

Problem 1

A weighed amount of brown algae (100 g) was extracted with water and the resulting solution irradiated with UV light in a closed reactor without removing oxygen until the complete transition of iodides into elemental iodine.

1. Write the reaction of iodine formation from inorganic iodide.

Note that the precipitate of iodine in the resulting solution did not form. After cetyltrimethylammonium bromide $C_{16}H_{33}(CH_3)_3NBr$ (CTMA) was introduced into the solution, a salt **A** containing the organic cation precipitated. The precipitate was washed, dried and weighed; its weight was 1.205 g. The precipitate was dissolved in the mixture of ethanol – water (1:1 vol.) in a volumetric flask of 100 mL capacity and adjusted to the mark; then a 10.00-mL aliquot was taken and titrated with a 0.1000 M sodium thiosulfate solution until the color disappeared, which required 3.9 mL of the titrant.

2. What is the amount of iodine contained in precipitate **A**? Record the probable composition of **A** and the reaction of its precipitation.
3. Calculate the iodine content in algae in g/100 g.

A weighed portion of NaI (8.0 mmol) was added to 100 mL of a 0.040 M solution of sodium iodate in 1 M HBr; as a result, after brief coloring, a nearly colorless solution of compound **B** was formed.

4. Write the reaction equation, if none of the substances was in excess. Note that the further addition of 12 mmol of solid NaI to the solution and an excess of CTMA yielded 12 mmol of precipitate **A**.
5. Write the reaction of transformation of **B** into **A**.
6. Write down the reaction of hydrolysis of **B**. What medium (acidic or alkaline) will promote hydrolysis? Confirm with a reaction equation.

Problem 2

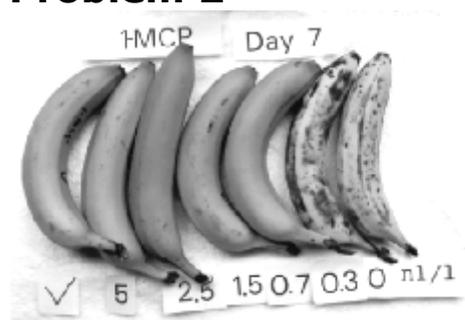
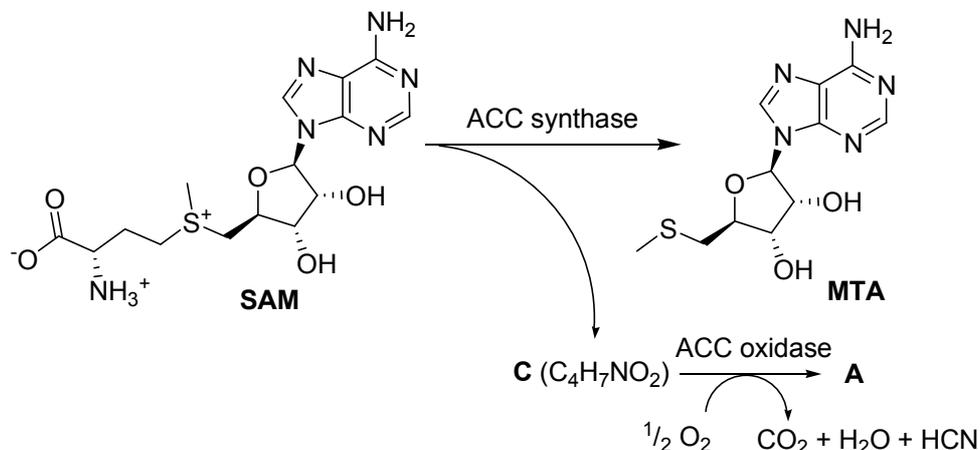
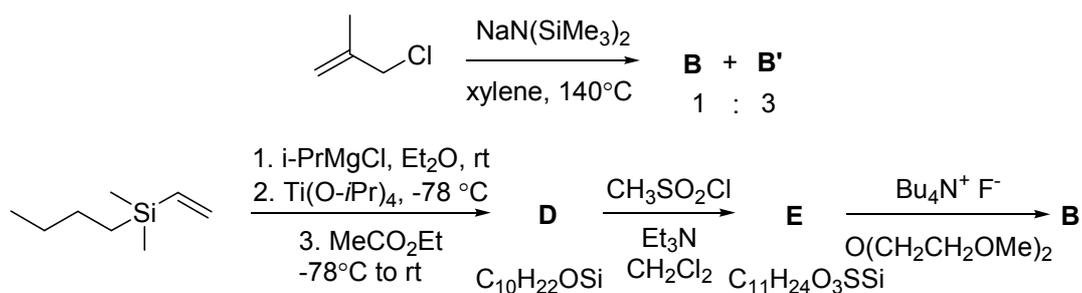


Figure. Bananas treated with compound **B** at concentration varied from 0 to 0.005 ppm followed by treatment with compound **A** (300 ppm) and keeping under air for 7 days.

