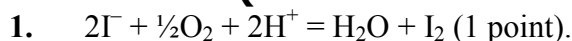
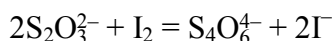
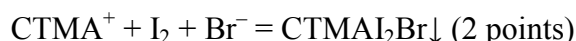


Problem 1 (author M.K. Beklemishev)

2. According to the equation of the reaction between thiosulfate and iodine:



one atom of molecular iodine requires one thiosulfate anion in titration. For this reason, the volume of thiosulfate shown in the problem situation corresponds to 0.39 mmol of I, and 3.9 mmol of I correspond to the whole amount of the precipitate (accounting for the volume of the flask and aliquote) (1 point). Then the molar weight of the compound containing in the precipitate will be equal to $1.205 / 0.0039 \cdot n = 309 \cdot n$ (where n is the number of iodine atoms in the molecule), which can be 309, 618, 927, ... g/mol. The molecular weight of CTMA cation is 284 g/mol, that is, we have to consider the values starting from 618 g/mol. In that case, the anion weight should be 334 g/mol, and since it should contain two iodine atoms, the rest of mass of the anion will equal $334 - 2 \cdot 127 = 80$ g/mol (1 point), which is close to the weight of bromide ion. In that case, the simple formula of the precipitate will be $CTMAI_2Br$, with I_2Br being a part of the anion. We can suppose that I_2Br^- is an analogue of triiodide ion I_3^- . Then the reaction of formation of CTMA salt will look like the following:



3. The amount of iodine extracted from 100 g of algae was 0.0039 mol, or 0.495 g \sim 0.5 g/100 g (0.5 points).

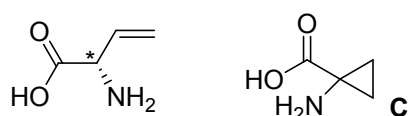
4. Based on the given quantities of substances, iodide is in twofold excess to iodate: $2NaI + NaIO_3 + nHBr \rightarrow \mathbf{B}$. Fading color was caused by iodine formed by the reaction of $5\Gamma + IO_3^- + H^+ \rightarrow 3I_2$, however, there was an excess of iodate, so the oxidation passed on. By problem situation, only one product was formed, that can only be iodine monobromide: $2\Gamma + IO_3^- + 6H^+ = 3IBr + 3H_2O$, or, if a possibility of complexation of \mathbf{B} with bromide ion is taken into account, $2\Gamma + IO_3^- + 6H^+ + 6Br^- = 3IBr_2 + 3H_2O$ (that particular form of Γ^+ is actually present in the solution; 1.5 points for any of the equations of formation of IBr).

5. The amount of IBr (or IBr_2^-) formed was equal to 8 mmol (iodide) + 4 mmol (iodate) = 12 mmol. IBr reacts with 12 mmol of iodide, hence the equation of that reaction may only look like that: $IBr + \Gamma^- = I_2 + Br^-$ or I_2Br^- (1.5 points). Next, \mathbf{A} is formed again: $CTMA^+ + I_2 + Br^- = CTMAI_2Br \downarrow$ (0 points, if this equation has been already written above, and 2 points, if not).

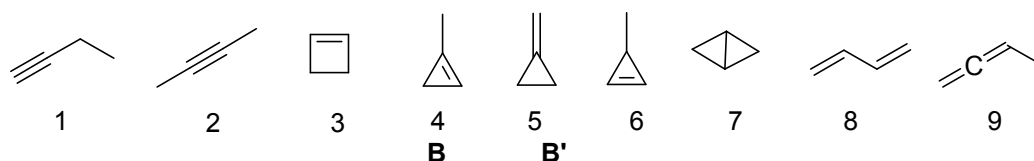
6. Hydrolysis of \mathbf{B} : $IBr + H_2O = HOI + H^+ + Br^-$ (1 point). Since the acid is formed, the equilibrium of hydrolysis is shifted to the right by the alkali: $IBr + 2OH^- = OI^- + Br^- + H_2O$ (0.5 points).

