# Preparatory problems

## 47th International Chemistry Olympiad
## (IChO-2015)

Moscow State University
Baku Branch
Azerbaijan

Edited by: Vadim Eremin, Alexander Gladilin

e-mail:
vadim@educ.chem.msu.ru
alexander.gladilin@simeon.ru

Released January 31, 2015

## Contributing authors

### Moscow State University, Baku Branch, Azerbaijan

M. Beklemishev
A. Drozdov
A. Dubenskiy
V. Eremin
A. Gladilin
E. Karpova
I. Kas'yanov
M. Korobov
M. Kovalchuk
E. Lukovskaya
P. Matveev
V. Nikitina
A. Prokhorova
G. Rusakova
E. Skokan
I. Trushkov
V. Zelikman

### Medical clinics No 33, Ufa, Russia

B. Garifullin

### Belarusian State University, Minsk, Belarus'

Yu. Halauko

### Aix-Marseille University, Marseille, France

D. Kandaskalov

### Kazan' Federal University, A.Butlerov Institute of Chemistry, Russia

I. Sedov

### Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev

D. Volochnyuk

### Multidisciplinary Lyceum, Vologda, Russia

A.Z. Lisitsyn

# PREFACE

**Dear friends!**

We are happy to present you the Booklet of Preparatory problems. Members of the Science Committee really did their best to prepare interesting tasks. The set covers all major parts of modern chemistry. All the tasks can be solved by applying a basic knowledge of chemistry, even in case a problem refers to a topic of advanced difficulty. Still, we expect it will take some time and efforts of yours to find the correct answers. Thus, most probably we know how you will spend some of your time in the coming months. We wish you much pleasure while working with this set of problems. And never forget that

**LIFE IS A HUGE LAB!**

## Note to mentors

In addition to the problems, you will find in the Booklet:

- The list of topics of advanced difficulty
- The Safety rules and recommendations set by the IChO International Jury
- The hazard warning symbols, their designations and explanations

Worked solutions will be posted at the website by the end of May, 2015.

**We pay great attention to safety.** In the section preceding the practical preparatory problems you will find safety precautions and procedures to be followed. At the registration in Baku we will ask every head mentor to sign a form stating that his/her students are aware of the safety rules and adequately trained to follow them. Prior to the Practical Examination all students will have to read and sign safety instructions translated into their languages of choice.

Despite our great proof reading efforts, some mistakes and misprints are still possible. We appreciate your understanding and will be happy to get your feedback. Please address your comments to icho2015@msu.az. You may also write your comments on our website http://www.icho2015.msu.az/. Please explore our official website on a regular basis, since corrections/upgrades of the preparatory problems, if any, will posted there.

On behalf of the Steering Committee (SC), we encourage you to visit its recently launched homepage https://www.ichosc.org/. You can also directly access SC by writing a letter to sc@ichosc.org.

Sincerely yours,
Members of the IChO-2015 Science Committee

# Contents

## Theoretical problems

## Practical problems

## Physical Constants, Formulas, and Equations

Avogadro's constant: $N_A = 6.0221 \times 10^{23} \text{mol}^{-1}$

Universal gas constant: $R = 8.3145 \text{ J·K}^{-1}\text{·mol}^{-1}$

Faraday's constant: $F = 96485 \text{ C·mol}^{-1}$

Standard pressure, $p° = 1 \text{ bar} = 10^5 \text{ Pa}$

Atmospheric pressure: 1 atm = 1.013 bar

Zero of the Celsius scale, 273.15 K

1 nanometer (nm) = $10^{-9}$ m

The First Law of thermodynamics: $\Delta U = Q - W$[1]

Reversible adiabatic process for an ideal gas: $pV^{1+R/C_V} = \text{const}$

Work made by an ideal gas in an adiabatic process: $W = nC_V (T_1 - T_2)$

Work made by an ideal gas in a reversible isothermal process: $W = nRT \ln\frac{p_1}{p_2}$

Gibbs energy: $G = H - TS$

Relation between equilibrium constant, standard electromotive force and standard Gibbs energy:

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{nFE^\circ}{RT}\right)$$

Dependence of Gibbs energy of reaction on concentrations: $\Delta G = \Delta G^\circ + RT\ln\frac{c_{\text{prod}}}{c_{\text{reag}}}$

Dependence of electrode potential on concentrations: $E = E^\circ + \frac{RT}{nF}\ln\frac{c_{\text{ox}}}{c_{\text{red}}}$

---

[1] You may use the First Law written in IUPAC convention: $\Delta U = Q + W$ (in this case, work is positive if it is done on the system)

## Topics of advanced difficulty

### Theoretical

1. The First Law of thermodynamics: thermodynamic cycles, adiabatic processes, work of adiabatic processes.
2. The Second Law of thermodynamics: spontaneous chemical reactions. Dependence of Gibbs energy of reaction on concentrations. Relation between equilibrium constant, electromotive force and standard Gibbs energy. Latimer diagrams.
3. Integrated rate law for first order reactions, half-life, mean life time. Analysis of complex reactions using steady-state and quasi-equilibrium approximations, mechanisms of catalytic reactions, determination of reaction order for complex reactions.
4. Inorganic complexes: structure and isomerism. Crystal field theory. Trans-effect.
5. Preparation and chemical properties of carbonyl compounds.
6. Oxidoreductase- and transferase-catalyzed reactions in metabolism of nucleotides and xenobiotics.

### Practical

1. Advanced procedures in organic synthesis: heating under reflux, vacuum filtration, vacuum distillation, determination of refraction index, use of a nomogram.
2. Kinetics of chemical reactions: photometric studies and analysis of experimental data with the English version of Microsoft Excel software.

**Note.** The hereunder topics met in the Preparatory problems:

- Clapeyron equation for phase transition
- Rate of heterogeneous reactions
- Claisen rearrangement
- Determination of a melting point
- Calculation of solubility in the presence of complexing agents
- Rotary evaporation
- Liquid-liquid extraction
- Deciphering a compound structure using NMR and mass spectrum data

are inalienable parts of the proposed tasks. *We do not expect students to get an advanced training in the above skills and concepts, since these will not appear neither in the Practical, nor in the Theoretical Exam set.*

# Theoretical problems

## Problem 1. Brayton cycle

Students have made a device capable to operate in a mode that is close to the ideal Brayton cycle. This thermodynamic cycle has once been proposed for development of internal combustion engines. The device consists of a cylinder with 1 mole of helium fitted with a computer-controlled movable piston. A Peltier element which can heat or cool the gas is mounted in the cylinder wall. The device can operate in the following modes: 1) reversible adiabatic expansion or compression, 2) reversible isobaric cooling or heating.

Through a number of cooling and compression steps, helium is going from the initial state with the pressure of 1 bar and the temperature of 298 K into the final state with the pressure of 8 bar and the temperature of 298 K. (The total number of cooling and compression stages can be from two up to infinity).

1. What is the minimum work that should be done on the gas for this? Compare this value to the work during a reversible isothermal compression.
2. What is the maximum work that can be done on the gas in this process?
3. Let the process be accomplished in three steps. At each step helium is first cooled and then compressed. At the end of each step the pressure increases twice and the temperature returns to the value of 298 K. What is the total heat removed from the gas by a Peltier element?

Once the gas is compressed, it is returned to the initial state (1 bar and 298 K) in two stages (heating and expansion).

4. What is the range of possible values of the formal efficiency $\eta$ for the resulting cycle? $\eta$ is the ratio of the useful work done by the gas to the amount of heat given to the gas during the heating stage.
5. In one of the experiments, the gas has been compressed from 1 bar and 298 K to 8 bar and 298 K in several steps (like in question 3). At the end of each step the pressure is increased by $x$ times and the temperature returns to 298 K. Then helium has been returned to the initial state in two stages – heating and expansion. Theoretical value of $\eta$ for this cycle is 0.379. How many steps were used?

In fact, Peltier elements also consume electric energy during the cooling stage. Assume that they consume as much energy as is removed from the gas.

6. What is the maximum possible efficiency of the considered cycle, taking into account energy consumption during cooling?

*Hint*: in reversible adiabatic process for helium $pV^{5/3} = const$. Isochoric molar heat capacity of helium is $3/2R$.

## Problem 2. Liquefied natural gas

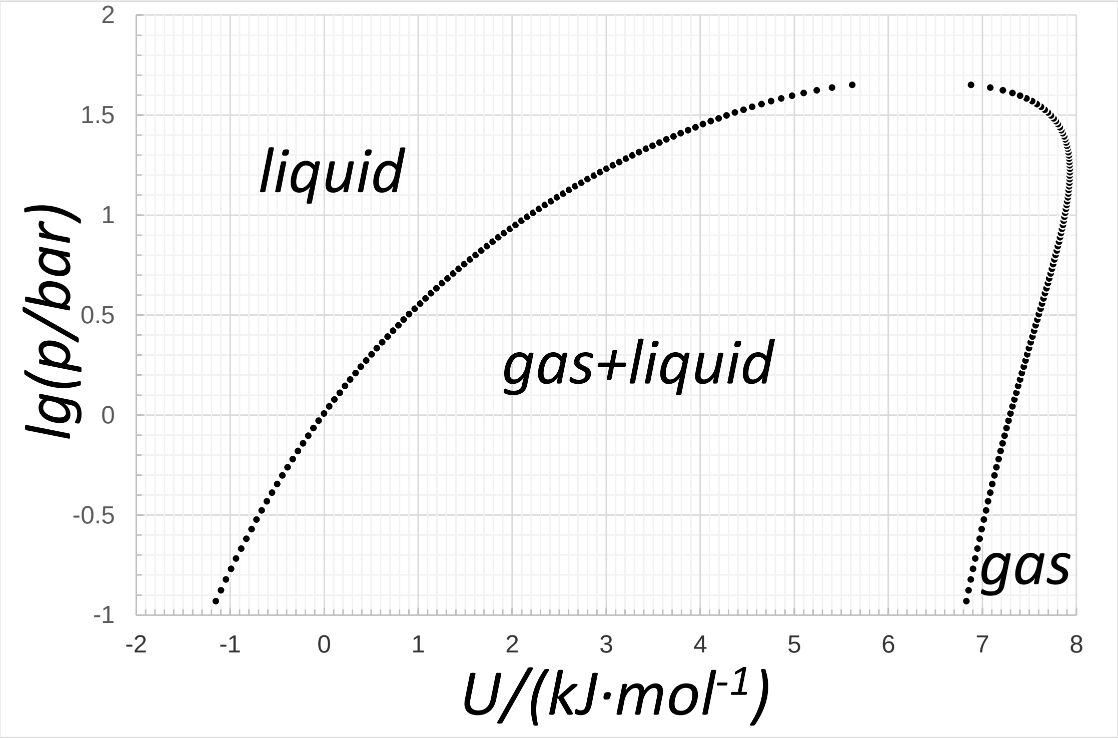
Liquefied natural gas (LNG) is being produced in the world in increasing amounts. It has a high energy density in comparison with the compressed natural gas, so that liquefaction is advantageous for transportation over long distances, especially by sea. The main component of LNG (> 95%) is methane. The dependence of the boiling point of methane on pressure is well described by the empirical equation:

$$\log (p/\text{bar}) = 3.99 - 443 / (T/\text{K} - 0.49)$$

1. What is the boiling point of methane at atmospheric pressure?

A typical cryogenic tank for marine transportation of the LNG has a volume of 40 000 $m^3$, in which it is stored at –159 °C. This tank has no external cooling, and the pressure inside it is kept constant. Initially the tank is fully loaded with 16 800 tons of liquid methane, but during the sailing time it partially evaporates. The evaporated gas can be used as a fuel in the engine of the marine vessel.

2. Estimate how many times larger is the energy density per unit volume of liquefied methane than that of gaseous methane in cylinders under 300 bar pressure at room temperature (298 K). (The compressibility factor of methane at these conditions is close to 1, and thus the ideal gas law can be applied.)

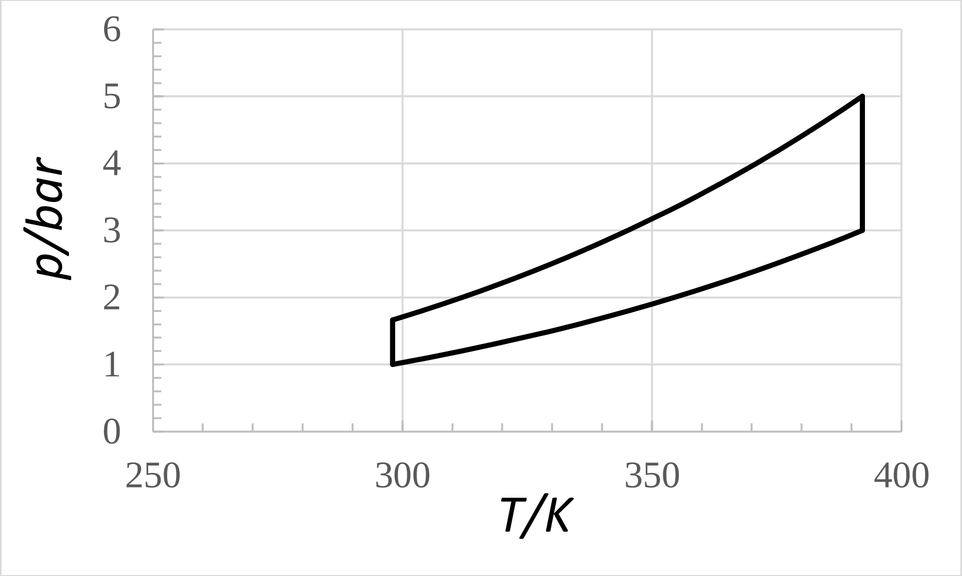


A phase diagram of methane given above is plotted in the coordinates 'logarithm of pressure in bars (log *p*) – internal energy (*U*)'. It is based on the experimental data [Setzmann and Wagner, 1991]. The area encircled by black dots (data points) corresponds to equilibrium coexistence of liquid and gaseous methane, while out of it methane is either completely liquid or completely gaseous. Using the diagram, answer the following questions:

3. What is the enthalpy of vaporization of methane under conditions of its transportation?
4. What percent of methane will evaporate after 15 days of sailing, given that the total heat leakage through the cryogenic tank is 50 kW?
5. For long term storage of LNG, it was suggested not to discharge evaporating methane but to seal the tank. A pilot experiment has been conducted with the same tank initially filled with liquid methane (at temperature –159 °C) up to exactly a third of its volume. After 9 months of storage, the pressure inside the tank grew up to 16.4 bar. Which part of methane has evaporated inside the tank? Assume that the heat leakage is the same as in the previous question.
6. What can be the maximum temperature of the liquefied methane? What would be the pressure in the reservoir containing it?

## Problem 3. Carnot cycle

In the following graph, a reversible Carnot cycle for an ideal gas is shown in «pressure-temperature» coordinates. A cycle consists of two isotherms and two adiabates.



Using this graph, calculate the following magnitudes or show that it is impossible:

1. The useful work of the cycle.
2. The efficiency η of the cycle.
3. The isochoric molar heat capacity of a gas.
4. The number of atoms in the molecule of a gas.