Two binary gaseous (under normal conditions) compounds **A** and **B** (containing 14.37% and 11.18% of element **X**, respectively), regulate ripening of fruit and widely used during the transportation and storage of fruit and vegetables. Compound **A** is synthesized in the Nature by Yang cycle fragment of which is given in the following Scheme:



Compound **B** is unnatural. Initially, it was synthesized by the treatment of methallyl chloride with a strong base. The side-product of this reaction is the compound **B'** which is more symmetrical than **B**. However, this method is not practical as the dosage of gaseous compound **B** cannot be taken easily. In 2012, this problem was solved by chemists from Erum Biotechnologies (South Korea). They proposed method given in Scheme 2. The possibility of the dosage of **B** is based in this method on the fact that compound **E** under treatment with the calculated quantity of fluoride ion produces quantitatively the required amount of compound **B**. **E** is obtained by mesylation of **D** which is the product of *Kulinkovich reaction*.



- Write down structural formulae of compounds **A**, **B**, **B'** and **C** accounting for fact that **B** and **B'** have the same carbon skeleton as that of the achiral compound **C**.
- Decipher structures **D** and **E** if it is known that these compounds are *trans*-isomers.
- Calculate the required quantity (in mL) of 2.3 M solution of Bu₄NF in DMF as well as minimum amount of **E** (in g) to obtain the concentration of **B** at 0.005 ppm level in the container with size of 12.0 · 2.3 · 2.4 m.

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Problem 3

The metal **A** obtained by coal reducing of its oxide **B** after sulfide burning. This sulfide is produced by processing polymetal (CuS, PbS) sulfide ores. Metal **A** is known as one of the major components of Wood's metal.

A is dissolved only in oxidizing acids. For example, reaction with 30% HNO₃ leads to nitrate **C**, which is easily hydrolysed in water forming the basic salts, one of which composition can be written as [A₆O₄(OH)₄](NO₃)₆·4H₂O. Therefore, metal salts of **A** are dissolved in solution of the corresponding acids.

Addition of alkali to **C** leads to the precipitation of hydroxide **D**. The compound **E** is produced by oxidation of **D** by potassium persulfate in alkaline medium. **E** is used in the practice of inorganic synthesis as a strong oxidant. Thus, the reaction of **E** with a transition metal sulfate affords another colored oxidant **F**, which solution has an intense broad absorption band in the green region (550 nm).

B is formed when **D** is heated to 150°C, (the weight loss in this process is 10.4%). Compound **B** is a yellow crystals, it is usually prepared by thermolysis of various metal organic compounds of **A**: acetates, β-diketonates and other MOCs. Sodium analogue of **E** is synthesized by fusion of **B** with sodium peroxide in an oxygen atmosphere.

1. Identify compounds **A** – **F** and write the mentioned reactions of their obtaining.
2. Specify the elemental composition of the Wood's metal, and select faithful answers of the Wood's metal usage from proposed in the answer sheet.
3. Draw six-core structure of the cation [A₆O₄(OH)₄]⁶⁺, if it is known that the structure contains such elements of symmetry as three two-fold axes and three mirror planes.
4. What is the color of the compound **F**? According what model (VBT, CFT, MOT) can be the appearance of **F**'s color explained?

The problem of obtaining **B** has acquired a special significance in recent decades, since HTSC properties of complex oxide materials containing **A** have been discovered.

5. Specify features of the superconducting state among the options listed in the answer sheet.

Problem 4

Aimed at minimizing the environmental impact, The Coca-Cola Company has developed and implemented production of the plastic bottles, which (as reported by the manufacturer) contain up to 30% of phylogenous materials. In reality, such bottles are molded of a single polymer **X**, a product of ethylene glycol condensation with diprotic aromatic carboxylic acid $C_8H_6O_4$.



1. Suggest three isomeric structures of **X** and choose the one that is most likely used in the industrial production.
2. Based on the content of the phylogenous materials in the plastic packing (without the label and cap), determine what component of the plastics is produced from biological raw material.

Sugar-cane is predominantly used as a raw material for the production of biobottles, since it is among the plants, which most actively absorb atmospheric CO_2 and efficiently utilize photosynthesis.