Problem 2 (author D.M. Volochnyuk)

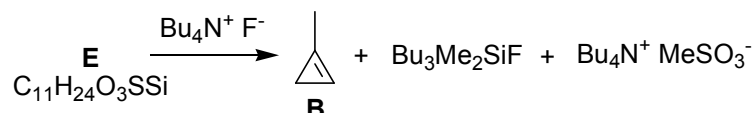
1. It is clear that elements forming compounds **A** and **B** are carbon and hydrogen. Then brutto-formula of **A** is $(\text{CH}_2)_n$. Accounting for gaseousness of **A**, n should be between 2 and 4. To determine structure of **A** we need consider its biosynthesis presented in problems. The transformation of *S*-adenosyl-*L*-methionine (SAM) into 5'-methylthioadenosine (MTA) proceeds with elimination of amino acid residue. Therefore, structure of **C** consists of α -amino acid fragment. This is partially supported by results of the oxidation of **C**. There are two amino acids with formula of $\text{C}_4\text{H}_7\text{NO}_2$, one of them is chiral, another one is achiral. The last one is the compound **C**. Analyzing biochemical oxidation of **C** (formation of CO_2 and HCN requires two carbon atoms) we can conclude that $n = 2$, and **A** is ethene, $\text{H}_2\text{C}=\text{CH}_2$.



From the content of hydrogen in compound **B** it is possible to determine that brutto-formula of **B** is $(\text{C}_2\text{H}_3)_n$. In this case n should be equal to 2 (formula is senseless for odd n , if $n > 2$, **B** cannot be gaseous). Let us write down possible isomers having formula of C_4H_6 . Only compounds **4** – **6** have the carbon skeleton identical to that of compound **C**. Among them, compound **4** has the lowest symmetry than **5** and **6**. Therefore, **4** is compound **B** (1-methylcyclopropene, 1-MCP). The choice between **5** and **6** should be based on the number of double bond “migrations” during its formation from methallyl chloride as well as thermodynamic consideration (in **5** only one sp^2 carbon has abnormal valence angle, in **6** both sp^2 carbon atoms have these strains). Both considerations lead to the conclusion that **B'** is compound **5** (structural formulae of **A** and **B** – 2 points for each; structural formulae of **B'** and **C** – 1 point for each, 6 points in total).



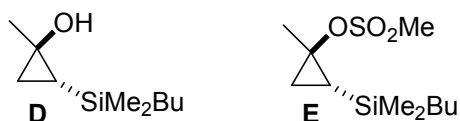
2. Considering molecular formulae of **D** and **E**, it is possible to conclude that **D** is alcohol, and **E** is its mesylate. Accounting for high affinity of silicon to fluorine, the generation of 1-MCP can be represented by reaction below.



For the regioselective formation of 1-methylcyclopropene the eliminating fragments should be connected to the carbon atoms forming the double bond. We know that **D** is formed by the cyclopropanation of $\text{BuMe}_2\text{SiCH}=\text{CH}_2$. Therefore, silyl group should be connected to CH-moiety.

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At last, **D** is *trans*-isomer. Taking all these data together, we can write down structural formulae of **D** and **E** (1 point for each structural formula, 2 points in total).



3. To achieve the required concentration of 1-MCP, it is needed:

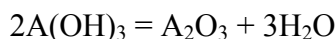
$v(1\text{-MCP}) = 5 \cdot 10^{-9} \cdot (12.0 \cdot 2.3 \cdot 2.4 \cdot 10^3) / 22.4 = 14.79 \cdot 10^{-6}$ mol. To prepare this amount of 1-MCP, the minimum amount of **E** should be: $v(1\text{-MCP}) \cdot M(\text{E}) = 14.79 \cdot 10^{-6} \cdot 264.46 = 3.91 \cdot 10^{-3}$ g **E**. Analogously we can calculate the volume of Bu_4NF solution in DMF. This is $14.79 \cdot 10^{-6} / 2.3 = 6.43 \cdot 10^{-6}$ L (or $6.43 \cdot 10^{-3}$ mL) (2 calculations, 1 point for each, 2 points in total).

Problem 3 (author M.S. Likhanov)

1. Unknown metal **A** is bismuth. This easily can be determined by performing the calculation of weight loss upon the metal hydroxide's heating to its oxide:



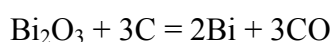
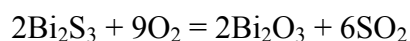
Examining the oxidation degrees of the metal, we can find that if the oxidation state is +3:



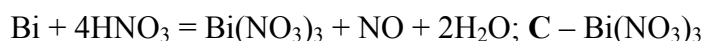
The weight loss = $\frac{3M(\text{H}_2\text{O})}{2M(\text{A}(\text{OH})_3)} = \frac{3 \cdot 18}{2 \cdot (x + 3 \cdot 17)} = 0.104$, hence $x = 208.6$, **A** – bismuth.

