70 (2H, *), 2.08–1.79 (6H, гм), 1.73 (3H, с), 1.65 (3H, с), 1.47 (1H, м)	7.38 (2H, д), 7.15 (2H, д), 5.35 (1H, д), 5.03 (1H, д), 2.36 (3H, с), 2.15 (3H, с)	4.10 (2H, т), 2.05 (3H, с), 1.68 (1H, м), 1.52 (2H, м), 0.92 (6H, д)	7.92 (2H, м), 7.57 (1H, м), 7.47 (2H, м), 4.70 (2H, с)
^{13}C ЯМР (δ, м. д.)	179.6, 19.7, 12.5	150.1, 133.7, 120.8, 108.5, 41.2, 30.9, 30.7, 28.1, 23.5, 20.8	143.2, 138.5, 137.3, 129.0, 125.5, 111.7, 22.0, 21.2	172.2, 63.6, 37.3, 25.1, 22.5, 21.1	191.1, 134.2, 134.0, 128.9, 128.5, 46.0
^{17}O ЯМР (δ, м. д.)	199	–	–	355, 197	540

5.1 Decipher substances **1, 2, 2', 3, 4**.

5.2 Provide formulae for all possible stereoisomers of the above compounds.

Answer Boxes for 5.1 and 5.2

1	**2**	**2'**
3	**4**	You may use the remaining space, as necessary, for **5.2**.

5.3 What is the ratio of signal intensities in the mass spec of compound **4**?

5.4. What is the operating frequency of the NMR spectrometer used, if the distance between one of the neighboring pairs signals in the 1H spectrum of compound **3** is 1230 Hz?