3. Suggest the industrial method of production of the demanded component of the plastics from sugar-cane. Write down the corresponding reactions.
4. Is it possible to distinguish between the biobottle and the conventional plastic bottle, provided the geometry, size, surface morphology, etc. of the bottles are identical?

In a science educational review, the content of the biocomponent in the plastics produced by The Coca-Cola Company was calculated using two different approaches. The reported values were of 20% and 31.25%.

5. Demonstrate the ways of calculation leading to the reported results. For each variant, write down the corresponding math and/or chemical equations and formulae.

The PlantBottle technology was launched in 2009. 20 billion biobottles have been produced by the beginning of 2014. The Coca-Cola Company reported that this allowed saving 445000 barrels of oil (1 barrel = 159 L).

6. Estimate the mass of the bottle used in the calculations done by the Coca-Cola Company Marketing Department to demonstrate the ecological effect of the novel packing.

Problem 5

The procedure for the synthesis of the substance **A** is described below.

In the first stage, a 31.5 g of oxalic acid dihydrate is dissolved in 200 mL of water at 70–75°C. Then a 6.32 g of finely pounded potassium permanganate is added to the solution in small increments while stirring. After the reaction, 6.90 g of potassium carbonate was added slowly, and the resulting solution was cooled to 4–5°C and diluted with 160 mL of chilled water.

1. Write down the chemical equation occurring in the first stage of synthesis of **A**.

The second stage of synthesis should, if possible, be carried out in complete darkness. 1.58 g of potassium permanganate ground into a fine powder is added to the solution obtained in the first stage of the synthesis. The mixture is then vigorously stirred for 10 min at 0–2°C. The resulting red-violet solution is cooled and filtered cold, then 200 mL of strongly chilled ethanol is added to it. The solution is left to crystallize in a mixture of ice and salt for 2 hours. The crystalline precipitate (potassium mass fraction is 23.92%) is separated on a sintered glass filter and dried at the room temperature in the air.

2. Determine the chemical formula of **A** and write down the equation that occurs in the second stage of the synthesis.
3. Write down the total equation of **A** synthesis described above and calculate its actual yield if the mass of the resulting product was 12.8 g.

If recovery of **A** is carried out in the light, it is contaminated by the substances **B** and **C** (mass fraction of potassium 22.65%).

4. Write down chemical formulas of **B** and **C** and the chemical equation of their formation.

Concentrated aqueous solutions of **A** has deep red-violet color. When diluted or acidified, the solution color changes to yellow-brown.

5. What causes the color change upon dilution or acidification of the aqueous solution of **A**? Write down the chemical reaction.

Problem 6

In 1888 Rydberg and Ritz discovered an empirical formula which determines the positions of spectral lines of hydrogen atoms by light absorption:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right),$$

where λ – wavelength, R – Rydberg constant, n_1 and n_2 – natural numbers. A given spectral series corresponds to transfer (jump) of electron from different states n_2 to a given state n_1 .

Spectral series	n_1	n_2	λ , nm
Layman	1	3	~100
	1		121
Brackket	4		1456
Ballmer		3	

1. Using the data from the table, calculate the Rydberg constant R and complete this table with the absent data.

In 1913 Bohr developed his model of Hydrogen atom. This model is based on the supposition that the atom has stationary circular orbits where electron is located without emission of energy. Electron transfer from orbit n_1 to n_2 is accompanied by absorption or emission of light (photon) with specific wavelength.

The potential energy of electron in the electrostatic field of the nuclei is

$$E_n = -\frac{e^2}{4\pi\epsilon_0 r_n},$$

where $e = 1.6 \cdot 10^{-19}$ C – elementary charge, $\epsilon_0 = 8.85 \cdot 10^{-12}$ F/M – electric constant, r_n – radius of n^{th} orbit. And $r_n = a_0 n^2$, a_0 – radius of 1st Bohr orbit (Bohr's radius).

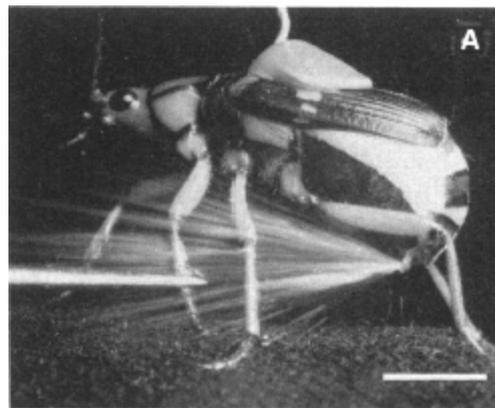
It is known that the value of kinetic energy of electron in Hydrogen atom is twice smaller than those of potential energy and it is opposite in sign.