*Hint*: in reversible adiabatic process for an ideal gas, $pV^{(1+R/C_V)} = \text{const}$ where $C_V$ is the isochoric molar heat capacity.

## Problem 4. Quasi-equilibrium model

Equilibrium constants are often included into the rate equations for complex chemical reactions. For some rapid reversible steps the ratio of concentration of products to concentration of reactants is assumed to be equal to equilibrium constant, though reaction as a whole still proceeds and chemical equilibrium is not attained. This is *quasi-equilibrium approximation*. The concept of quasi-equilibrium makes rate equations much simpler which is vitally important for complex reactions.

I. Consider kinetics of a complex reaction

$$A + B \xrightarrow{k_{\text{eff}}} C + D$$

The following mechanism was proposed

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AB \xrightarrow{k_2} AB^* \xrightarrow{k_3} C + D$$

The rates of the forward and reverse reaction of the first step are almost equal,

$$r_1 \approx r_{-1}$$

i.e., quasi-equilibrium is reached.

1. Calculate $k_{\text{eff}}$, if $k_1 / k_{-1} = 10\ \text{M}^{-1}$, $k_2 = 20\ \text{s}^{-1}$.

Metallic platinum loses its mass interacting with the flow of atomic fluorine at $T$ = 900 K. Partial pressure of F in the incident flow near the surface is $10^{-5}$ bar, see Fig.1.

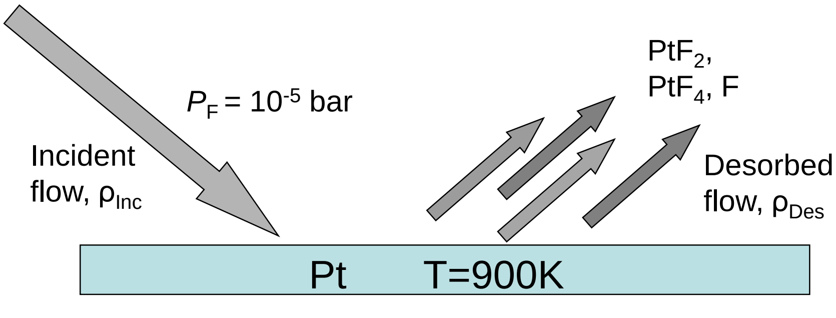


Fig. 1. Gasification of Pt by a flow of atomic fluorine

No solid products of interaction of Pt with F were found on the surface. Gaseous species $PtF_4$ и $PtF_2$ were detected in the flow desorbed from the surface. The ratio $\frac{p^2_{PtF_2}}{p_{PtF_4}}$ was equal to $10^{-4}$ bar and did not vary with the change of the incident atomic fluorine flow.

Use the data in the Table to answer the following questions:

2.1. Find the maximum partial pressure of molecular fluorine near the platinum surface under the given experimental conditions. Assume first that gasification does not proceed.

2.2. Why is the ratio $\frac{p^2_{PtF_2}}{p_{PtF_4}} = 10^{-4}$ bar constant near the surface?

2.3. Make the necessary assumptions and estimate the partial pressure of atomic fluorine in the desorbed flow.

2.4. Put forward the quasi-equilibrium model to account for the rate of gasification of Pt with atomic fluorine,

$$r_{Pt} = \frac{dn_{Pt}}{dt} \; \{\text{mol of Pt / Pt surface area / time}\}$$

Make use of the dimensionless *equilibration probability*,α, which is equal to the fraction of incident fluorine flow involved in gasification. Consider other steps of gasification as quasi-equilibrium. The flow $\rho_i$ of each gaseous species $i$ is related to its partial pressure $p_i$ as

$$\rho_i = c\frac{p_i}{(m_i)^{1/2}}$$

where $m_i$ is a molecular mass, $c$ is constant.

2.5. Estimate the *equilibration probability* α under the experimental conditions, described in the Table.

2.6. How many grams of Pt will be gasified from 1 cm$^2$ of the Pt surface in 15 minutes, if the incident flow of atomic fluorine is $2\cdot10^{18}$ atoms/cm$^2$/s?

Table

| Reaction | $K_p$ (900 K), bar$^{-1}$ | Gaseous species | $p$(900 K), bar |
|---|---|---|---|
| $2F(g) = F_2(g)$ | $1.7\cdot10^3$ | $PtF_2$ | $2\cdot10^{-6}$ |
| $Pt(s) + 2F(g) = PtF_2(g)$ | $5\cdot10^8$ | $PtF_4$ | $4\cdot10^{-8}$ |

## Problem 5. The Second Law of thermodynamics applied to a chemical reaction

When does chemical reaction proceed spontaneously? The Second Law gives the answer.

Consider *a system*, a chemical reactor in Fig. 1. Pressure $p$ and temperature $T$ inside the reactor are kept constant. There is no transfer of matter into or out of the system.

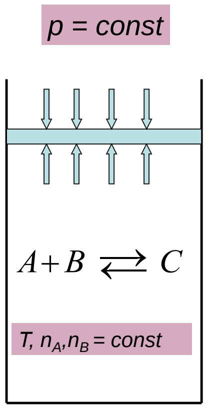


Fig. 1. Chemical reaction inside a reactor

According to the Second Law, every spontaneous process in such a reactor leads to the decrease of the Gibbs free energy, $G_{\text{system}}$, i.e. $\Delta G_{\text{system}} < 0$.

If the chemical reaction, e.g., A + B = C (a), is the only process inside the reactor

$$\begin{aligned} &\Delta G_{\text{System}} = \Delta G_{\text{Reaction}}(a)\Delta\xi(a) \\ &\Delta\xi(a) = \Delta n_C = -\Delta n_A = -\Delta n_B \end{aligned} \qquad (1)$$

where $\Delta G_{\text{Reaction}}$ and $\Delta\xi$ are the Gibbs free energy and *the extent of reaction* (a), respectively, $\Delta n_{\text{A}}$, $\Delta n_{\text{B}}$, $\Delta n_{\text{C}}$ are changes of the numbers of moles of A, B, C in the reaction (a).

1.1. Relate $\Delta\xi$ to $\Delta n_i$ of reactants and products of the following reaction

$$\frac{1}{6}\text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O} \qquad \text{(b)}$$

1.2. Prove that, according to the Second Law, $\Delta G_{\text{Reaction}} < 0$ for any single spontaneous chemical reaction in the reactor (Fig.1).

2. The Gibbs free energy of the chemical reaction (a) is:

$$\Delta G_{\text{Reaction}} = \Delta G^{\circ}_{\text{Reaction}} + RT\ln\frac{[\text{C}]}{[\text{A}][\text{B}]} < 0 \qquad (2)$$

where [C], [A], [B] are time variant concentrations inside the reactor in the course of spontaneous reaction. Using the law of mass action, relate $\Delta G_{\text{Reaction}}$ to the ratio of rates of forward $r_1$ and reverse $r_{-1}$ reaction (a). Consider both reactions as elementary ones.

3.1. Derive the expression (2) for $\Delta G_{\text{reaction}}$ of the following chemical transformations:

(a') $H_2(g) + Br_2(g) = 2HBr(g)$

(a'') $H(g) + Br_2(g) = Br(g) + HBr(g)$

(a''') $CaCO_3(s) = CaO(s) + CO_2(g)$

3.2. For which of these reactions the relation between $\Delta G_{\text{Reaction}}$ and $r_1$, $r_{-1}$ derived in Problem 2 is valid?

4. The *observed rate* of chemical reaction, $r_{\text{obs}}$, is defined as $r_{\text{obs}} = r_1 - r_{-1}$.

Let reaction (a) proceed spontaneously. At a certain moment

$r_{\text{obs}} / r_1 = 0.5$, [A] = 0.5 M, [B] = 1 M, [C] = 2 M.

Find the equilibrium constant, $K$, of the reaction (a), T=298K.

5. Plot $r_{\text{obs}}$ as a function of

a) $r_1$, at $\Delta G_{\text{Reaction}} = \text{const}$;

b) $r_1$, at $r_{-1} = \text{const}$;

c) $\Delta G_{\text{Reaction}}$, at $r_1 = \text{const}$.

6. Which thermodynamic and kinetic parameters of a chemical reaction are influenced by a catalyst? Put plus (+) into the cell of the Table if a catalyst may cause a change of the corresponding parameter, (–) otherwise.

Table

| $r$ | $r_1$ | $r_1/r_{-1}$ | $\Delta G_{\text{Reaction}}$ | $r/r_1$ |
|---|---|---|---|---|
| | | | | |

## Problem 6. Catalytic transformation of a single molecule on a single nanoparticle

Use of catalytic nanoparticles opens new ways to study and to understand catalysis. The exiting measurements were performed at Cornell University (NY, USA). The researchers observed the catalytic transformation of single molecules on the surface of a spherical nanoparticle ($d$ = 6 nm) formed by Au atoms.

The experimental design is shown in Fig.1. The dissolved A was transformed into dissolved B in the presence of Au nanoparticles, adsorbed on the glass slide.

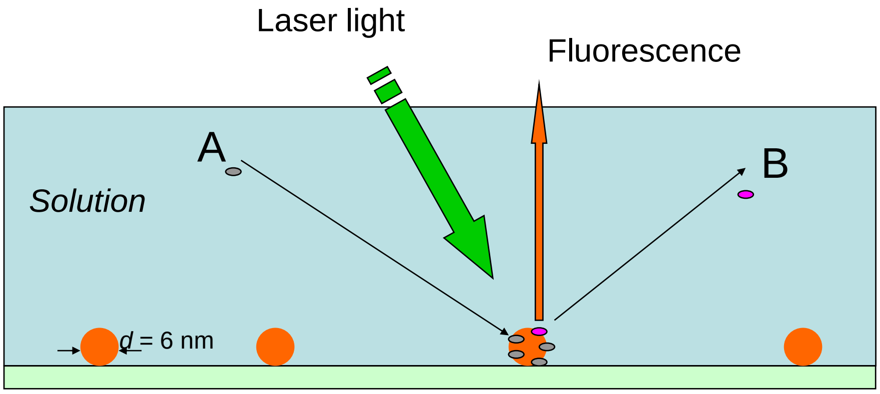


Fig.1. The experimental design

The reaction product B is a fluorescent molecule while the reagent A is not. Continuous laser light producing fluorescence was focused within a small surface area containing a single Au nanoparticle. The time dependence of fluorescence on the wavelength characteristic for B, adsorbed on the Au nanoparticle is shown in Fig.2.

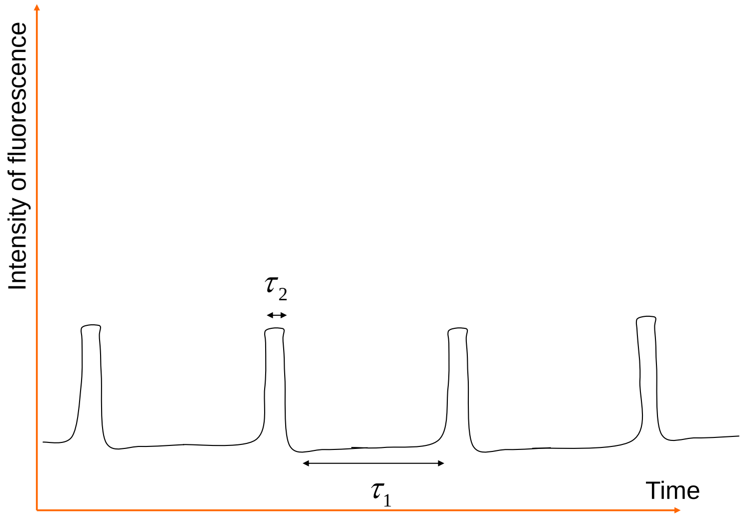


Fig. 2. Time dependence of intensity of fluorescence coming from a single cluster

The fluorescence of B in the solution could not be detected under the experimental conditions. The same intensity of fluorescence was observed periodically for the time intervals $\tau_2$. The fluorescence disappeared during the time intervals $\tau_1$ between the peaks (see Fig.2). The researchers have performed their measurements for long periods of time and for many different single Au nanoparticles. As a result the averaged values of $[\tau_1]$ and $[\tau_2]$ were obtained.

Answer the following questions about this experiment and the conclusions made by its authors.

1. Estimate the number of the Au atoms in a single nanoparticle if it's density is equal the bulk density of Au, 19.32 g/cm$^3$. What fraction of Au atoms is involved in the catalysis if catalytically active is the surface layer with the depth equal to two atomic diameters of Au ($d_{\mathrm{Au}}$ = 0.350 nm)?

2. The resolution of the instruments made it possible to measure the fluorescence emitted from 1 μm$^2$ area. The number density of Au nanoparticles on the glass slide was 0.035 particle·μm$^{-2}$. What was the probability (%) of observing fluorescence from a single Au nanoparticle?

3. The authors claimed that each peak in Fig. 2 corresponds to the fluorescence of a single molecule B adsorbed on Au nanoparticle. What was the main argument of the authors?

Consider adsorption of A on Au nanoparticles to be a fast reversible process. Let *m* catalytic sites exist on the surface of a single nanoparticle. The fraction of catalytic sites occupied by molecules A, is equal to

$$\theta_{\mathrm{A}} = \frac{K_{\mathrm{ads}}[\mathrm{A}]}{1 + K_{\mathrm{ads}}[\mathrm{A}]}$$

4. Relate $[\tau_1]$ and $[\tau_2]$ to the rates of catalytic production/desorption of a single molecule B on/from a single Au nanoparticles.
5. Plot $[\tau_1]^{-1}$ and $[\tau_2]^{-1}$ as a function of concentration of A in the solution.
6. How will $[\tau_1]^{-1}$ and $[\tau_2]^{-1}$ change with the increase of nanoparticle diameter from 6 to 12 nm?

## Problem 7. Esterification of a dicarboxylic acid

Dicarboxylic acid is mixed with ethanol in a molar ratio 1 : $X$ ($X > 1$) in the presence of a catalyzer. The system reached equilibrium. The equilibrium constants for the formation of monoester from an acid and ethanol and that for the formation of diester from monoester and ethanol are the same: $K_1 = K_2 = 20$.

1. At what $X$ the yield of monoester is maximal?
2. Find the maximum yield.
3. Answer the questions 1 and 2 at arbitrary $K_1$ and $K_2$.

## Problem 8. Three elements

Three elements – **A**, **B**, and **C** form three binary compounds. Each element has the same valence in these compounds. The mass fraction of **A** in the compound with **B** is 75%, and the mass fraction of **B** in the compound with **C** is 7,8%. Determine the mass fraction of **C** in the compound with **A** and find all the elements.

## Problem 9. Simple experiments with copper(II) chloride

Copper(II) chloride forms brown crystals soluble in water.

1. The color of the solutions depends on concentration. Explain this fact.
2. Draw the structure of at least three copper containing species that can be present in the solution.
3. To the aliquots of the copper chloride(II) solution in the test tubes (a) zinc powder and the solutions of (b) sodium iodide, (c) sodium nitrate, (d) sodium sulfide were added dropwise. What changes happen if they are? Provide equations. In what cases copper is completely or partly reduced?
4. Suggest a synthetic route to copper chloride(II) starting from copper(II) sulfate aqueous solution.