Thus **B** – Bi_2O_3 .

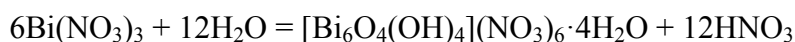
The obtaining of bismuth from sulfide:



Bismuth dissolution in nitric acid:



Example of bismuth salts hydrolysis reaction:



The obtaining of bismuth hydroxide:

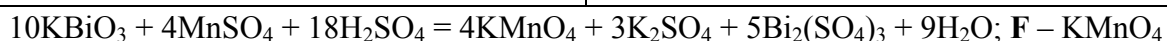


Oxidation of bismuth hydroxide by potassium persulfate in an alkaline medium leads to the formation of potassium bismuthate:

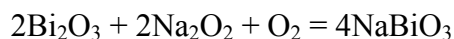


It is widely known that potassium bismuthate able to oxidize manganese's salt to permanganate, which has a deep crimson color that corresponds to the absorption band in the green region.

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Decomposition of bismuth hydroxide to oxide and its subsequent fusion with sodium peroxide to produce sodium bismuthate.



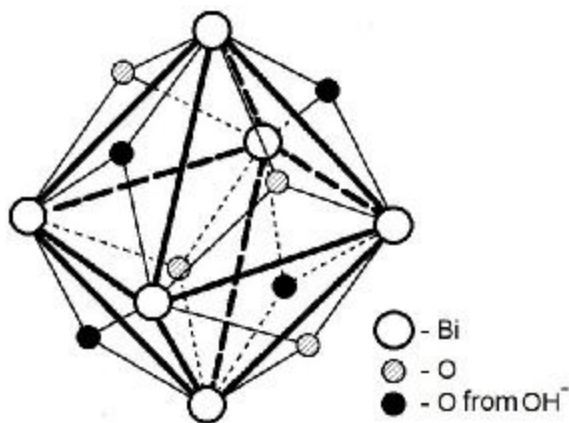
Example of bismuth oxide production from its MOC:



(0.5 points for each substance and 0.3 points for each reaction, 5.4 points in total)

2. Wood's metal consists of Bi, lead, tin and cadmium (0.5 points). Wood's metal is used as a low-temperature heating bath in a chemical laboratory, in precision castings, in galvanoplastics, for sensors in the fire alarm system (0.1 points for each feature, 0.9 points in total).

3. Taking into account mentioned elements of symmetry, structure of the six-core complex has the view (1.5 points in total):

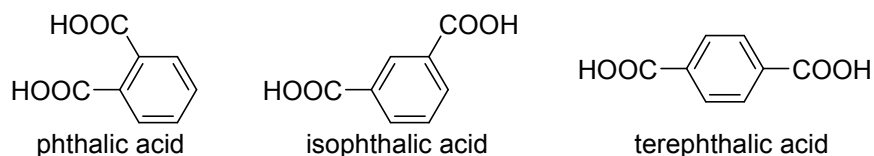


4. F is KMnO_4 . F has a deep crimson color, and concentrated solutions have purple and almost black color (0.2 points). Color of permanganate ion is explained by MOT, since the transition with the charge transfer from atomic orbitals localized predominantly on oxygen to anti-bonding orbitals localized on the manganese takes place (0.8 points, 1 points in total).

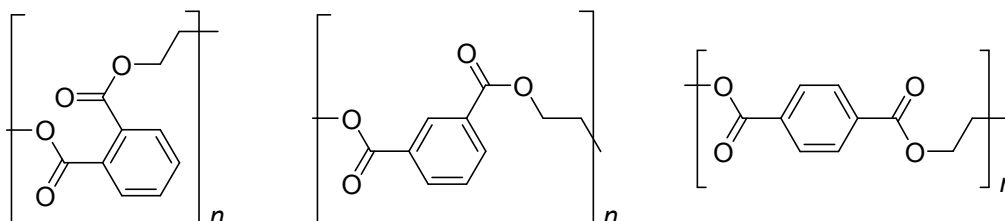
5. The main sign of the superconducting state appearance is zero resistance. In addition, the superconducting state is characterized by the Meissner effect (the effect of the full expulsion of the magnetic field from a superconductor volume (perfect diamagnetism)) and the Josephson effect (the effect of the superconducting current flowing through a thin isolator layer separating two superconductors) (0.4 points for each feature, 1.2 points in total).

