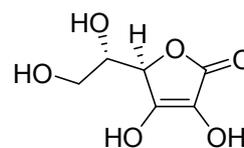


Problem 1

Ascorbic acid (AA) is an important vitamin and antioxidant. Its quantity in pharmaceuticals is determined by titration with potassium iodate in 0.5 M HCl medium in the presence of starch, during which dehydroascorbic acid $C_6H_6O_6$ (DHA) and iodide ion are formed.



1. Write down the equations of titration reaction and reaction producing iodine that gives color to the indicator. Calculate the amount of AA in the sample (in mol), if 9.5 mL of 0.100 M KIO_3 solution was spent for its titration.

DHA is slowly converted into xylosone $C_5H_8O_5$ as a result of addition of a water molecule and decarboxylation. Xylosone rapidly (much more rapid than during the previous stage) is reduced by the second molecule of AA to yield xylose $C_5H_{10}O_5$ and another molecule of DHA. Then xylose slowly cyclizes to give furfural $C_5H_4O_2$.

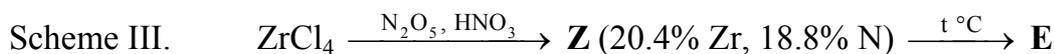
Having started a titration of AA (total amount: 1.00 mmol) with iodate as described in question 1, the analyst left the lab, and when he returned, he found no ascorbic acid in solution. At the same time, xylose and furfural were found in solution, their total amount being 0.55 mmol.

2. Write down the reactions of DHA and xylosone transformations during storage of the solution using chemical formulas (no structures).
3. What was the volume of 0.100 M iodate solution that the analyst had spent before he left the lab?
4. What other organic components, beside xylose and furfural, and in what quantities were present in solution by the time the analyst returned, if the system reached equilibrium?
5. What side reaction except for the mentioned ones could also lower the AA concentration in solution during its storage?

If titration of AA by iodate is performed in the medium of 5 M HCl, then iodate will be also reduced to iodide, but 7.00 mL of 0.100 M iodate solution will be spent for 0.300 mmol of AA.

6. What will be the product of oxidation of AA under these conditions? Write down the reaction of titration and the structure of this product if no other carbon-containing compounds are formed in the reaction.

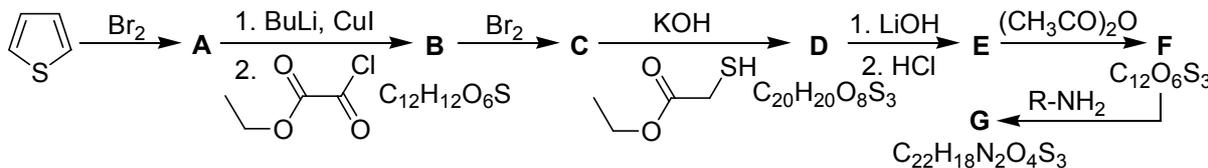
To synthesize some other anhydrous nitrates (for example, zirconium nitrate **E**) one can use N_2O_5 undergoing a dissociation into ions in the presence of anhydrous HNO_3 . The salt **Z** (see scheme III) is built up similarly to **Y**.



1. Write down the equations for the autoionization of N_2O_4 and N_2O_5 taken place in corresponded solutions.
2. Determine the **A – E**, **X**, **Z** formulae and the ions forming **Y** and **Z** complex salts.
3. Write down the equations for the reactions described.
4. Draw the graphic formula for N_2O_4 and N_2O_5 .

Problem 4

Thiophene molecules are the efficient building blocks for production of organic transistors because they are structurally inflexible and relatively stable but can be easily functionalized. In 2011, it was synthesized derivative of thiophene which was shown to be efficient for preparation of organic transistors:



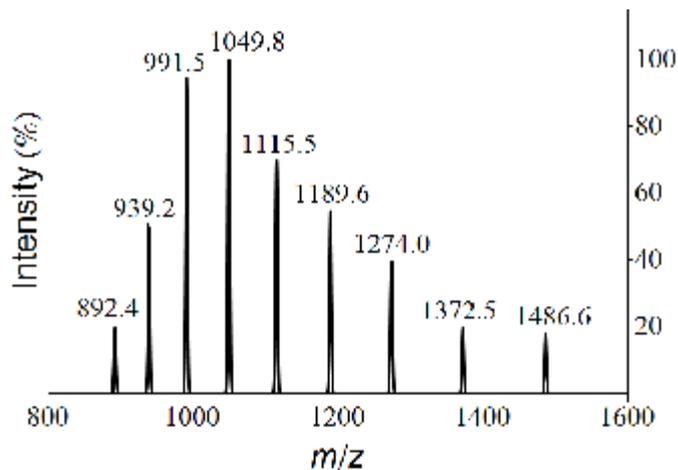
1. Which aromatic compound – thiophene or benzene – is more reactive in the electrophilic substitution reactions?
2. Thiophene nitration produced a mixture of two mononitroderivatives in a ratio of $\sim 100:1$. Write down the structural formula of the main product.
3. Write down the structural formula of amine RNH_2 if it is known that its ^{13}C NMR spectrum contains 3 signals (molecule has 3 types of carbon atoms).
4. Decipher scheme of synthesis accounting for fact that ^1H NMR spectrum of **D** contains four signals with the relative intensities of 2:2:3:3.