## Problem 10. An element typical for Azerbaijan mud volcanoes expelled water

Azerbaijan is famous for mud volcanoes. About 400 active mud volcanoes are present in this region, both onshore and offshore - more than half the total throughout the world. Mud volcanoes come in a variety of shapes and sizes, but those most common in Azerbaijan have several small cones, or vents, up to about four meters in height. Mud volcanic eruptions in Azerbaijan normally last for less than a few hours, and are characterized by vigorous extrusion of mud breccias, hydrocarbon gases, and waters. Bakhar is a mud volcano with a high seep activity in the dormant period. The reservoirs formed by the volcanoes' activity contain the expelled waters. Those of Bakhar volcano have a composition with Na and Cl as dominant ions. The analyzed waters are enriched in metals and in an element **X** that causes flame coloration. Its' concentration in seeping water of 250 ppm represents a 55-fold enrichment in comparison to seawater. Being concentrated, the expelled water gives the white crystals, among them the compound **Y**, one of the main sources of **X**. The common oxide of **X** contains 31.0% of the element, whereas the compound **Y** – 11.3% only.

1. What are the element **X** and the compound **Y**?
2. Calculate the mass of **Y** that can be obtained from 1 L of expelled water.
3. The mass loss under gentle heating of **Y** is 37.8%. Draw a possible structure of anion in **Y**, knowing that it contains two different types of **X** atoms (three- and four-coordinated).

## Problem 11. The Prussian blue

The Prussian blue is a component of black and bluish inks for printing. The precipitate formed upon the dropwise addition of potassium ferrocyanide to the ferric chloride solution contains 34.9% (mass) of iron.

1. Give a formulae of the precipitate and write the chemical equation. (Use 55.8 for atomic mass of iron).
2. Using the crystal field theory show the *d*-orbital splitting pattern for all Fe atoms in the Prussian blue.
3. What causes the intense color of the pigment?
4. What product initially forms from potassium ferrocyanide and ferric chloride solution in the inverse-mixing-order route? Give the equation.

## Problem 12. Substitution in square planar complexes

For platinum (II) and (IV) a large number of complexes is known. For most of them the isomers were isolated.

1. Explain what is the reason for the existence of different isomers and draw the structures for all $Pt(NH_3)_2Cl_2Br_2$ species.
2. The reaction of thiourea with $[Pt(amine)_2Cl_2]$ isomers results in different products. Explain this fact and give the reaction scheme.
3. Give an example of $PtX(amine)Cl_2$ isomeric complexes reacting with thiourea with the formation of one and the same product.
4. Explain why do the reactions of $[PtCl_4]^{2-}$ and $[AuCl_4]^{-}$ with iodide result in different products.

## Problem 13. Redox equilibria in aqueous solutions

Using the Latimer diagrams (pH = 0):

$$[Au(H_2O)_6]^{3+} \xrightarrow{1.401\ V} [Au(H_2O)_6]^{+} \xrightarrow{1.692\ V} Au$$

$$[AuCl_4]^{-} \xrightarrow{0.926\ V} [AuCl_2]^{-} \xrightarrow{1.154\ V} Au$$

$$[AuBr_4]^{-} \xrightarrow{0.810\ V} [AuBr_2]^{-} \xrightarrow{0.960\ V} Au$$

answer the following questions:

1. Is Au(I) stable to disproportionation in aqueous solutions in the absence and in the presence of chloride and bromide ions? Support your answer by calculations.

2. Is it possible to oxidize gold powder by pure oxygen ($p(O_2)$ = 1 atm, $E^\circ_{O_2,H^+/H_2O}$ = 1.229 V) in the aqueous solution in the presence of chloride ions?

3. At what pH interval is it possible to oxidize gold powder by hydrogen peroxide ($E^\circ_{H_2O_2,H^+/H_2O}$ = 1.763 V) in the presence of chloride-ions? Assume that the activities of all ions in the solution except $H^+$ are 1.

## Problem 14. Determination of acetylsalicylic acid purity

Aspirin – acetylsalicylic acid – is used to treat pain and to reduce fever, at low doses, to prevent heart attacks, strokes, and blood clot formation. It is one of the most widely used medications in the world, with an estimated 80 billion of tablets of it being consumed each year. Aspirin tablets can be contaminated with salicylic acid – the reagent for synthesis of acetylsalicylic acid. The content of salicylic acid is controlled in accordance with national pharmacopoeias. It must not exceed 0.1–0.3 %. Redox titration using bromine as an oxidation agent is one of the possible techniques to determine salicylic acid in aspirin.

4.4035 g portion of powdered aspirin tablets was dissolved in 250.0 mL volumetric flask. For redox titration, reagent (bromine) was generated *in situ* (in the same titration flask). Bromide-bromate mixture was made of potassium bromide (0.5950 g) and potassium bromate (0.1670 g) in 100 mL of water. 25.00 mL aliquot was transferred to a titration flask, also sulfuric acid and 20.00 mL of the above mixture was added. The volume was made up to 50.0 mL with water. Flask was corked up and stirred for 10 min.

1. Write the balanced equations of the reactions described.
2. At what maximal pH bromide will react with bromate? The standard redox potentials are:

$$E^{\circ}_{2\mathrm{BrO}_3^-,\mathrm{H}^+/\mathrm{Br}_2} = 1.52\ \mathrm{V},\ E^{\circ}_{\mathrm{Br}_2/2\mathrm{Br}^-} = 1.09\ \mathrm{V}.$$

Solution obtained after filtration of the reaction mixture was titrated against a 0.02015 M solution of $NaAsO_2$ and a mean titre of 9.93 mL was obtained.

3. Write the balanced equations of the reactions described.
4. Calculate the percentage of salicylic acid in tablets by mass.
5. Do the tablets meet the regulatory requirements?

## Problem 15. Chemical dosimeter

Chemical dosimeters are widely used for remote determination of high-level doses of radiation. Most common type of dosimeter is a ferrous-ferric sulfate dosimeter. When ionizing radiation passes through the solution, lots of products (radicals, ions, and molecules) are formed. Most of them can oxidize $Fe^{2+}$ into $Fe^{3+}$.

1.1. Choose the electronic configuration of $Fe^{2+}$ cation:

A) $3d^6 4s^0$  B) $3d^5 4s^0$  C) $3d^4 4s^2$  D) $3d^5 4s^1$

1.2. Write the balanced equations for oxidation of $Fe^{2+}$ with the following particles:

A) $H_2O^+$  B) $OH\cdot$  C) $H_2O_2$

The resulting solution is then titrated and the amounts of Fe(II) and Fe(III) are calculated. For these purpose, permanganatometric and iodometric titrations can be used.

2.1. Write down the balanced redox equation for the reaction between:

a) iron(II) sulfate and potassium permanganate in acidic media;

b) iron(III) sulfate and potassium iodide;

c) sodium thiosulfate and iodine.

2.2. Calculate concentrations of cations $Fe^{2+}$ and/or $Fe^{3+}$in each of the following cases:

a) To titrate 20.00 mL of Fe(II) solution, 12.30 mL of 0.1000 M potassium permanganate solution was spent.

b) 1.00 mL of solution containing Fe(III) was diluted up to 20.00 mL, to resulted solution an excess of potassium iodide solution was then added. The iodine formed was titrated with 4.60 mL sodium thiosulfate solution (0.0888 M).

c) An aliquot 5.00 mL was titrated with 0.1000 M potassium permanganate solution, the average volume being equal 7.15 mL. After that, an excess of potassium iodine solution was added to the flask. Titration of the resulting solution required 13.70 mL of 0.4150 M sodium thiosulfate.

Frequently, chemical dosimeters are used for measuring doses near nuclear reactors where large amounts of various radionuclides are accumulated.

3.1. Match mother and daughter radionuclide, indicate the type of decay (α or $\beta^-$) in each case:

Mother radionuclide:

a) $^{60}Co$ b) $^{90}Sr$ c) $^{226}Ra$ d) $^{137}Cs$ e) $^{212}Po$

Daughter radionuclide:

1) $^{90}Zr$ 2) $^{137}Xe$ 3) $^{214}Rn$ 4) $^{222}Rn$ 5)$^{137}Ba$ 6) $^{60}Ni$ 7) $^{60}Fe$ 8) $^{208}Pb$ 9) $^{90}Y$

Radioactivity $A$ is directly proportional to the number of particles $N$ of a substance ($A = \lambda N$), where $\lambda$ is the decay constant related to half-life by the equation $\lambda = \ln 2 / T_{1/2}$. Radioactivity is measured in becquerel (symbol Bq) units: 1 Bq is one decay per second.

3.2. Using values of half-lives, calculate (in GBq) radioactivity of samples containing:

a) 1.3141 g $^{226}RaCl_2$

b) 1.0 mg $^{90}Sr(NO_3)_2$ and 0.5 mg $^{137}CsNO_3$

$T_{1/2}(^{226}Ra)$ = 1612 years, $T_{1/2}(^{90}Sr)$ = 29 years, $T_{1/2}(^{137}Cs)$ = 30 years.

3.3. Explain why $^{226}Ra$ is dangerous for humans?

3.4. It is well known that radionuclide $^{64}Cu$ decays to $^{64}Ni$ (this is attributed to electron capture, process when nuclei absorb inner electron) and $^{64}Zn$ ($\beta^-$ decay). Half-life for electron capture is 20.8 hours, for $\beta^-$ decay is 32.6 hours.

a) Calculate the average half-life of $^{64}$Cu.

b) How much time is required for radioactivity of a $^{64}$Cu sample to decrease by 10 times?

## Problem 16. Determination of water in oil

Oil is the most important mineral for Azerbaijan. From chemist's point of view it is a mixture of a great number of substances of different nature – both organic and inorganic. At all stages of petroleum refining, it is important to control the content of inorganic impurities, including water, in oil. One of the popular chemical methods for the determination of water in various organic matrices is named Karl Fischer titration. The method is based on the reaction described by R. Bunsen:

$$I_2 + SO_2 + H_2O \rightarrow HI + H_2SO_4$$

1.1. Indicate the oxidant and reductant in the reaction.

1.2. Put the coefficients in this reaction. Sum of the least integer coefficients is

A) 14 B) 9 C) 7 D) 10

Reagent which was proposed by the German chemist Karl Fischer is a mixture of pyridine, sulfur dioxide, iodine, and methanol. In this case, the following reactions occur during titration:

$$SO_2 + CH_3OH + H_2O + I_2 \rightarrow 2HI + CH_3OSO_3H$$

$$Py + HI \rightarrow PyH^+I^-$$

$$Py + CH_3OSO_3H \rightarrow PyH^+\ CH_3OSO_3^-$$

2.1. What is the role of pyridine in the composition of Fisher reagent?

2.2. What substance(s) could be used instead of pyridine?

A) Imidazole B) Pyrrol C) Hydrazine D) Butylamine

2.3. However, the above composition of titrant may lead to various side reactions. Write the possible reactions taking place between the components of the Fisher reagent and the following substances:

a) Aldehydes, RC(O)H

b) Ketones, RC(O)R

c) Mercaptans, RSH

d) Organic peroxides, ROOH

Indicate if an overestimation or underestimation of the water content is observed in each case.

3.1. Fischer reagent is to be standardized prior to use, i.e. it is necessary to set amount of water corresponding to one volume of a titrant. The reagent was prepared by the following procedure: 49 g of iodine were dissolved in 158 g of pyridine, then 38.5 g of liquid sulfur dioxide was introduced while cooling. Thereafter, mixture was diluted up with methanol to 1 liter.

a) Using the above data, calculate the theoretical titre of the Fischer reagent (in mg/mL).

b) Calculate the practical titre (in mg/mL) of Fischer reagent, if to reach the endpoint for the titration of 5 g of a mixture of methanol and water (water content of 1% by volume), 19 mL of titrant was spent.

c) Why do the results obtained differ?

d) Calculate the water content (in %) in the sample of sour oil, if the content of mercaptan in sulfur recalculation is 1 wt.% and titration of 1.00-g sample of sour oil dissolved in methanol required 7.5 mL of titrant.

3.2. The modern version of water determination in different samples is coulometric Karl Fischer titration. During the titration iodine is generated electrochemically and the water content is defined as the total amount of current passing through the coulometer. Titration is stopped when the generation of iodide stops in the system.

a) Using Faraday's law, calculate the mass fraction of water in the oil sample (10.0 g), if 375.3 Coulombs passed through a coulometer.

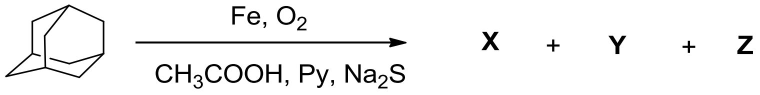
b) 1.000 g portion of sugar was dissolved in 15 mL of methanol and chloroform mixture. Calculate the molar and mass fractions of water and sugar, if for a coulometric titration of sugar a total charge of 567.2 Coulombs was required, while 31.1 Coulombs were required to titrate solvent.

## Problem 17. Oxidation and inspiration

> ***With every breath, I breathe in so much of inspiration.***
> ***I feel if there is one thing as free and as important as oxygen, it's inspiration.***
> ***(Sharad Sagar)***

Oxygen is not only chemical element but also the essential element of life. Its most stable form, dioxygen, $O_2$, constitutes 20.8% of the volume of the Earth's atmosphere. All forms of oxygen are able to oxidize various compounds, especially organic ones. The type of oxygen-containing functionalities in organic compounds could be efficiently determined by IR spectroscopy. Thus, C=O groups are characterized by intense absorption at 1750-1660 $cm^{-1}$ and O–H group is characterized by absorption in the region of 3600-3000 $cm^{-1}$.

The most typical oxidation of saturated hydrocarbons with $O_2$ is the burning process. However, some reaction have been developed producing various oxygenated products. For example, Gif reaction (which received this name in honor of Gif-sur-Yvette where Prof. Derek Barton was working when he disclosed this transformation) represents the oxidation of saturated hydrocarbons with air oxygen at room temperature. Thus, the oxidation of adamantane leads to three products:



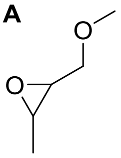
Products **X** and **Y** are isomers. The compound **Y** can be easily transformed to **Z**. IR spectra of the compounds **X** and **Y** contain a band around 3300 $cm^{-1}$, while IR spectrum of compound **Z** contains band 1720 $cm^{-1}$.

1. Write down the structural formulae of compounds **X**–**Z**.

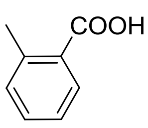
Without catalysts $O_2$ has, fortunately, very low reactivity. Otherwise, all living organisms should be oxidized by air. A wide variety of oxidizing reagents have been developed for selective or undiscriminating oxidation of various functional groups in high yield. Below 7 organic molecules are given. They were synthesized by oxidation with 7 indicated reagents.