Problem 4 (authors B.N. Garifullin, Yu.S. Holovko)

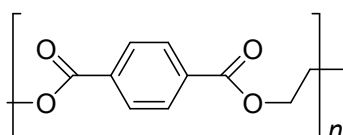
1. The three isomers of the diprotic aromatic carboxylic acid with the molecular formula of $C_8H_6O_4$ are:



The following polyesters are produced by polycondensation of these acids with ethylene glycol:



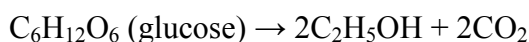
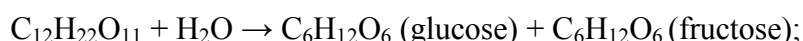
The most probable choice is polyethylene terephthalate (PET), a thermoplastic widely used for food packing (0.25 points for each isomer, 0.25 point for the correct choice, 1 point in total):



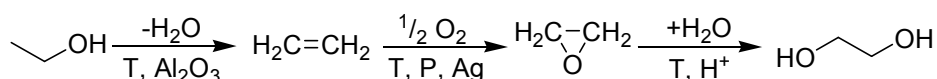
2. Any of the above mentioned polycondensation reactions describes the interaction of ethylene glycol with a carboxylic acid. The hereunder calculation confirms that about 30% of the polymer mass originates from ethylene glycol (EG) (1 point):

$$\omega(\text{EG}) = \frac{62}{62 + 166} = 27\% \approx 30\%$$

3. Sugar-cane (attention to the name!) contains substantial amount of sucrose (up to 21 wt% in the stem) that is converted into ethanol upon fermentation:



In turn, ethanol can be transformed into ethylene glycol in three stages via the industrial processes (0.5 point for each reaction, 2.5 points in total):



4. The bottles can be distinguished by means of the isotopic analysis. The conventional packing produced via processing of a fossil fuel contains practically no ^{14}C isotope, since its half-decay period (5700 years) is far below the date of the fossil fuels formation (tens of millions years). On the contrary, the packing produced from contemporary phylogenous raw materials contains almost maximum possible fraction of the ^{14}C isotope that was assimilated by the plant used in the bottle production from atmosphere upon vegetation (2 points).

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5. The first value is obtained if one takes into account the number of carbon atoms in the polymer structure originating from ethylene glycol:

$$\omega(\text{C}) = \frac{2}{2+8} \cdot 100\% = 20\%$$

The second value is obtained if one takes into account the fraction of the ethylene glycol moiety $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ in the structure of the repeating unit of **X** (based on the esterification mechanism elucidated by using alcohols labeled with oxygen isotopes) (1 point for calculation of each value, 2 points in total):

$$\omega(\text{moiety}) = \frac{60}{192} \cdot 100\% = 31.25\%$$

6. Taking 0.85 kg/L as oil density (an estimate! The actual values are found between 0.82 and 0.95 kg/L depending on the brand; any value within 0.6–1 kg/L is accepted) and 85% as the mass fraction of carbon in oil (calculated for octane; any value within 83–85% is accepted), one gets the mass of carbon in the preserved volume of oil as:

$$m(\text{C}) = 445000 \text{ bl} \cdot 159 \text{ L/bl} \cdot 850 \text{ g/L} \cdot 0.85 \approx 5 \cdot 10^{10} \text{ g}$$

As found before, ethylene glycol brings only each fifth carbon atom in the **X** structure; hence, the mass of the produced polymer is

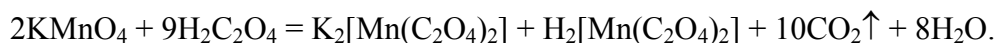
$$m(\text{X}) = \frac{5 \cdot 10^{10} \text{ g} \cdot 5}{0.63} \approx 4 \cdot 10^{11} \text{ g},$$

or about 20 g per bottle (this is close to the mass of a 0.33 L PET bottle, you can double check the validity of the value yourself) (1.5 point).