Problem 5

Electrospray is a method for ionization of molecules in solutions. The main advantage is low fragmentation. A liquid passes through a thin capillary and leaves the needle tip in the form of small charged droplets. The droplets move under electric field, growing smaller in size due to vaporization of the solvent and spontaneous fragmentation into smaller parts. As a result, micro-droplets are generated, containing only one charged molecule (ion). After vaporization

of the last portions of the solvent the ions are directed to a mass spectrometer to be analyzed by the mass-to-charge ratio (m/z).

Electrospray is used for determination of the molecular mass of proteins. The peaks of multiply protonated ions $[A + nH]^{n+}$, where n – the number of protons, attached to the molecule **A**, are registered by mass spectrometer. In the figure the mass spectrum of lysozyme **A** is shown. The charges of neighboring ions differ by one unit.

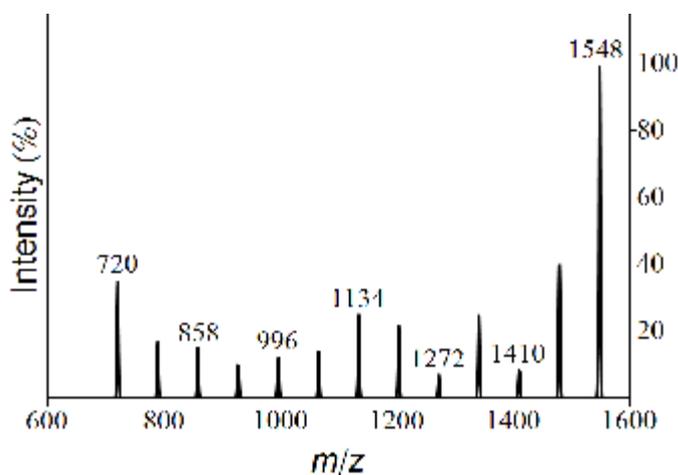


1. In the mass spectrum choose any two peaks and from the values m/z calculate the molecular mass M of **A**. Express the mass in daltons ($1 \text{ Da} = 1 \text{ a.m.u.} = 1.66054 \cdot 10^{-27} \text{ kg}$) and round it off to the nearest whole number. The proton mass $m_p = 1.0073 \text{ Da}$.
2. Find the charges (z) of all the ions, presented in the mass spectrum (whole numbers in elementary charges $e = 1.602 \cdot 10^{-19} \text{ C}$).

The stability of a charged droplet with respect to ruptures is conditioned by competition between electrostatic and cohesion (surface) energy. For a spherical droplet, $U_{el} = q^2 / 8\pi\epsilon_0 r$, where q – charge of the droplet, r – radius, $\epsilon_0 = 8.854 \cdot 10^{-12} \text{ J}^{-1}\text{C}^2\text{m}^{-1}$, $U_{surf} = \sigma S$, where S – area of the droplet surface, σ – surface tension.

3. From energetic considerations derive the stability condition for a spherical droplet with respect to rupture into two parts of the same shape and volume (with charges $q/2$). Inequality, expressing the condition, should contain q, r as the variables, and σ, ϵ_0 as the constants.
4. Determine the maximum charge q (in elementary charges e), which can bear a water droplet with $r = 10^{-5} \text{ cm}$? Round off the answer to the whole number. Surface tension of water $\sigma = 7.28 \cdot 10^{-2} \text{ J}\cdot\text{m}^{-2}$.

Distinguished from electrospray, molecules under electron impact ionization undergo, as a rule, considerable fragmentation. Mass spectrum of fullerene derivative $C_N(\text{CX}_3)_n$, obtained from its vapor, is shown in figure. The element **X** is halogen. All the peaks represent ions with

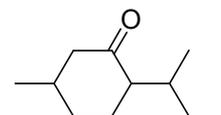


the charge +1, but different numbers of CX₃-groups.

5. a) How many carbon atoms (*N*) does the fullerene molecule, (CX₃-derivative of which was studied) contain? b) Determine the element **X**; c) Determine the number of functional groups (*n*) in the studied compound.

Problem 6

Essential oils of some herbs are source of menthone (**I**) which has a number of stereoisomers:



1. Cycloalkanones are often synthesized by pyrolysis of calcium salts of the appropriate acids. In particular, this method was utilized to confirm structure of menthone by counter synthesis. Write down structural formula of acid pyrolysis of which calcium salt produces **I**.