**Products**

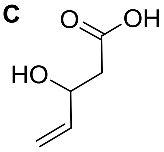
**A**



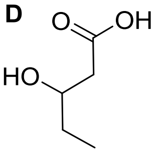
**B**



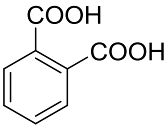
**C**



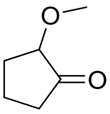
**D**



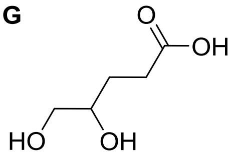
**E**



**F**



**G**



**Oxidants**

**a** $Me_2SO + (COCl)_2$, then $Et_3N$ (Swern oxidation)

**b** $CrO_3 + H_2SO_4$; acetone (Jones oxidation)

**c** $SeO_2$

**d** $KMnO_4$, 20 °C, pH 7-7.5

**e** $KMnO_4$, $H_2SO_4$, Δ

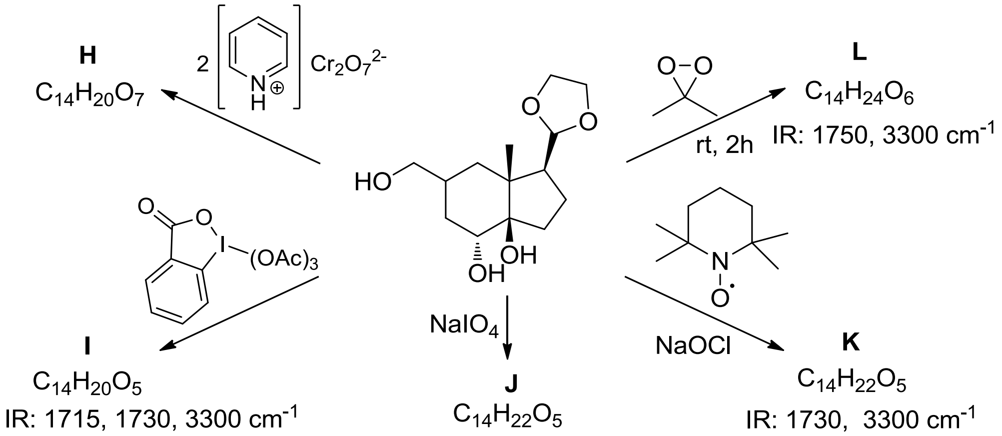
**f** *meta*-chloroperbenzoic acid (mCPBA)

**g** $Ag(NH_3)_2OH$, then $H^+$

These oxidation reactions proceed without C–C cleavage.

2. Put the correspondence between the products and the oxidants and determine the starting organic compounds.

Examples of the chemoselective oxidation of the same substrate with different oxidants affording different reaction products are given below.



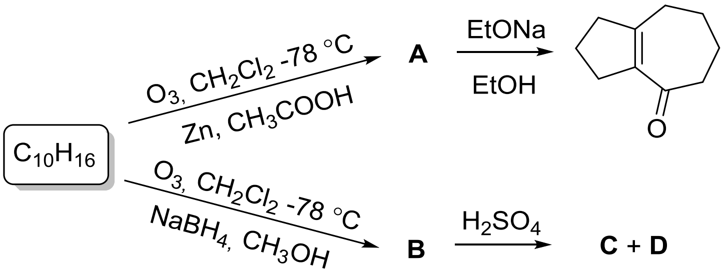
Compounds **I**, **J**, and **K** react with $Ag(NH_3)_2OH$ solution producing the metallic silver precipitation. Compound **H** could be formed by oxidation of **J**. The treatment of 1.44 g of **L** with metallic sodium produces 0.224 L ($P$ = 1 atm, $T$ = 273 K) of hydrogen gas.

3. Write down the structural formulae of compounds **H**–**L**.

## Problem 18. Essential ozone

Until NMR became the main method for the determination of structures of organic molecules, the ozonolysis reaction, disclosed by Schönbein in 1840, was intensively used for the ascertainment of the unsaturated bond(s) position(s) in molecules. Imagine that you are in a similar situation (but with modern reagents). You have found that some hydrocarbon $C_{10}H_{16}$ participates in the transformations given in Scheme 1.

Scheme 1

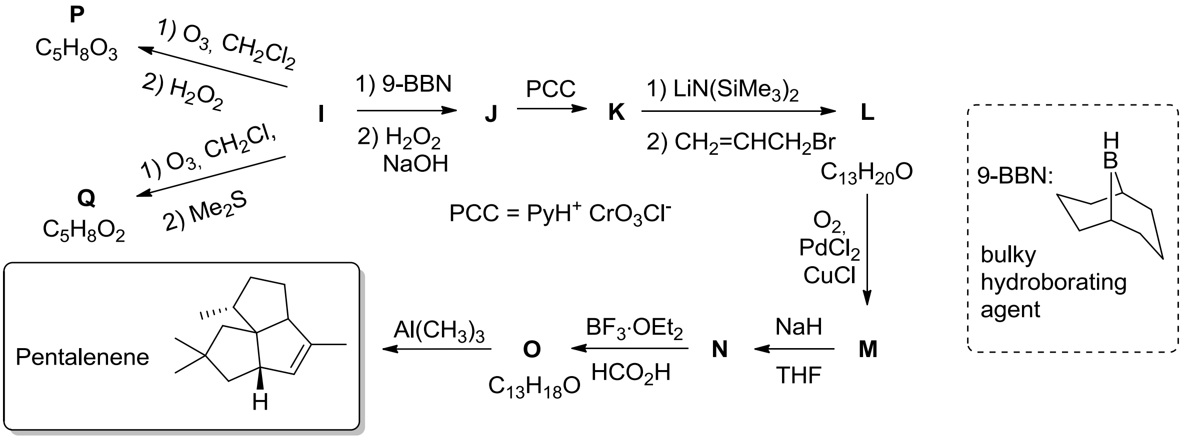


1. Determine the structural formulae of the hydrocarbon $C_{10}H_{16}$ and the molecules **A**–**D** accounting for the fact that compounds **C** and **D** are isomers of the initial hydrocarbon; the ozonolysis of **C** followed by the treatment of the reaction mixture with alkaline $H_2O_2$ produces a single product while the same transformations of **D** afford two compounds.

Some other hydrocarbon **E** ($\omega_C = 90.6\%$) under ozonolysis (1. $O_3$, $CH_2Cl_2$, –78 °C; 2. $Me_2S$) forms three carbonyl compounds – **F** ($C_2H_2O_2$), **G** ($C_3H_4O_2$), and **H** ($C_4H_6O_2$) in a ratio of 3:2:1. Initial hydrocarbon **E** doesn't decolorize bromine water.

2. Write down the structural formulae of hydrocarbon **E** and products of its ozonolysis **F**–**H**.

Hydrocarbon **I** having center of symmetry was used as an initial material in the total synthesis of *pentalenene* (Scheme 2):

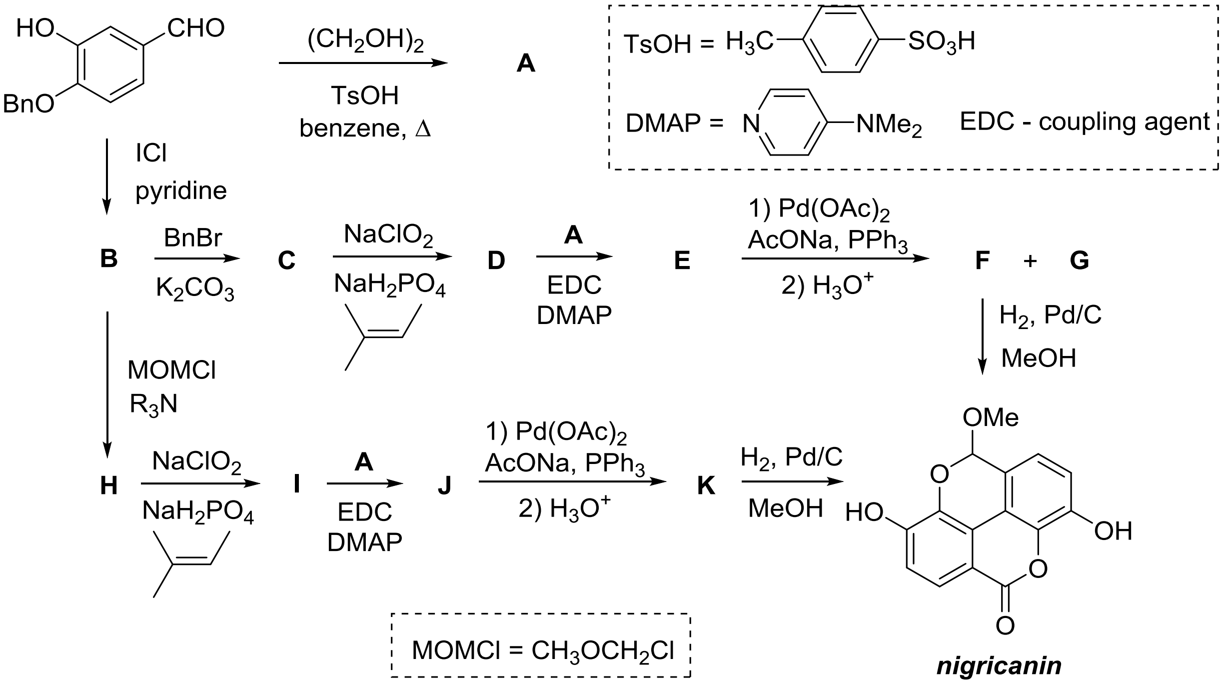


The ozonolysis of hydrocarbon **I** furnishes a single compound **P** or **Q** depending on the treatment of the ozonolysis product. Under treatment with $I_2$ and NaOH, compound **Q** forms a yellow precipitate containing 96.7% of iodine. Under basic conditions compound **Q** is transformed into compound **R** containing 4 types of hydrogen atoms (4 signals in $^1$H NMR spectrum with integral intensity of signals 1:1:2:2). Molecular formula of **R** is $C_5H_6O$. Molecule of compound **N** has bicyclic framework containing **R** as a fragment. Molecule of **O** consists of three rings.

3. Descript the scheme of the synthesis of ***pentalenene***.

## Problem 19. Two in one

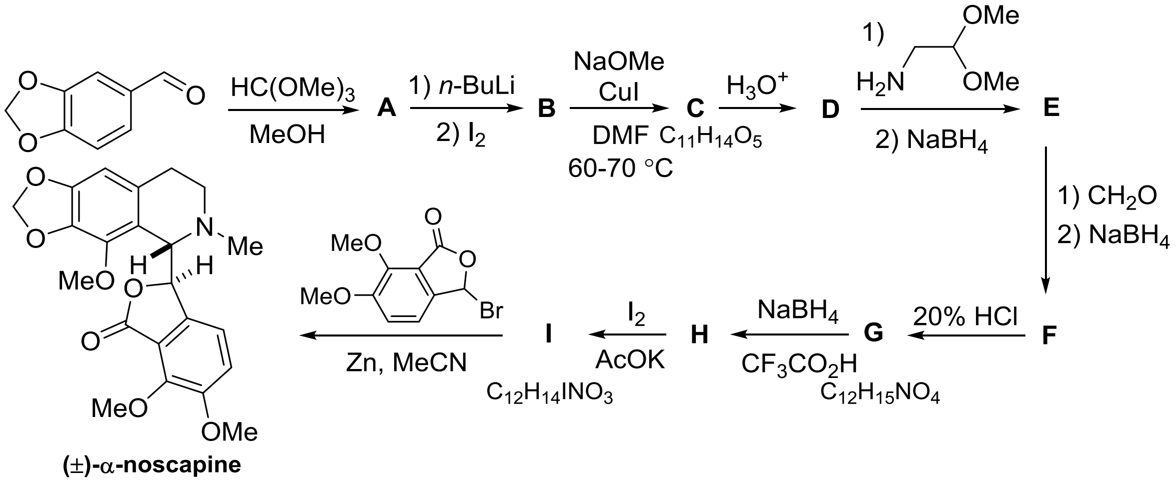
Ellagic acid and its family exhibit antioxidant, anti-cancer, and other types of biological activity. Very recently, the first total synthesis of *nigricanin*, one of the ellagic acid congeners, was described (Scheme 1).



Decipher this scheme. Write down the structural formulae of compounds **A**–**K** accounting for the facts that **F** and **G** are isomers; molecular formulae of **D** and **E** are $C_{21}H_{17}IO_4$ and $C_{37}H_{31}IO_7$, respectively.

## Problem 20. Antitussive "narcotine"

(-)-α-Noscapine is an alkaloid isolated from *Papaver somniferum L.* in 1817 by P. Robiquet which named this compound as "narcotine". This agent demonstrates significant painkilling and antitussive activities. It is also used for treatment of cancer, stroke, anxiety, and so on. Clinically used (-)-α-noscapine is provided through extraction from natural sources or resolution of synthetic racemic compound. There are some syntheses of (±)-α-noscapine. One of them is given in the scheme below.

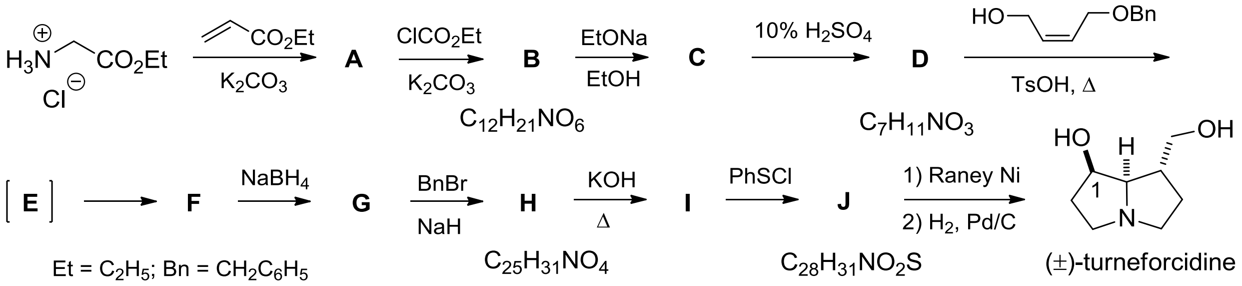


Decipher this scheme. Write down the structural formulae of compounds **A**–**I** if **G** is a tricyclic compound.

## Problem 21. Pyrrolizidine alkaloids

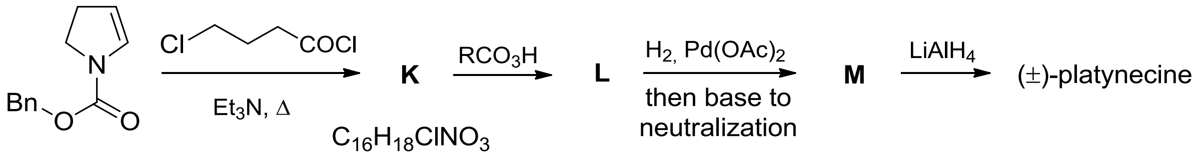
Pyrrolizidine alkaloids and their unnatural analogues occupy the important place in organic chemistry due to a broad variety of physiological activities. Polyhydroxylated pyrrolizidines form a sub-class of these alkaloids, members of which are often referred to as aza-sugars (or imino sugars) and inhibit various glycosidases that can be useful for the treatment of diabetes, influenza, HIV and other diseases. The synthesis of dihydroxypyrrolizidine alkaloid, (±)-turneforcidine, is given in the Scheme 1. In this scheme **E** is an unstable intermediate which spontaneously undergoes the Claisen rearrangement producing **F**.