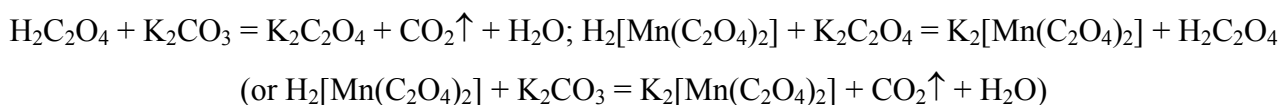
Problem 5 (author V.N. Khvalyuk)

1. In the first stage, the reaction between oxalic acid $\text{H}_2\text{C}_2\text{O}_4$ and potassium permanganate KMnO_4 occurs; the former acts as a reductant [it can only be oxidized to carbon(IV)], while the latter is an oxidant. The oxidation state of manganese (from +2 to +6) in the reduction product of KMnO_4 depends on the acidity of the reaction medium.

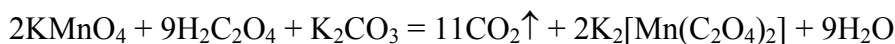
In the first stage, $\frac{31.5}{126} = 0.250$ mol of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\frac{6.32}{158} = 0.0400$ mol of KMnO_4 were mixed. Reduction of manganese(VII) to Mn(II) requires the reagents to be in the molar ratio of 5:2 (not taking into account acid-base interaction). Here, the ratio is much higher and is equal to $0.250:0.0400 = 12.5:2$. Therefore there is a large excess of $\text{H}_2\text{C}_2\text{O}_4$ and the reaction medium will be acidic, which means the product of KMnO_4 reduction should be Mn(II) (another indicator is the reaction temperature and the order in which reagents are mixed). Since the medium is acidic and the temperature is high (70–75°C), the final oxidation state of $\text{H}_2\text{C}_2\text{O}_4$ will be CO_2 . The Problem states that at the end of the first stage “*solution is cooled*”, which means there is no MnC_2O_4 precipitate. This can only be if oxalate complex of manganese(II) is formed, as there are no other anions in the solution. The equation of the reaction is:



Adding potassium carbonate leads to the reactions:



Hence the equation of the first step of synthesis is (1 point):



2. In the second step, the compounds containing Mn(II) (reductant) and Mn(VII) (oxidant) react with each other. Obviously, the resulting product should have Mn in the oxidation state between +2 and +7.

In the first stage, 0.0400 mol of the Mn(II)-containing compound was formed, and $\frac{1.58}{158} = 0.0100$ mol of KMnO_4 , was added to it, i.e. the molar ratio of Mn(II) : Mn(VII) was 4:1.

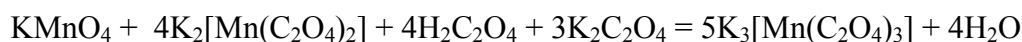
Electron-balanced equation	Molar ratio of Mn(II) : Mn(VII)
$4 \text{ Mn(II)} + 1 \text{ Mn(VII)} = 5 \text{ Mn(III)}$	4 : 1
$3 \text{ Mn(II)} + 2 \text{ Mn(VII)} = 5 \text{ Mn(IV)}$	3 : 2
$2 \text{ Mn(II)} + 3 \text{ Mn(VII)} = 5 \text{ Mn(V)}$	2 : 3
$1 \text{ Mn(II)} + 4 \text{ Mn(VII)} = 5 \text{ Mn(VI)}$	1 : 4

As shown above, in the second stage, the molar ratio of reagents is 4 : 1, which means the product of the second stage is substance containing Mn(III). Since the only anion in the reaction media is $\text{C}_2\text{O}_4^{2-}$, and the only cation is K^+ , the compound is $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3]$. Crystallization yields

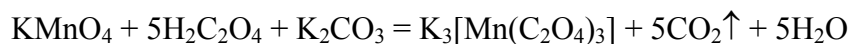
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$\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3] \cdot x\text{H}_2\text{O}$ precipitate. Based on the mass fraction of potassium, $x = 3$. Hence the formula of **A** is $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ (1 point).

In the second stage, the reaction is (1 point):



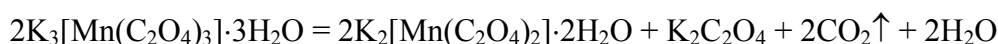
3. The total chemical equation leading to **A** is (1 point):



Overall, $0.0400 + 0.0100 = 0.0500$ mol of KMnO_4 was used in the synthesis, hence at the end one should have 0.0500 mol, or $0.0500 \cdot 490 = 24.5$ g of $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$. The actual yield is $\frac{12.8}{24.5} = 52\%$ (1 point).