2. Write down IUPAC name for **I** and structural formulae of all its stereoisomers.

In (–)-menthone carbon atom, connected to CH₃ group, has *R*-configuration. In aqueous CH₃COOH solution (–)-**I** undergoes epimerization at 20°C producing the equilibrium mixture of (–)-menthone and (+)-isomenthone [(+)-**isoI**]. This mixture has specific rotator power of –3°. The transformation (–)-**I** ⇌ (+)-**isoI** proceeds via the intermediate formation of unstable compound **X** which is isomer of (–)-**I** and (+)-**isoI**. IR spectrum of **X** contains a broad band at 3500 – 3200 cm⁻¹.

3. Calculate content of (%) (–)-**I** ($[\alpha]_D^{20^\circ\text{C}} = -30^\circ$) and (+)-**isoI** ($[\alpha]_D^{20^\circ\text{C}} = +92^\circ$) as well as equilibrium constant *K*. Write down structural formula of **X**.

4. Accounting for your answer on question 3, propose structural formulae of (–)-**I** and (+)-**isoI**, using cyclohexane conformations giving in the answer sheet.

Problem 7

Chemistry of isotopes has different useful applications in many fields of science and industry. For example, it is used for studies of reaction mechanisms and kinetics, for catalysis studies, diffusion, adsorption, *etc.* In geology, one of the applications of isotopes is determination of the age of rocks and other objects, such as meteorites.

One of such methods, based on samarium and neodymium isotopes, was developed by Langmar in 1947. The ¹⁴³Nd quantity increase due to ¹⁴⁷Sm decay ($\tau_{1/2} = 1.06 \cdot 10^{11}$ years) from initial value $n_0(^{143}\text{Nd})$ at the moment of object formation (*n* – number



of moles). The quantity of ^{144}Nd does not change in time, permitting determination of the sample age, measuring the ratios $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ by mass spectrometry.

In 1940, in Australia, there was found a meteorite, named Moama. It is believed that the age of this meteorite is comparable to the age of Solar system. In 1978 two minerals were extracted from Moama – plagioclase and pyroxene, which were analyzed:

| Mineral | $n(^{143}\text{Nd}) / n(^{144}\text{Nd})$ | $n(^{147}\text{Sm}) / n(^{144}\text{Nd})$ |
|-------------|---|---|
| Plagioclase | 0.510 | 0.111 |
| Pyroxene | 0.515 | 0.280 |

1. a) Write down the decay reaction for ^{147}Sm ; b) Determine the decay constant.
2. Determine the initial ratio $n_0(^{143}\text{Nd}) / n_0(^{144}\text{Nd})$ at the moment of meteorite formation using table data. Remember that $n_0(^{143}\text{Nd}) / n(^{144}\text{Nd})$ is the same for both minerals.
3. Calculate the age of Moama.
4. Is it possible, using Langmar's method, to determine the age of rocks, which were formed in 3 – 5 millennium B.C.? Confirm the answer by a numerical example.

Problem 8

The President of the Palestinian National Authority, Nobel Peace Prize laureate Y. Arafat died suddenly under strange circumstances in November 2004. In 2012 the Y. Arafat's body was exhumed as insisted by his widow, and the tissue samples were subjected to analysis. The results demonstrated the probability of Y. Arafat's death because of the fatal poisoning with the substance containing an isotope of **X**.

The numbers of α -particles emitted in a unit of time by 1.00 mg sample of ($T_{1/2} = 138.4$ days) and 4.55 g sample of ^{226}Ra ($T_{1/2} = 1601$ year) are identical.

1. Write down the equation of radioactive decay of ^{226}Ra isotope.
2. Calculate the molar mass of **X**.
3. When the exhumation of Y. Arafat's body (70 kg) would have become meaningless due to decreasing of the total α -radioactivity of the organism tissues up to 0.3 Bq/kg, if:
 - a) the minimal lethal dose of **X** is 1 μg ;
 - b) in norm, the α -activity (A_α) of human body (70 kg) is 0.2 Bq/kg, this value staying unchanged for many years;
 - c) a non-radioactive isotope is formed from **X** in the process of its α -decay.

The ratio of the number of neutrons to protons (N/Z) in **X** equals 1.50.

4. Determine **X**.

More than 90% of **X** is produced in Russia. The ^{209}Bi isotope is used as the target in the one-step procedure for obtaining **X**.

5. Write down the theoretically possible equations of nuclear reactions if the total mass of all the rest (but **X** and ^{209}Bi) particles in the reaction does not exceed 1 a.m.u.

A sample of **X** of 1 cm^3 ($\rho_{\text{X}} = 9.2\text{ g/cm}^3$) evolves significant energy per time unit (1210 W), which is comparable to that of an electric iron. This is behind the extreme toxicity of **X** for living things.

6. Calculate the initial kinetic energy (in MeV) of the α -particle formed in **X** decay supposed the kinetic energy completely transforms into the heat one ($1\text{ eV} = 1.6 \cdot 10^{-19}\text{ J}$).