Scheme 1



Epimer of turneforcidine at C(7) atom, (±)-platynecine, was synthesized by the reaction sequence given in Scheme 2. It is noteworthing that **K** is the product of [2+2]-cycloaddition.

Scheme 2



Decipher these schemes. Write down the structural formulae of compounds **A**–**M** as well as of (±)-platynecine.

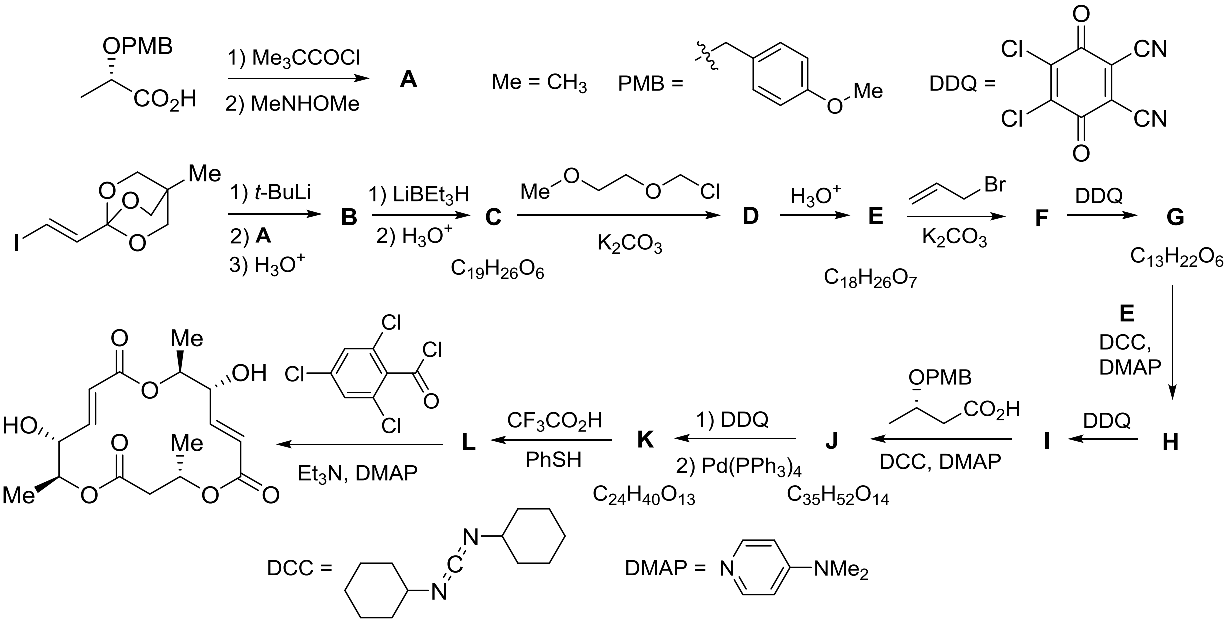
## Problem 22. Delightful odor of truffle

For many people the taste and odor of truffles are so delightful that truffles cost more than their weight in gold. The compound **X** is responsible for the divine smell of the black truffle. The treatment of 0.108 g of compound **X** with the acidified solution of $HgSO_4$ leads to the formation of some precipitate **Z**. The treatment of the formed organic compound **A** with the excess of $Ag(NH_3)_2OH$ afforded 0.432 g of metallic silver. Gas formed as a result of the burning of 0.648 g of compound **X** was divided into two equal parts. One part was passed through the $Ba(OH)_2$ solution, 3.075 g of precipitate was formed. Another part was passed through NaOH solution. After some time the excess of $BaCl_2$ solution was added. It led to the formation of 3.171 g of precipitate.

Write down the structural formulae of compounds **X**, **Z**, **A**. Determine the weight of the precipitate **Z.** Assume that all reactions proceed with 100% yield.

## Problem 23. Synthesis of large rings. The magic or routine work?

The synthesis of large rings is a challenging problem of the synthetic organic chemistry. On the contrary, Nature solves this problem efficiently. Thus, various fungus produce macrolactone polyketides. One of them, Macrosphelide A, attracts attention as potent, orally bioavailable inhibitor of the interaction between cancer and endothelial cells. A number of syntheses of this molecule was reported. One of them was based on the utilization of lactic (2-hydroxypropionic) acid derivative according to Scheme below.



1. Decipher this scheme. Write down the structural formulae of compounds **A-L**.
2. Write down the IUPAC name of compound **E**.

## Problem 24. What Time is it in Baku or Cheating the Death

*One looking at the puddle, sees in her dirt, and another – reflected in her star*

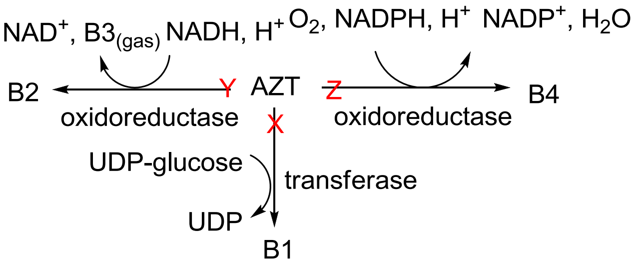
*Immanuel Kant*

People use acronyms for convenience sake. Still, sometimes the meanings are not absolutely unambiguous. Thus, AZT generally standing for Azerbaijan time has acquired an alternative meaning in pharmacology denoting one of the most usable anti-HIV drugs. Nucleoside **A1**, a major component of nucleic acids, was used as a starting material in AZT synthesis. Under complete combustion with subsequent condensation of water **A1** gives a gas undergoing an 11-fold volume decrease when bubbled through the 1 M KOH solution.

$$\mathrm{A1} \xrightarrow[\text{2. } CH_3SO_2Cl,\ Et_3N]{\text{1. } Ph_3CCl} \mathrm{A2} \xrightarrow{NaOH} \mathrm{A3} \xrightarrow[\text{then } H_3O^+]{\mathrm{A4}} \mathrm{AZT}$$

1. What are the building blocks of nucleosides?
2. Deduce the structures of all of **A1** to **A4**. Note that:
   - When arranged in any order the numbers of atoms in **A1** are not described by either arithmetic or geometric progression
   - all the synthetic steps are $S_N$-type reactions
   - **A4** is a binary compound (85.8 % N by mass)
   - O is the heaviest element in both **A3** and AZT
3. How many stereoisomers of AZT do exist?
4. Give the full wording for the pharmaceutical AZT acronym.
5. Propose the mechanism of AZT antiviral action.

Metabolism of AZT is diverse and includes several pathways (X, Y, and Z) shown in the hereunder scheme (all balanced equations). X, the major of these, leads to a higher soluble product **B1** excreted with urine. Y provides the cytotoxic product **B2** with the same number of atoms as that in AZT. Z is found in patients infected with a specific bacteria, the product **B4** retaining the AZT-type activity.



6. Draw the structures of **B1-B4**.

"Dallas Buyers Club", a movie from 2013, received numerous awards including three Oscars. It is based on a true story describing ambiguous results of the first clinical AZT trials. The protagonist suffering from AIDS lacks a positive effect from AZT and switches over to drugs unauthorized by US FDA. One of the latter is based on the substance **D**.

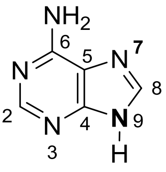
**D** (51.17 % C by weight) and nucleoside **N** (a major component of nucleic acids; 47.57 % C by weight) differ by one atom only. Under complete combustion with subsequent condensation of water, the mixture of **D** and **N** of any composition gives gaseous products undergoing a 7-fold decrease of their total volume when bubbled through the 1 M KOH solution. It was found that **D** imitates AZT with respect to the mechanism of its action.

7. Calculate the number of C and N atoms in **D** without deciphering its structure.
8. Draw the structures of **D** and **N**.
9. Do you support the “Dallas Buyers Club” principal character in his belief that **D** possesses a major clinical advantage over AZT? Comment why physicians used to administer AZT and **D** in a combination.

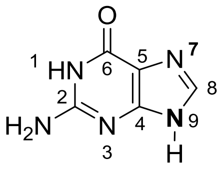
The compound **D** turns out to be a prodrug. Its active metabolite **M** (17.23 % P and 35.62 % O by mass) is produced by a number of manufacturers for research (non-clinical) purposes only.

10. Draw the structure of **M**.

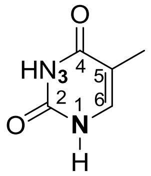
*Note*: *If you feel like watching the above movie, check the film rating system accepted in your country.*



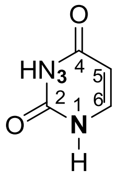
adenine



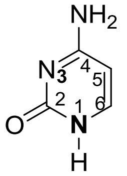
guanine



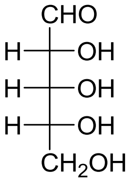
thymine



uracil



cytosine

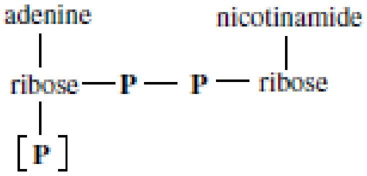


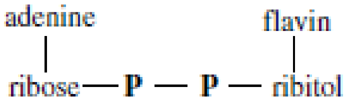
D-ribose

## Problem 25. Number One Enzyme

Enzymes rule over in biochemical processes. Enzyme Commission (EC) numbers have been proposed in order not to be lost in the vast variety of biocatalysts. This is a four-level classification based on the types of enzymatic reactions, each specific reaction being described by four numbers separated by periods. Number 1 of 6 top-level EC numbers is attributed to oxidoreductases, enzymes catalyzing oxidation/reduction reactions (transfer of H and O atoms or electrons from one substance to another). These reactions are of a great importance for both energy transformation and xenobiotic metabolism.

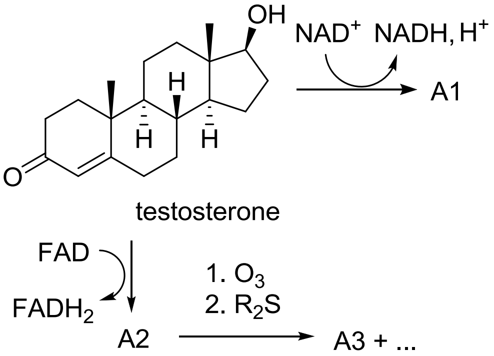
Changes of the oxidation state of a molecule can be achieved in different ways, which makes possible a more detailed classification of oxidoreductases. Many of these require a cofactor or coenzyme. Thus, *dehydrogenases* remove two hydrogen atoms from an organic substrate and pass them over to a suitable acceptor like nicotinamide adenine dinucleotide {phosphate} ($NAD^+$ {$NADP^+$}) or flavin adenine dinucleotide (FAD).





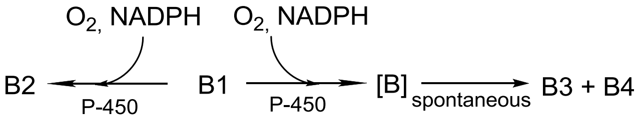
1. Write down the equation of ethanol oxidation involving $NAD^+$ as the coenzyme. Show the changes in the nicotinamide moiety.

2. Sometimes the route of dehydrogenase reaction is determined by the coenzyme/cofactor involved. Predict the structures of **A1**–**A3** in the following scheme if it is known that 1.00 g of **A3** gives 7.52 g of silver precipitate under Tollens` reagent treatment.



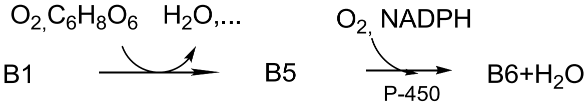
*Oxygenases* catalyze direct addition of oxygen atoms originating from $O_2$ to an organic substrate. These enzymes are further subdivided into *mono-* and *di-oxygenases* depending on the number of incorporated atoms (one and two, respectively). In the case of monooxygenases the other oxygen atom is reduced to water by an appropriate reactant. Cytochrome P-450-dependent monooxygenase is an exceptionally important representative of the class.

An aromatic compound **B1** contains 77.75% C and 14.80% O by mass. **B1** metabolism in rat liver microsomes develops in two ways (see on the hereunder scheme). **B2** reveals 4 signals in. **B2** and **B3** undergo color changes when added to 1% $FeCl_3$ solution, whereas the **B1** color is unaffected by such treatment. All of **B1** to **B4** are composed of the same elements. **B4** is a gas under STP.



3. Decipher **B1** to **B4**. Write down the balanced equations.

Under oxygen deficiency **B1** partially converts into **B5**, an isomer of **B2**. This transformation requires a vitamin as the oxygen acceptor. Further oxidation of **B5** leads to **B6** characterized by 2 signals in $^1$H-NMR spectrum.



4. Draw the structures of **B5** and **B6** as well as of both forms of the vitamin.

Like dehydrogenases, o*xidases* remove hydrogen atoms from an organic substrate transferring these either to the molecular oxygen or **X**, which finally results in water formation in both cases. The phenol oxidation can be described by the following equation:

$$2\text{Phenol} + \mathbf{X} = \mathbf{Y} + 2H_2O$$

The reaction develops *via* a free radical intermediate and leads to a mixture of isomers of **Y** (77.4 % C by mass).

5. Decipher **X**. Draw the isomers of **Y** that show a sole peak in the phenolic region of $^1$H-NMR spectra at low temperatures.

## Problem 26. Holy War against Four Horsemen of the Apocalypse

For centuries the Caspian Sea is widely known for its oil fields. Nowadays it attracts ever increasing attention of researches as a treasury of biological resources, in particular, of algae which can be considered as virtually inexhaustible source of unique chemicals. These studies are in line with the global fight of Enlightened Humanity against the four Horsemen of the Apocalypse – Conquest, War, Famine, and Death.

Substances **X** and **Y** have been isolated from red algae *Asparagopsis armata*. These substances are rarely found in nature and belong to the same class of organic compounds. A sample of 1.000 g of **Y** was combusted in an excess of oxygen at high temperature followed by complete absorption of colorless gaseous (25°C, 1 atm) mixture of products with an excess of aqueous calcium hydroxide solution leading to 1.620 g of a white precipitate. Addition of the supernatant to an excess of silver nitrate solution provided 1.786 g of a colored precipitate.

It is also known that:

- cooling of **Y** combustion products from 150 down to 0°C does not result in any condensed phase;
- white precipitate is an individual compound;
- the molar masses of each of **X** and **Y** are less than 275 g/mol;
- the number of atoms of any element in the molecules of **X** and **Y** does not exceed 3.

1. Without revealing the molecular formula, deduce which elements may be found in **Y**.
2. Without revealing the molecular formula of **Y**, write down the equation that includes numbers of atoms in the molecule as unknowns. Can this equation be of help in establishing the **Y** composition?
3. Determine the molecular formula of **Y** using all the data provided.
4. Will the substitution of silver nitrate by silver oxide in ammonia solution in the above experiment change the weight and color of the precipitate? To support the answer, calculate the solubility of AgBr ($K_{sp} = 5.4 \cdot 10^{-13}$) in 1.0 M $NH_3$ taking into account that the two first stepwise formation constants of silver-ammonia complexes are $10^{3.32}$ and $10^{3.92}$, respectively.