4. If the second stage of the reaction is conducted in the light, an intermolecular reaction – photolysis of **A** – occurs: $\text{Mn(III)} + \text{C(III)} = \text{Mn(II)} + \text{C(IV)}$

The actual products of this reaction are $\text{K}_2[\text{Mn}(\text{C}_2\text{O}_4)_2] \cdot y\text{H}_2\text{O}$ and CO_2 . From the potassium mass fraction, $y = 2$. The chemical equation is (1 point):



The formula of **B** is $\text{K}_2\text{C}_2\text{O}_4$ (1 point), the formula of **C** is $\text{K}_2[\text{Mn}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ (1 point).

5. A ligand exchange partially occurs in the solution (1 point):



Adding acid to the solution shifts the equilibrium to the right due to the formation of the oxalic acid; diluting solution also shifts the equilibrium to the right. The color change is due to the formation of $[\text{Mn}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$ complex (1 point).

Problem 6 (author D.V. Kandaskalov)

1. We can find Rydberg constant using the first line of the Table as it is only one which is completed. As the one wavelength is known approximately we will find approximate value of Rydberg constant:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \Rightarrow R = \frac{1}{\lambda} \cdot \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)^{-1} = \frac{1}{100} \cdot \left(\frac{1}{1^2} - \frac{1}{3^2} \right)^{-1} = 0.01125 \text{ nm}^{-1}$$

Then we can precise the Rydberg constant using the second line and calculating n_2 :

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \Rightarrow \frac{1}{121} \approx 0.01125 \cdot \left(\frac{1}{1^2} - \frac{1}{n_2^2} \right) \Rightarrow n_2 \approx 1.94$$

As n_2 – natural number, it must be $n_2 = 2$, thus one can calculate precise value of R :

$$R = \frac{1}{\lambda} \cdot \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)^{-1} = \frac{1}{121} \cdot \left(\frac{1}{1^2} - \frac{1}{2^2} \right)^{-1} = 0.01102 \text{ nm}^{-1}$$

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As $n_1 < n_2$, the Balmer series has $n_1 = 1$ or 2. $n_1 = 1$ – is Lyman series as we can see in the Table.

Thus, Balmer series has $n_1 = 2$ and wave length of electron transfer $2 \rightarrow 3$ is

$$\lambda = \frac{1}{R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)} = \frac{1}{0.01102 \cdot \left(\frac{1}{2^2} - \frac{1}{3^2} \right)} = 655 \text{ nm}$$

For Brackett series we have:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \Rightarrow \frac{1}{1456} = 0.01102 \cdot \left(\frac{1}{4^2} - \frac{1}{n_2^2} \right) \Rightarrow \frac{1}{n_2^2} = 0 \Rightarrow n_2 \rightarrow \infty$$

2. The ground state of atom corresponds to the electron on the first orbit. Thus, the corresponding series is the Lyman one.

3. The first formula could be seen as the energy difference between two orbits. Thus, the energy of the ground state of hydrogen atom ($n = 1$) is

$$E = h\nu = \frac{h \cdot c}{\lambda} = -R \cdot h \cdot c = -1.102 \cdot 10^7 \cdot 6.62 \cdot 10^{-34} \cdot 3 \cdot 10^8 = -2.189 \cdot 10^{-18} \text{ J}$$

To obtain the energy of 1 mole of atoms we should use the N_A factor: $E = -2.189 \cdot 10^{-18} \cdot 6.02 \cdot 10^{23} = -1.318 \cdot 10^6 \text{ J/mol}$.