2. Which series does correspond to transfer of electron to the ground state?
3. Knowing constant R , calculate the energy of 1 mole of hydrogen atoms in the ground state.
4. Calculate the Bohr's radius a_0 and minimal distance between 3rd and 2nd orbits.
5. Find the ionization energy of hydrogen atom.
6. Taking into account that the total energy of H_2 molecule is -3070 kJ/mol (energy is measured from the energy of nuclei and electrons at rest, situated at infinite distance from each other), calculate the bond energy between H atoms in this molecule.

Additional data: $h = 6.627 \cdot 10^{-34}$ J·s, $c = 3 \cdot 10^8$ m·s⁻¹.

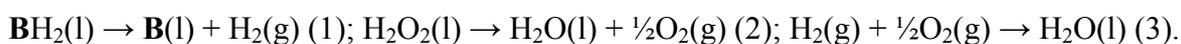
Problem 7

The bombardier beetles are known for the unique defense mechanism. In case of danger they excrete a hot stream of the repellent solution frightening away the aggressor (see the figure). The stream is formed via the chemical reaction involving a pair of compounds fed into the reaction chamber from the reservoirs in the beetle body. One of the reactants is a representative of the hydroquinones class (**BH**₂).



1. Mass fraction of oxygen in **BH**₂ is of 25.78%. Determine the compound structure.

Hydrogen peroxide is the second component of the reaction mixture. The following set of the reaction occurs in the reaction chamber in the presence of catalase and peroxidase enzymes:



2. Write down the resultant thermochemical equation of the reaction between **BH**₂ and H₂O₂.

Standard enthalpies of formation of H₂O(l) and H₂O₂(l) are of, -285.83 kJ/mol and -187.78 kJ/mol, respectively.

3. Determine standard enthalpy of reactions (2) and (3).

Standard potential of the (**BH**₂/**B**) electrode relative to the standard hydrogen electrode is of 0.7175 V at 0°C and of 0.6805 V at 50°C.

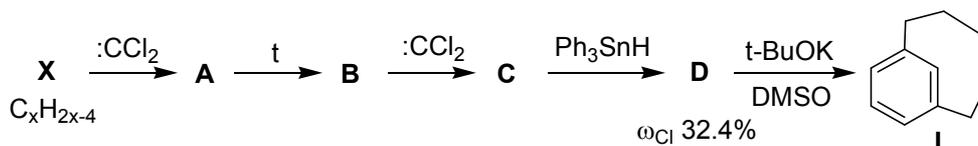
4. Determine standard enthalpy of reaction (1) and of the resultant reaction that you have reported in question 2.

The composition of the mixture in the reaction chamber of the beetle is as follows: 10 wt.% **BH**₂, 25 wt.% H₂O₂, and water.

5. Assuming that the thermophysical properties of the mentioned reaction components are approximately the same as for water (specific heat capacity 4.2 J/deg·g in the liquid phase and of 2 J/deg·g in vapor phase, specific heat of evaporation 2256 J/g), determine the final temperature of the excreted stream. Choose the proper type of the excreted mixture from the list in the Answers sheet.

Problem 8

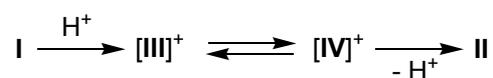
In 1984, L. W. Jenneskens and co-workers synthesized for the first time hydrocarbon **I** with very unusual structure. The starting compound in their synthesis was a monocyclic hydrocarbon **X**.



This is known that: *a*) compound **A** and its isomer **B** can be described as products of 1,2- and 1,4-addition of dichlorocarbene to **X**; *b*) **X** reacts with acrolein ($\text{CH}_2=\text{CH}-\text{CHO}$) affording bicyclic product **E**; *c*) ozonation of 1 mol of **X** followed by ozonide reduction with zinc in acetic acid produces 2 mol of CH_2O and 1 mol of **F**, ^1H NMR spectrum of which contains 3 signals with the relative intensities of 2:2:1; *d*) compound **D** has 4 diastereomers.

1. Write down structural formulae of **X**, **A** – **F**.
2. Write down structures of diastereomers of **D**.

Hydrocarbon **I** demonstrates chemical behavior different from that for the most arenes. Thus, it forms addition products in reactions with electrophiles; in the presence of acid **I** isomerizes into thermodynamically more stable compound **II**. The last reaction proceeds *via* the intermediate formation of isomeric carbocations $[\text{III}]^+$ and $[\text{IV}]^+$.



3. Write down structural formulae of compounds **II** – **IV**, accounting for fact that **I** and **II** are positional isomers.