Subjecting 1.000 g of **X** to the described above analysis sequence results in a colored gaseous (250°C, 1 atm) mixture of products leading to 0.756 g of a white individual precipitate after passing the mixture through an excess of aqueous calcium hydroxide solution. Addition of silver nitrate solution to the supernatant also provides a colored precipitate.

It is known that molecules of **Y** and **X** differ by one element, **Y** having one atom more. **X** can exist as a mixture of enantiomers, whereas **Y** reveals geometric isomerism. Furthermore, **Y** reacts with 0.1 M aqueous KOH solution at room temperature.

5. Deduce the molecular formula and draw the structure of **X**.

6. Draw all possible geometric isomers of **Y**.

7. Based on theoretical considerations decide which of the Horsemen of the Apocalypse can be potentially defeated by **X** and **Y**?

Substance **Z** (41.00% O by weight) belongs to the same class of compounds as **X** and **Y**. However, **Z** has been only detected in leaves of some plants, and never in algae.

Combustion of a 1.000-g sample of **Z** in a large excess of oxygen followed by complete absorption of colorless gaseous (25°C, 1 atm) products with an excess of aqueous calcium hydroxide solution leads to 3.065 g of a white precipitate. By contrast, no precipitate formed when the supernatant from the previous test was added to an excess of silver oxide in ammonia solution.

It is also known that:

- one of the gaseous products of **Z** combustion has the density of 1.43 g/L (measured at 34°C, 750 Torr);
- the number of atoms of any element in the molecule of **Z** does not exceed 3.

8. Find the molecular and structural formulae of **Z**.

   Both **Z** and its sodium salt are highly toxic to all mammals.

9. Knowledge of the area of organisms producing **Z** as well as of its metabolic pathway in mammals can be considered as a weapon against some of the Horsemen of the Apocalypse. Comment which of these, in your mind.

# SAFETY RULES AND REGULATIONS ADOPTED AT IChO

Extracts from the Regulations of the International Chemistry Olympiad (IChO)

## § 12 Safety

(1) During the experimental part, the competitors must wear laboratory coats and eye protection. The competitors are expected to bring their own laboratory coats. Other means of protection for laboratory work are provided by the organizer.

(2) When handling liquids, each student must be provided with a pipette ball or filler. Pipetting by mouth is strictly forbidden.

(3) The use of acutely toxic substances (GHS hazard statement H300, H310, H330) is strictly forbidden. The use of toxic substances is not recommended, but may be allowed if special precautions are taken. Substances with GHS hazard statements H340, H350, H360 (proven mutagens, carcinogens, and teratogens) must not be used under any circumstances (see Appendix B for definitions of these categories).

(4) Detailed recommendations involving students´ safety and the handling and disposal of chemicals can be found in Appendices A 1, A 2, and B.

a) Appendix A 1: Safety Rules for Students in the laboratory.

b) Appendix A 2: Safety Rules and Recommendations for the Host Country of the IChO.

c) Appendix B contains a reference to the hazard symbols and statements of the Globally Harmonized System of Classification of Chemicals (GHS), the use of which is expected in labeling and classifying materials used at the IChO.

## APPENDIX A

### A 1: SAFETY RULES FOR STUDENTS IN THE LABORATORY

All students of chemistry must recognize that hazardous materials cannot be completely avoided. Chemists must learn to handle all materials in an appropriate fashion. While it is not expected that all students participating in the International Chemistry Olympiad know the hazards of every chemical, the organizers of the competition will assume that all participating students know the basic safety procedures. For example, the organizers will assume that students know that eating, drinking or smoking in the laboratory or tasting a chemical is strictly forbidden.

In addition to the common-sense safety considerations to which students should have been previously exposed, some specific rules, listed below, must also be followed during the Olympiad. If any question arises concerning safety procedures during the practical exam, the student should not hesitate to ask the nearest supervisor for direction.

**Rules regarding personal protection**

1. Eye protection must be worn in the laboratories at all times. If the student wears contact lenses, full protection goggles must also be worn. Eye protection will be provided by the host country.
2. A laboratory coat is required. Each student will supply this item for himself/herself.
3. Long pants and closed-toed shoes are recommended for individual safety. Long hair and loose clothing should be confined.
4. Pipetting by mouth is strictly forbidden. Each student must be provided with a pipette bulb or pipette filler.

**Rules for Handling Materials**

1. Specific instructions for handling hazardous materials will be included by the host country in the procedures of the practical exam. All potentially dangerous materials will be labeled using the GHS symbols. Each student is responsible for recognizing these symbols and knowing their meaning (see Appendix B).
2. Do not indiscriminately dispose chemicals in the sink. Follow all disposal rules provided by the host country

.

## A 2: SAFETY RULES AND RECOMMENDATIONS FOR THE HOST COUNTRY OF THE INTERNATIONAL CHEMISTRY OLYMPIAD

Certainly it can be assumed that all students participating in the IChO have at least modest experience with safety laboratory procedures. However, it is the responsibility of the International Jury and the organizing country to be sure that the welfare of the students is carefully considered. Reference to the Safety Rules for Students in the Laboratory will show that the students carry some of the burden for their own safety. Other safety matters will vary from year to year, depending on practical tasks. The organizers of these tasks for the host country are therefore assigned responsibility in the areas listed below. The organizers are advised to carefully test the practical tasks in advance to ensure the safety of the experiments. This can best be accomplished by having students of ability similar to that of IChO participants carry out the testing.

**Rules for the Host Country (see also A 1):**

1. Emergency first-aid treatment should be available during the practical examination.
2. Students must be informed about the proper methods of handling hazardous materials.
   a) Specific techniques for handling each hazardous substance should be included in the written instructions of the practical examination.
   b) All bottles (containers) containing hazardous substances must be appropriately labeled using internationally recognized symbols (see Appendix B).
3. Chemical disposal instructions should be provided to the students within the written instructions of the practical examination. Waste collection containers should be used for the chemicals considered hazardous to the environment.
4. The practical tasks should be designed for appropriate (in other words, minimum) quantities of materials.
5. The laboratory facilities should be chosen with the following in mind:
   a) Each student should not only have adequate space in which to work, but should be in safe distance from other students.
   b) There should be adequate ventilation in the rooms and a sufficient number of hoods when needed.
   c) There should be more than one emergency exit for each room.
   d) Fire extinguishers should be nearby.
   e) Electrical equipment should be situated in an appropriate spot and be of a safe nature.
   f) There should be appropriate equipment available for clean-up of spills.
6. It is recommended that one supervisor be available for every four students in the laboratory to adequately ensure safe conditions.
7. The organizers should follow international guidelines for the use of toxic, hazardous or carcinogenic substances in the IChO.

**APPENDIX B**

## HAZARD WARNING SYMBOLS AND HAZARD DESIGNATIONS

Chemicals used in the IChO laboratory experiments need to be labeled according to the Globally Harmonized System of Labeling of Chemicals (GHS) standard developed by the United Nations. The organizing country should use the locally legislated GHS system (pictograms, hazard statements, etc.) if it exists. If such rules do not exist, the original GHS directives (http://www.unece.org/trans/danger/publi/ghs/ghs_welcome_e.html) and the GHS compliant documentation by the chemical providers should be used

# GHS HAZARD STATEMENTS

| Code | Hazard Statement |
|---|---|
| Physical Hazards | |
| H225 | Highly flammable liquid and vapor |
| H232 | May form combustible dust concentrations in air |
| H260 | In contact with water releases flammable gases which may ignite spontaneously |
| H271 | May cause fire or explosion; strong oxidizer |
| H272 | May intensify fire; oxidizer |
| H290 | May be corrosive to metals |
| Health hazards | |
| H301 | Toxic if swallowed |
| H302 | Harmful if swallowed |
| H303 | May be harmful if swallowed |
| H304 | May be fatal if swallowed and enters airways |
| H311 | Toxic in contact with skin |
| H314 | Causes severe skin burns and eye damage |
| H315 | Causes skin irritation |
| H316 | Causes mild skin irritation |
| H317 | May cause an allergic skin reaction |
| H318 | Causes serious eye damage |
| H319 | Causes serious eye irritation |
| H320 | Causes eye irritation |

| | |
|---|---|
| H332 | Harmful if inhaled |
| H333 | May be harmful if inhaled |
| H335 | May cause respiratory irritation |
| H336 | May cause drowsiness or dizziness |
| H351 | Suspected of causing cancer |
| H361 | Suspected of damaging fertility or the unborn child |
| H373 | May cause damage to organs through prolonged or repeated exposure |
| Environmental hazards | |
| H400 | Very toxic to aquatic life |
| H402 | Harmful to aquatic life |
| H410 | Very toxic to aquatic life with long lasting effects |
| H411 | Toxic to aquatic life with long lasting effects |
| H412 | Harmful to aquatic life with long lasting effects |

# PRACTICAL PROBLEMS

## Problem 27. Determination of nickel in nickel and copper-nickel alloys by complexometric titration

Nickel forms single-phase solid solutions with some metals such as copper, iron, and chromium. Nickel and copper feature unrestricted mutual solubility. Copper-nickel alloys, also referred to as cupronickels, possess different properties depending on their composition. The most used cupronickels contain 10 to 45% of nickel.

The main properties of copper-rich alloys (70–90% of copper) include high resistance to corrosion, electrical conductivity, ductileness, strength at elevated temperatures. These features make the alloys highly sought in various industrial applications: construction of sea water corrosion-resistant facilities including oil rig platforms (which is of particular importance for Azerbaijan!), condenser systems in desalination plants, cooling circuits, and ammunition. Small amounts of other elements are usually added for specific purposes; the two most popular alloys for marine applications contain up to 2% iron and manganese. The alloy composed of copper with 45% nickel content provide for almost exactly constant resistance regardless of temperature, and is thus used in the production of thermocouples and resistance wires in high precision resistors. The copper-nickel alloy containing 25% nickel with an additive of 0.05-0.4% manganese is commonly used in manufacturing coins and medals.

Precipitation of nickel as dimethylglyoximate followed by its weighing is widely used for accurate determination of this metal in steels and alloys. Nickel can also be assayed by treatment of a $Ni^{2+}$ containing solution with KI and KCN followed by titration with silver nitrate.

Only metal ions (Zn(II), Cu(II), Ca(II) or Mg(II)) rapidly forming EDTA complexes can be determined by direct titration with EDTA. Since the EDTA complex of nickel(II) is formed slower, the back titration is used in the latter case: EDTA is added in an excess and the unreacted EDTA is back titrated with Ca(II) or Mg(II), the metals that also form colored complexes with a suitable indicator (such as Eriochrome black T), still less stable than the nickel one.

In this task you will precipitate nickel from its ammonia solution with dimethylglyoxime in the presence of citric or tartaric acid as a masking agent* and then determine the metal content by complexometric titration with Eriochrome black T as the indicator.**

**Notes.**

*At this stage, gravimetric determination of nickel as dimethylglyoximate may be carried out. However, it requires drying to constant weight, which may be time consuming.

**The method gives best results with the alloys containing less than 0.5 mass % of Cu.

**Chemicals and reagents:**

- Alloy sample, ~0.5 g, or test solution (a solution containing about 1 g $L^{-1}$ of $Ni^{2+}$, 0.5-0.7 g $L^{-1}$ $Fe^{3+}$, 5-6 g $L^{-1}$ $Cu^{2+}$)
- Diluted nitric acid (1: 1, v/v)
- Diluted hydrochloric acid (1: 1, v/v)
- Diluted sulfuric acid (1: 1, v/v)
- Citric acid or tartaric acid
- Ammonia solution, concentrated
- Dimethylglyoxime (10 g $L^{-1}$ in ethanol)
- Ammonium chloride, 10%
- Sodium hydroxide (200 g $L^{-1}$)
- Hydrogen peroxide solution, 3%
- Eriochrome black T (as a mixture with NaCl, 1:100 w/w)
- Standard 0.05 M EDTA solution: dissolve 18.61 g of solid ethylenediamine tetraacetate disodium dihydrate in 500 mL of distilled water, place the mixture into a measuring flask and dilute to 1 L.
- Ammonia – ammonium chloride buffer solution, pH 10: dissolve 70 g of solid $NH_4Cl$ in 600 mL of concentrated (~15 M) ammonia and dilute to 1 L with distilled water.
- Magnesium sulfate solution (0.05 M): dissolve 12.33 g of solid magnesium sulfate heptahydrate in 500 mL of distilled water and dilute to 1 L.

| Substance | Name | State | GHS Hazard Statement |
|---|---|---|---|
| $HNO_3$ | Nitric acid | aqueous solution | H290, H314, H318 |
| $C_{10}H_{14}N_2O_8Na_2 \times 2H_2O$ | Ethylenediamine tetraacetate disodium dihydrate, $Na_2H_2EDTA \times 2H_2O$ | solid | H302, H315, H319, H335 |
| HCl | Hydrochloric acid | aqueous solution | H314, H318 |
| $H_2SO_4$ | Sulfuric acid | aqueous solution | |
| $C_6H_8O_7$ | Citric acid | solid | H319 |
| $C_4H_6O_6$ | Tartaric acid | solid | H315, H319, H335 |
| $NH_3$ | Ammonia | aqueous solution | H314, H400 |
| $C_4H_8N_2O_2$ | Dimethylglyoxime | solution in ethanol | H232 |
| $NH_4Cl$ | Ammonium chloride | aqueous solution | H302, H319 |
| NaOH | Sodium hydroxide | aqueous solution | H314 |

| | | | |
|---|---|---|---|
| $H_2O_2$ | Hydrogen peroxide | aqueous solution | H271, H302, H314, H333, H402 |
| $C_{20}H_{12}N_3O_7SNa$ | Eriochrome black T | solid | H319 |
| NaCl | Sodium chloride | solid | Not classified |
| $MgSO_4*6H_2O$ | Magnesium sulfate heptahydrate | solid | Not classified |

**Equipment and glassware:**

- Analytical balance (± 0.0001 g)
- Glass beaker, 250 and 400 mL
- Watch glass
- Hotplate stirrer
- Volumetric flask, 500 and 100 mL
- Paper filters (3 ea.)
- Funnel
- pH Indicator paper
- Burette, 25 or 50 mL (2 ea.)
- Funnels (to fill the burettes)
- Volumetric pipette, 10 mL
- Erlenmeyer flask, 100 mL (3 ea.)
- Graduated cylinders, 10 and 25 mL
- Wash bottle with distilled water

**Procedure**

**A. Standardization of $MgSO_4$ solution**

1) Fill a burette with the standard $Na_2H_2$EDTA solution. Transfer 5.00 mL of the solution into the 100-mL Erlenmeyer flask. Adjust pH to 10 with the ammonium buffer solution (3–4 mL). Add 20–30 mg of the Eriochrome black T indicator.