4. The total energy of hydrogen atom is the sum of potential and kinetic energy

$$E_{\text{total}} = E_{\text{pot}} + E_{\text{kin}} = E_{\text{pot}} - E_{\text{pot}} / 2 = \frac{-e^2}{4\pi\epsilon_0 r_n} - \frac{-e^2}{8\pi\epsilon_0 r_n} = \frac{-e^2}{8\pi\epsilon_0 r_n} = \frac{-e^2}{8\pi\epsilon_0 a_0 n^2} \Rightarrow$$

$$\Rightarrow a_0 = -\frac{e^2}{E_{\text{pot}} \cdot 8\pi\epsilon_0 n^2} = \frac{(1.6 \cdot 10^{-19})^2}{2.189 \cdot 10^{-18} \cdot 8 \cdot 3.14 \cdot 8.85 \cdot 10^{-12} \cdot 1^2} = 52.6 \cdot 10^{-12} \text{ m} = 52.6 \text{ pm}$$

The minimal distance between the 3rd and the 2nd orbits: $r_3 - r_2 = a_0 \cdot 3^2 - a_0 \cdot 2^2 = 5a_0 = 263 \text{ pm}$

5. The ionization energy corresponds to electron transfer from ground state ($n = 1$) to infinite state ($n = \infty$):

$$E_{\text{ion}} = E_{\infty} - E_1 = E_1 \cdot \left(\frac{1}{\infty^2} - \frac{1}{1^2} \right) = -E_1 = 2.189 \cdot 10^{-18} \text{ J}$$

6. Energy of H_2 is smaller than the double energy of H by the bond energy:

$$E_{\text{H}_2} = 2E_{\text{H}} - E_{\text{bond}} \Rightarrow E_{\text{bond}} = 2E_{\text{H}} - E_{\text{H}_2} = 2 \cdot (-1318) + 3070 = 434 \text{ kJ/mol}$$

Problem 7 (author E.A. Карпушкин)

1. Hydroquinone are the derivatives of 1,4-dihydroxybenzene, the latter containing 29.06 wt.% of oxygen. Hence, **BH₂** contains additional substituent(s) in the benzene ring. Since the oxygen fraction given in the task is lower than that in the unsubstituted hydroquinone, it is reasonable to assume that the additional substituents do not contain oxygen. The molar mass is then $M(\text{BH}_2) = 2 \cdot 16.00 / 0.2578 = 124.1 \text{ g/mol}$. The mass of the $\text{C}_6(\text{OH})_2$ moiety is of 106.1 g/mol, the residue of 18 g/mol corresponds to three hydrogen atoms and a methyl group. Hence, **BH₂** is 2-methylbenzene-1,4-diol (1 point).

2. $\text{BH}_2 + \text{H}_2\text{O}_2 = \text{B} + 2\text{H}_2\text{O} + \text{Q}$ (1 point)

3. By definition, standard enthalpy of reaction (3) equals standard enthalpy of water formation (-285.83 kJ/mol). Standard enthalpy of reaction (2) equals the difference between the enthalpies of formation of the products ($-285.83 + 0 \text{ kJ/mol}$) and the starting compounds (-187.78 kJ/mol), and is equal to -98.05 kJ/mol (2 points).

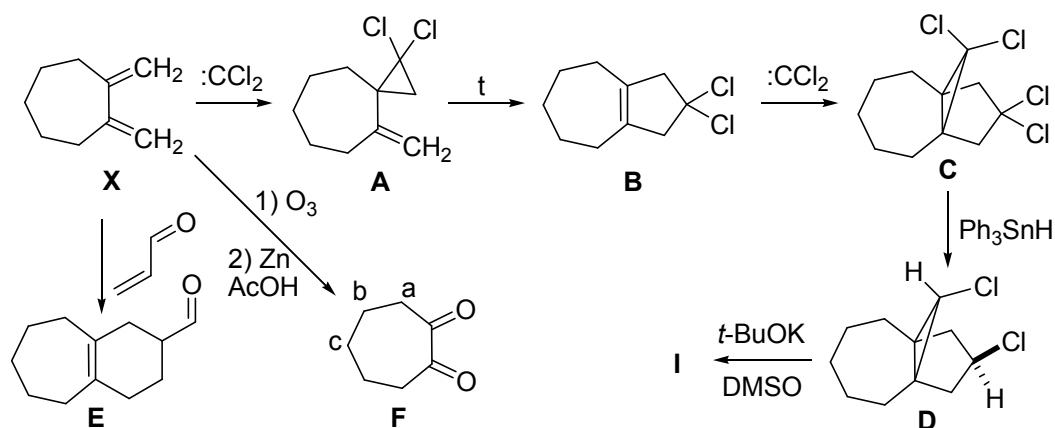
4. $\Delta G = -nFE = \Delta H - T\Delta S \rightarrow \Delta H = -nF \cdot d(E/T)/d(1/T)$ ($n = 2$ – is the number of electrons involved in the electrode reaction, F is the Faraday constant). Replacing with the numerical values given in the task, one gets $\Delta H = +177.5 \text{ kJ/mol}$ (2 points). The resultant reaction mentioned in question 2 is a sum of the reactions (1) – (3). The enthalpy of the resultant process is the sum of enthalpies of these reactions (Hess's law). Finally $-285.83 - 98.05 + 177.5 = -206.4 \text{ kJ/mol}$ (1 point).