2) Fill the other burette with $MgSO_4$ solution. Titrate the prepared EDTA solution with $MgSO_4$ under continuous stirring until the blue color sharply turns into purple (the change must be irreversible). Record the volume of $MgSO_4$ solution consumed in titration. Repeat the titration until your get consistent results.

The concentration of $MgSO_4$ solution (M) is found from the following equation:

$$C_1=V_0\cdot C_0/V_1,$$

where $V_0$ is the volume of $Na_2H_2$EDTA taken for titration, mL,

$V_1$ is the volume of magnesium sulfate consumed in titration, mL,

$C_0$ – the concentration of $Na_2H_2$EDTA solution.

## B. Dissolution of the alloy sample (the experiment should be carried out under a fume hood)

*(Skip this stage and proceed to part **C** if you are analyzing a test solution rather than an actual alloy sample)*

1) Accurately weigh out the alloy sample, place it into a 250-mL beaker and carefully dissolve in 15 mL of nitric acid (diluted with water, 1:1 v/v). Cover the beaker with the watch glass.

2) Gently heat the solution and boil it on a hot plate until dissolution is complete (the residual volume should be of about 5 mL). Transfer the solution into the 500-mL volumetric flask, rinse the watch glass and the beaker with distilled water, add the wash water to the volumetric flask, and dilute to the mark using the wash bottle.

3) If the alloy sample cannot be totally dissolved (as it may contain W and/or Si), heat the mixture to dryness, add 10 mL of HCl (1:1 v/v) and heat to dryness again. Dissolve the dry residue in 10 mL of concentrated HCl and dilute it with 100 mL of distilled water. Filter off the precipitated tungstic acid using two filters and a long-stem funnel. Wash the precipitate with hot diluted HCl solution (1:10 v/v) until no $Ni^{2+}$ ions are detected in wash waters (test with dimethylglyoxime).

4) If the sample contains more than 0.1 mass % of Si, add 10 mL of $H_2SO_4$ (1:1 v/v) and evaporate till abundant evolving of sulfuric acid fumes. Cool the slurry and carefully add about 10 mL of cold water. Then add 100 mL of hot water and dissolve the residue under heating. Filter off the precipitated silicic acid with filter paper and wash the precipitate with hot water. Transfer the filtrate obtained after W and/or Si separation to a 500-mL volumetric flask and dilute to the mark.

## C. Precipitation of nickel dimethylglyoximate

1) Transfer 50.00 mL of the test solution into the 400-mL beaker, adjust the volume with water to 200 mL and add 6–8 g of solid tartaric or citric acid. Heat the solution on the hot plate until dissolution of the acid is complete. Neutralize the mixture to pH 4–5 with 5–10 mL of ammonia solution (check against the pH indicator paper).

2) Add 25 mL of the dimethylglyoxime solution in ethanol dropwise under intensive stirring, add 2–3 mL of the concentrated ammonia solution to obtain pH 10 and then the other 2–3 mL portion of the same solution to provide for $NH_3$ excess. You will observe the precipitation of nickel dimethylglyoximate.

3) If iron hydroxide precipitates as the solution turns alkaline, add more tartaric or citric acid.

4) Heat the solution with the precipitate on the hot plate until boiling (do not allow boiling!) and store it in a warm place for 40–50 min.

5) Filter the precipitate using the filter paper and wash it with 4–5 portions of hot distilled water. Then wash the precipitate off to the 400-mL beaker, first with 30–50 mL of HCl (1:1 v/v) and then hot water. If you failed dissolving the precipitate, heat the solution and slightly boil it with stirring.
6) Cool the solution down to room temperature, transfer to a 100-mL volumetric flask and dilute to the mark with distilled water.

### D. Determination of $Ni^{2+}$

1) Transfer 10.00 mL of the prepared $Ni^{2+}$ solution into the 100-mL Erlenmeyer flask. Adjust pH to 10 with the ammonium buffer solution (4–6 mL) and add 10.00 mL of the standard $Na_2H_2EDTA$ solution from the burette. Add 20–30 mg of the Eriochrome black T indicator to obtain a blue colored solution.
2) Fill the burette with the standard $MgSO_4$ solution and take the initial reading of the burette. Titrate the blue nickel(II) solution with the standard $MgSO_4$ solution until the color becomes permanently purple. Take the final reading of the burette. Repeat the titration until your get consistent results.
3) Calculate the amount of $Na_2H_2EDTA$ spent for $Ni^{2+}$ titration based on the volumes of the $Na_2H_2EDTA$ solution added and the $MgSO_4$ solution consumed in the titration.

### Questions and Data Analysis

**1.** Write down the balanced chemical equations for the reactions occurring:

- when the sample of the alloy is dissolved in nitric acid;
- when the test solution is titrated with the magnesium sulfate solution.

**2.** Explain the role of citrate or tartrate when in the process leading to nickel dimethylglyoximate? Write down the corresponding chemical equations.

**3.** Explain the necessity of the nickel dimethylglyoximate precipitation. How do Cu and Mg present in the test mixture interfere with the determination of nickel? Write down appropriate chemical equations.

**4.** Explain why the pH value of the titrated solution should be kept below 10. In calculations, use the following constants of complex formation: $K[Ni(EDTA)]^{2-} = 4.2\times10^{18}$, $K([Mg(EDTA)]^{2-} = 4.9\times10^{8}$.

**5.** What is the most stable form of EDTA at pH 10? Compare the molar fractions of $HEDTA^{3-}$ and $EDTA^{4-}$. Note that $H_4EDTA$ is a weak acid with the following acidity constants: $K_1 = 1.0 \cdot 10^{-2}$, $K_2 = 2.1 \cdot 10^{-3}$, $K_3 = 6.9 \cdot 10^{-7}$, $K_4 = 5.5 \cdot 10^{-11}$.

**6.** Derive the formulae for calculation of the $Ni^{2+}$ concentration in the test solution. Calculate the mass fraction of Ni in the alloy.

## Problem 28. Titrimetric determination of lead and silver in their mixture

Lead and silver are often both present in alloys (such as tin-lead-silver or lead-silver), which are successfully applied in bearing assembly, ballast, casting, step soldering, and radiation shielding. The alloys usually contain 30–90 % of lead and 1–5 % of silver. Redox titration was found to be a precise standardless method allowing determination of these metals.

In this work, you will determine lead and silver in a solution by redox titration.

**Chemicals and reagents:**

- A sample of lead and silver containing alloy, or test solution simulating a dissolved alloy (a standard solution containing about 500–1000 mg Pb and 70–190 mg Ag in 0.1 L)
- Ammonia aqueous solution (25% ammonium solution and water, 1:1 v/v)
- Oxalic acid, saturated solution at room temperature
- Potassium permanganate, 0.0100 M standard solution
- Sulfuric acid, 1 M solution
- Nitric acid, 4 M solution
- Ammonium iron(III) sulfate, saturated solution
- Ammonium thiocyanate, 0.0100M standard solution.

| Substance | Name | State | GHS Hazard Statement |
|---|---|---|---|
| $NH_3$ | Ammonia | aqueous solution | H314, H400 |
| $C_2H_2O_4$ | Oxalic acid | aqueous solution | H314, H318 |
| $KMnO_4$ | Potassium permanganate | aqueous solution | H272, H302, H400, H410 |
| $H_2SO_4$ | Sulfuric acid | aqueous solution | H314, H290 |
| $HNO_3$ | Nitric acid | aqueous solution | H290, H314, H318 |
| $NH_4Fe(SO_4)_2$ | Ammonium iron(III) sulfate | aqueous solution | H315, H319 |
| $NH_4SCN$ | Ammonium thiocyanate | aqueous solution | H332, H412 |

**Equipment and glassware:**

- Analytical balance (± 0.0001 g)
- Hot plate
- Filter paper or glass filter
- Burette, 25 mL (2 ea.)
- Funnels (to fill the burettes)
- Volumetric pipette, 10.00 mL
- Pipette filler
- Erlenmeyer flask, 100 mL
- Volumetric flask, 100 mL
- Glass beaker, 100 and 250 mL
- Graduated cylinders
- Waste bottle for oxalate solution

### Procedure

### A. Decomposition of the alloy sample

(Optional and may be omitted; if so, a model solution of metal salts is to be prepared; see *Chemicals and reagents* for the solution composition)

Take a precise weight of the metal (~250 mg) and place it in a beaker. Carefully add 5 mL of concentrated nitric acid (to be done under a fume hood because of gaseous $NO_2$ evolvement). Heat the beaker slightly on the hot plate to provide for an effective dissolution. When the digestion is complete evaporate the solution to near dryness to remove the major part of the acid (avoid evaporating to dry salts, since hydrolysis may occur. If still so, add a minimal amount of $HNO_3$ to dissolve the residue). Allow the beaker cooling down to room temperature.

***ATTENTION!*** *Nitric acid is very corrosive! You will have to deal with hot solutions in the above and subsequent steps. Be careful and beware of steam!*

### B1. Separation of lead

Using the hot plate, remove the excess of the acid by evaporating the solution obtained at stage **A** to dryness and dissolve the residue in water (skip this step if a model test solution is used rather than a real alloy solution). Bring the solution to boiling, then add about 10 mL of the saturated solution of oxalic acid and observe a precipitate formation. Avoid large excess of oxalic acid. To partially dissolve the precipitate, add aqueous ammonia solution (1:1 v/v) dropwise.

***ATTENTION!*** *The ammonia solution is corrosive and has a very strong smell! Keep the bottle stoppered when not in use.*

**C. Determination of lead**

Heat the solution above the precipitate on the hot plate to remove the excess of ammonia, and cool the mixture quickly under the running tap water. Filter the slurry through the glass filter. Keep the filtrate for next step. Wash the filter cake with cold water and then dissolve it in hot 1M $H_2SO_4$ adding the acid in small portions. Collect the obtained solution in the 100-mL volumetric flask and make it up to the mark with water. Titrate oxalate in the prepared solution (take 10.00 mL aliquots) with 0.0100 M solution of potassium permanganate.

***ATTENTION****! Oxalate solutions are toxic. Do not pour the solutions down a sink. Instead, dispose these in a special waste bottle.*

**D. Determination of silver**

Add 10 mL of 4M nitric acid solution and 1–2 mL of saturated iron(III) ammonium sulfate solution to the filtrate (from step **C**). Use burette to add the standard solution of ammonium thiocyanate until vanishing reddish-brown color is observed. Shake the flask and continue titrating until the color is stable.

**Questions and Data Analysis**

**1.** Write down balanced chemical equations for the reactions that take place upon:

a) formation of the precipitate (step **B**),

b) partial dissolution of the precipitate in ammonia (step **B**),

c) dissolution of lead oxalate (step **C**),

d) oxalate titration with permanganate (step **C**).

**2.** Explain the role of iron(III) at step **D**.

**3.** Calculate the lead and silver content in the sample (starting alloy or test solution).

## Problem 29. Complexometric determination of iron, chromium, and zinc in an alloy

Ferrochrome is an alloy of iron and chromium mostly (over 80% of world consumption) used in stainless steel production. To improve the corrosion resistance of steel it is often coated with zinc, the process being referred to as galvanization. It is of extreme importance to accurately control the contents of zinc, iron, and chromium in the resultant galvanized steel. Typically samples of steel are dissolved in concentrated nitric acid and the content of major components in the obtained solution is determined by different methods.

Analysis of multicomponent systems is often hindered by the interference between the components. Various separation techniques (precipitation, extraction) or masking are the usual steps towards avoiding such interference. Still, nowadays researches are mainly focused at analytical methods allowing sequential determination of components in the same solution without any separation procedures. These methods are typically based on simple manipulations like changing the pH.

In this task you will apply one of such methods for sequential determination of iron(III), chromium(III) and zinc(II) simultaneously present in an aqueous solution.

**Chemicals and reagents:**

- Test solution simulating a digested sample of galvanized steel (a standard solution containing $Fe^{3+}$, $Zn^{2+}$ and $Cr^{3+}$ ions within the concentration range of 0.1–0.3 M)
- Hydrochloric acid, 1 M
- $Na_2H_2EDTA$ standard solution, 0.025 M
- Acetate buffer solution, pH 5.5–6.0, 0.1 M in acetate
- Copper(II) sulfate standard solution, 0.025 M
- Distilled water
- Indicators:
  - aqueous solution of 5-sulfosalicylic acid, 5% (w/w)
  - solution of 1-(2-pyridylazo)-2-naphthol (PAN) in ethanol, 0.1% (w/w)
  - universal pH indicator paper

| Substance | Name | State | GHS Hazard Statement |
|---|---|---|---|
| $C_{10}H_{14}N_2O_8Na_2$ | Ethylenediamine tetraacetate disodium dihydrate, $Na_2H_2EDTA$ | aqueous solution | H302, H315, H319, H335 |
| HCl | Hydrochloric acid | aqueous solution | H314, H318 |

| | | | |
|---|---|---|---|
| $C_2H_3NaO_2$ | Sodium acetate | aqueous solution | H303, H316, H320, H333 |
| $CuSO_4$ | Copper(II) sulfate | aqueous solution | H301, H400, H410 |
| $C_7H_6O_6S$ | 5-Sulfosalicylic acid | aqueous solution | H315, H319 |
| $C_{15}H_{11}N_3O$ | 1-(2-Pyridylazo)-2-naphthol (PAN) | ethanol solution | Not classified |

**Equipment and glassware:**

- Hot plate
- Funnels (to fill the burettes)
- Paper filters
- Volumetric flask, 100 mL
- Volumetric pipettes, 1 and 10 mL
- Burette, 25 or 50 mL (2 ea.)
- Erlenmeyer flask, 200 mL (3 ea.)
- Graduated cylinder, 10 mL (2 ea.)
- Glass dropper

## Procedure

### A. Sample preparation

Prepare 100 mL of your working solution by a 10-fold dilution of the test solution provided. Use the 100 mL volumetric flask and distilled water. The $Fe^{3+}$, $Zn^{2+}$ and $Cr^{3+}$ ions content in the working solution would be within the concentration range of 0.01 – 0.03 M.

### B. Determination of $Fe^{3+}$

Place 10.00 mL of the working solution into a 200 mL Erlenmeyer flask, add about 20 mL of distilled water and adjust the pH to 1 by adding about 5 mL of 1M HCl (check the pH value against the indicator paper). Finally, supplement 1 mL of 5% aqueous solution of sulfosalicylic acid (the indicator) and mix thoroughly.

Titrate the flask contents with 0.025 M EDTA standard solution until the color changes from violet to yellow-green. Record the volume of the standard solution ($V_1$, mL). Repeat the titration as necessary.

### C. Determination of $Zn^{2+}$

Adjust the pH of the solution obtained in step **B** to 5–6 by adding 5–6 mL of the acetate buffer solution, then add 3–5 drops of PAN solution (the indicator) and mix thoroughly.

Titrate the flask contents with 0.025 M EDTA standard solution until the color changes from pink to yellow-green. Record the volume of the standard solution ($V_2$, mL). Repeat the titration as necessary.

**D. Determination of $Cr^{3+}$**

Direct titration of $Cr^{3+}$ with EDTA solution is impossible because of the low rate of complex formation. Thus, the method of back titration is used: an excess of EDTA standard solution is introduced, and the unreacted EDTA is titrated with $Cu^{2+}$.