5. Let us determine the composition of 1 g of the reaction mixture: 0.1 g (0.8 mmol) of **BH₂**, 0.25 g (7.3 mmol) of H_2O_2 and 0.65 g of water. Hence, the resultant reaction (see question 2) will consume the stoichiometric amount of hydrogen peroxide (0.8 mmol), and the residual peroxide (6.5 mmol) will decompose via reaction (2). The total heat emission by 1 g of the system is $206.4 \cdot 0.8 + (98.05 \cdot 6.5) = 802 \text{ J}$. Heating of 1 g of the system from 25 to 100°C will consume $4.2 \cdot 75 = 315 \text{ J}$, and the complete evaporation of the mixture would require 2256 J. Hence, the mixture will be heated up to boiling, and $(802 - 315) / 2256 \approx 1/5$ of the mixture will be evaporated. The excreted stream can be therefore regarded as liquid aerosol (small droplets of the solution heated to boiling in the gas mixture as the continuous phase) (3 балла).

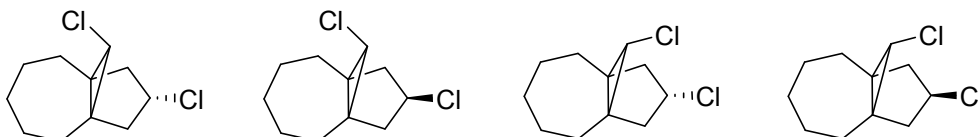
Problem 8 (author S.G. Bahtin)

1. According to the problem condition, compounds **A** and **B** can be described as products of 1,2- and 1,4-addition of dichlorocarbene to cyclic hydrocarbon **X**. This shows directly that **X** is 1,3-diene. The formation of 2 mol of CH_2O during the reductive ozonolysis of 1 mol **X** demonstrates that **X** has two $\text{C}=\text{CH}_2$ fragments. From the given formula of **X** it is possible to conclude that this is 1,2-bis(methylene)cycloalkane. Product of its ozonolysis **F** – cycloalkane-1,2-dione – contains three types of hydrogen atoms in a ratio of 2:2:1. This information allows for concluding that **F** is

cycloheptane-1,2-dione. Therefore, **X** is 1,2-bis(methylene)cycloheptane. It reacts with acrolein via Diels-Alder cycloaddition furnishing bicyclic product **E**. Compound **A** is the product of 1,2-addition of $:\text{CCl}_2$, *i.e.* this is the corresponding cyclopropane. **B** is the cyclopentene derivative (formally this is the product of 1,4-addition of $:\text{CCl}_2$ despite the real mechanism of its formation is the sigmatropic rearrangement of **A**). The reaction of $\text{C}=\text{C}$ bond in **B** with dichlorocarbene produces three-membered ring. From the chlorine content in **D** we can determine its molecular formula as $\text{C}_{11}\text{H}_{16}\text{Cl}_2$. It means that reaction of **C** with Ph_3SnH leads to the substitution of two chlorine atoms by two hydrogens. Compound **D** has diastereomers only if two substitutions proceed at two different carbon atoms. The final step of compound **I** synthesis is the elimination of HCl under treatment with strong base – potassium *tert*-butoxide. This elimination is accompanied by the fragmentation of the cyclic system (7 structural formulae, 1 point for each, 7 points in total)



2. Structural formulae of diastereomers of **D** (4 formulae, 0.25 points for each, 1 point in total):



3. The Friedel-Crafts alkylation is the reversible process. So, in the presence of acids, alkylbenzenes can be protonated at the substituted carbon atom of the aromatic ring affording the corresponding σ -complex **III**. The alkyl group migration leads to the new σ -complex **IV** which has no steric strains intrinsic to the compound **I** and cation **III**. The deprotonation of cation **IV** accomplishes the transformation of **I** into **II**. (Structural formula of **II** – 1 point, structural formulae of **III** and **IV** – 0.5 points for each; 2 points in total).