Supplement an excess of 0.025 M standard solution of EDTA (20 mL) to the solution obtained in step **C**, mix thoroughly and boil the mixture for 5 min. Add 3-5 drops of PAN solution (the indicator) to the cooled mixture and mix thoroughly.

Titrate the flask contents with 0.025 M $CuSO_4$ standard solution until the color changes from wine-red to blue-violet. Record the volume of the standard solution ($V_3$, mL). Repeat the titration as necessary.

**Questions and Data Analysis**

**1.** Write down balanced chemical equations for the reactions that take upon:

a) the sample of alloy is dissolved in concentrated nitric acid

b) the working solution is titrated with $Na_2H_2EDTA$

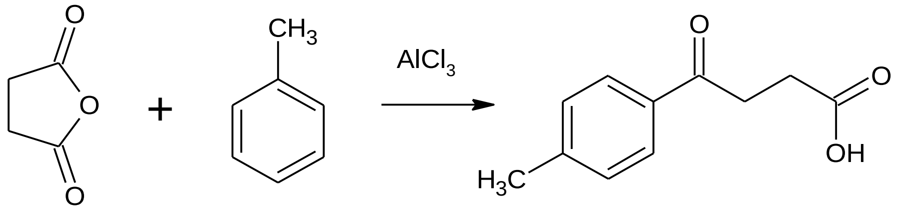
**2.** Derive the formulae for calculation of the $Fe^{3+}$, $Zn^{2+}$ and $Cr^{3+}$ concentration in the test solution. Calculate the concentrations of the ions.

**3.** Calculate the molar fraction of $H_2EDTA^{2-}$ at pH 1. EDTA is a weak acid with the following acidity constants: $K_1 = 1.0\cdot10^{-2}$, $K_2 = 2.1\cdot10^{-3}$, $K_3 = 6.9\cdot10^{-7}$, $K_4 = 5.5\cdot10^{-11}$.

## Problem 30. Synthesis of 3-(4-methylbenzoyl)propionic acid

The Friedel-Crafts reactions are a family of processes (acylation, alkylation, and some other less important) developed by C. Friedel and J. Crafts in 1877 at the Sorbonne.

The Friedel-Crafts acylation allows introducing of an acyl group into the aromatic ring with a suitable acylating agent (acyl halide or carboxylic acid anhydride) and a strong Lewis acid as a catalyst. Nowadays it is an important synthetic method providing aromatic and alkyl-aromatic ketones, which are important intermediates in the production of pharmaceuticals, dyes and other valuable compounds.



The Friedel-Crafts alkylation is less sought, since may lead to a mixture of polyalkylated products. Remarkably, a solution comes from the Friedel-Crafts acylation, since the acylation products are readily reduced to the corresponding alkanes (e.g. via Clemmensen or Wolff-Kishner reactions).

**Chemicals and reagents**

- Toluene (dry), 25 g
- Succinic anhydride, 5 g
- Aluminium chloride anhydrous, 13.3 g
- Dichloromethane (Methylene chloride), 100 mL
- Hexane, 75 mL
- Hydrochloric acid, concentrated, 25 mL
- Sodium sulfate, calcined, 20 g
- Distilled water, 100 mL

| Substance | Name | State | GHS Hazard Statement |
|---|---|---|---|
| $C_7H_8$ | Toluene | liquid | H225,H304, H315, H336, H361, H373 |
| $C_4H_4O_3$ | Succinic anhydride | solid | H302, H319, H335 |
| $AlCl_3$ | Aluminium chloride | solid | H315, H319, H335, H402 |
| $CH_2Cl_2$ | Dichloromethane | liquid | H302, H315, H320, H351 |
| $C_6H_{14}$ | n-Hexane | liquid | H225, H304, H315, H335, H336,H361, H373, H411 |
| HCl | Hydrochloric acid | aqueous solution | H302, H314, H318, H335, H402 |
| $NaSO_4$ | Sodium sulfate | Solid | H317 |

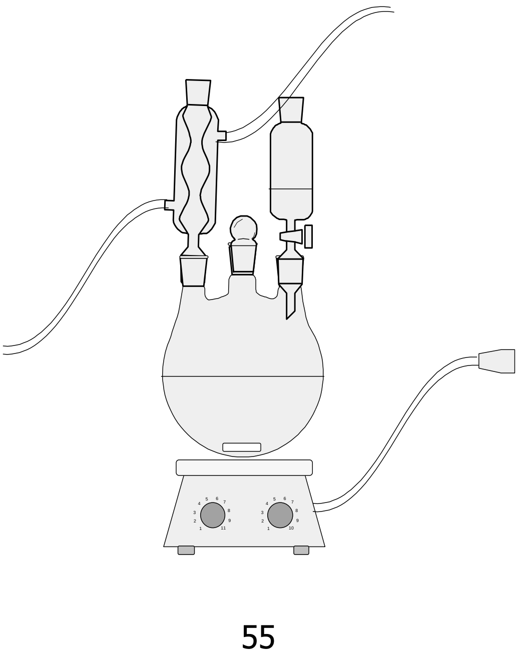
**Equipment and glassware**

- Laboratory stand with clamps
- Three-necked flask, 250 mL
- Reflux condenser with breather tube
- Dropping funnel, 100 mL
- Magnetic stirrer with heating
- Teflon magnetic stir bar
- Hoses
- Thermometer with a tapered joint
- Tapered joint stopper
- Ice bath
- Graduated cylinder, 50 mL
- Beaker, 100 mL
- Separating funnel, 250 mL
- Rotary evaporator
- Paper filter
- Fritted glass filter, porosity 2-3
- Bunsen flask for vacuum filtration
- Glass rod
- Melting point apparatus
- Capillary for melting point determination (2-3 ea.)
- Glass tube for capillary filling
- Spatula
- Teflon sleeves for tapered joints or vacuum grease
- Analytical balances (± 0.001 g)

**Procedure**

**A. Assembly of the apparatus**

Assemble the apparatus as shown in the hereunder picture. Equip every joint with the Teflon sleeve or apply vacuum grease.



### B. Preparation of the reagents and synthesis of the product

Fix the three-necked flask at the laboratory stand over the magnetic stirrer. Place 25 g of toluene and 5 g of succinic anhydride into the flask and equip it with the reflux condenser with a breather tube, the dropping funnel and the stir bar. Start stirring the mixture. Use the neck left open to add 13.3 g of the finely-powdered anhydrous aluminum chloride in portions at continuous stirring. When finished, fix the neck with the thermometer so that its tip is submerged into the reaction mixture. Switch on heating. Close the neck with the stopper and vigorously stir the reaction mixture for 1 h at 60 °C.

### C. Isolation of the product

Cool the flask down to room temperature and then place it in the ice bath. Fill the dropping funnel with 60 mL of ice-cooled water. Add slowly (dropwise) all the water from the funnel to the reaction mixture at constant vigorous stirring. When finished, add dropwise 25 mL of concentrated hydrochloric acid add 60 mL of dichloromethane. Transfer the reaction mixture to the separatory funnel and tightly close it with the stopper.

Keep shaking the reaction mixture vigorously (turning the separatory funnel up and down) for a few minutes, and then allow the phase separation. Add extra 10 mL of water and 10 mL of dichloromethane if phase separation is not satisfactory. Segregate the well defined organic phase. For better extraction, add 20 mL of dichloromethane to the aqueous phase and repeat separation as described above two times. Combine the organic phases in the separatory funnel and wash with 30 mL of water. Pour out the organic phase and dry it over calcined $Na_2SO_4$ for 1 h. Filter the desiccant off using the paper filter or fritted glass filter. Evaporate the filtrate on the rotary evaporator to approximately 20% of the original volume.

### D. Purification of the product

Transfer the residue left after the rotary evaporation into the beaker and add 30 mL of hexane, which will initiate the crystallization process. Place the beaker in the ice bath for 20 min to complete crystallization. Filter out the precipitate using the fritted glass filter and wash the product three times with 15 mL of hexane each.

### E. Analysis of the product

Weigh the product. Calculate the yield.

Place the non-sealed end of the capillary into the product crystals, then turn it the sealed end down and throw several times down through a glass tube. Check that the sealed end side of the capillary is filled with the product. Apply the ready capillary to the melting point apparatus and record the melting point of the product. Compare the value with the reference data and draw a conclusion about the product purity.

**Note.** The resulting product, if pure, can be used as the starting compound in Problem 31.

**Questions**

**1.** Is it possible to introduce two acyl groups in the ring via the Friedel-Crafts electrophilic substitution reaction? Propose the way to obtain 1,4-diacetylbenzene.

**2.** Compare the activity of phenol, *p*-nitrophenol and *p*-methoxyphenol in the O-acylation reaction in neutral medium (*e.g.* in THF). Suggest the reaction scheme of the most active compound (according to your choice) with propionic acid chloride.

**3.** Why is the Friedel-Crafts acylation more often used as compared to the Friedel-Crafts alkylation?

**4.** Which other reagents (besides that considered in the Problem) can be used in the Friedel-Crafts acylation?

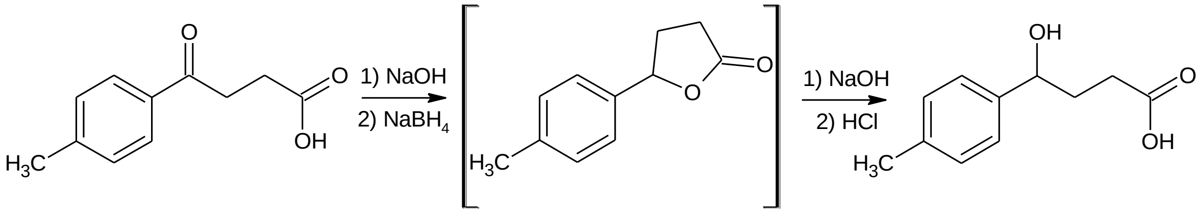
**5.** Why are the ice-cooled water and concentrated hydrochloric acid added to the mixture once the reaction is complete?

**6.** Why aluminum chloride is taken in the two-fold excess?

## Problem 31. Synthesis of 4-(4-methylphenyl)-4-hydroxybutanoic acid

The intermediate oxidation state of carbon in carbonyl compounds specifies its ability to take part in oxidation-reduction reactions. Depending on the selected reaction conditions the reduction of a carbonyl group can lead either to alcohols (primary in the case of aldehydes and secondary in the case of ketones) or saturated hydrocarbons. The latter are typically formed as a result of hydrogenation at elevated temperature and high pressure, still can also be obtained under relatively mild conditions (e.g. via Clemmensen or Wolff-Kischner reactions).

Reduction of carbonyl compounds to alcohols can be successfully carried out by catalytic hydrogenation. Still, the preference is nowadays given to other chemical processes due to the simplicity of experimental procedures and accessibility of reagents. Hydride complexes of aluminum (or boron) and alkaline metals are indispensable in organic synthesis due to their high reducing ability in a wide range of temperatures and the possibility of choosing appropriate complexes applicable in solvents with different polarity. In this task you will get acquainted with one of such reagents, sodium borohydride.



**Chemicals and reagents**

- β-(4-methylbenzoyl)-propionic acid, 4 g
- Sodium borohydride, 0.8 g
- Sodium hydroxide, 2.5 M aqueous solution, 24 mL
- Hydrochloric acid, 6 M aqueous solution, 20 mL
- Distilled water, 100 mL

| Substance | Name | State | GHS Hazard Statement |
|---|---|---|---|
| $C_{11}H_{12}O_3$ | β-(4-methylbenzoyl)-propionic acid | solid | H315, H319, H335 |
| $NaBH_4$ | Sodium borohydride | solid | H260, H301+H311, H314 |
| NaOH | Sodium hydroxide | aqueous solution | H314 |
| HCl | Hydrochloric acid | aqueous solution | H302, H314, H318, H335, H402 |

**Equipment and glassware**

- Laboratory stand with clamps
- Three-necked flask, 250 mL
- Reflux condenser with breather tube
- Dropping funnel, 100 mL
- Magnetic stirrer with heating
- Teflon magnetic stir bar

- Hoses
- Thermometer with a tapered joint
- Tapered joint stopper
- Ice bath
- Beaker, 100 mL (2 ea.)
- pH indicator paper
- Fritted glass filter, porosity 2-3
- Glass rod
- Melting point apparatus
- Capillary for melting point determination (2-3 ea.)
- Glass tube for capillary filling
- Spatula
- Teflon sleeves for tapered joints or vacuum grease
- Analytical balances (± 0.001 g)

### Procedure

### A. Assembly of the apparatus

Assemble the apparatus as shown in the picture in Problem 30. Equip every joint with the Teflon sleeve or apply vacuum grease.

### B. Preparation of the reagents and synthesis of the product

Prepare the solution of 0.8 g of sodium borohydride in 12 mL of water and pre-cool it to 0-5°C. Fix the three-necked flask at the laboratory stand over the magnetic stirrer. Weigh out and admeasure the required amounts of the reagents. Place 4 g of β-(4-methylbenzoyl)-propionic acid and 12 mL of 2.5 M aqueous solution of NaOH in the flask and equip it with the reflux condenser with a breather tube, the dropping funnel and the stir bar. Switch on stirring. Fix the unused neck with the thermometer so that its tip is submerged into the reaction mixture. Place the ice-water bath under the flask. When the reaction mixture gets cooled down to 0-5°C, quickly add with intensive stirring the pre-cooled sodium borohydride solution. Remove the ice-bath and let the reaction mixture warm up to room temperature. Gently heat up the mixture to boiling and keep refluxing for 40 min. Then add 12 mL of 2.5 M aqueous solution of NaOH to the heated reaction mixture and continue refluxing for another 20 min.

### C. Isolation of the product

Switch off the heating. Cool the flask down to room temperature and then place it in the ice-water bath containing sodium chloride. Fill the dropping funnel with 15 mL of 6 M HCl and add the acid solution slowly to the flask under vigorous stirring continuously monitoring the pH of the reaction mixture with the pH indicator paper (capture a drop of the reaction mixture with the glass rod through the neck of the flask and apply it to the test paper). **Important!** The temperature of the reaction mixture **must not** exceed 5°C. Instantly control the temperature keeping the tip of the thermometer submerged into the reaction mixture. Adjust the pH to 2 and observe precipitation of white crystals. Filter out the product using the fritted glass filter and wash it 2-4 times with ice-cold water until the pH of the filtrate attains 4-5.

Air-dry the resulting white precipitate on a filter paper for a few hours. To accelerate the process the precipitate may be placed in a round-bottom flask and dried out on a rotary evaporator under reduced pressure. Control the dryness of the product by determining its melting point.

### E. Analysis of the product

Weigh the product. Calculate the yield.

Place the non-sealed end of the capillary into the product crystals, then turn it the sealed end down and throw several times down through a glass tube. Check that the sealed end side of the capillary is filled with the product. Apply the ready capillary to the melting point apparatus and record the melting point of the product. Compare the value with the reference data and draw a conclusion about the product purity.

### Questions

**1**. What effects does an alkali produce on the starting materials and the reaction intermediates? Write down the equation of sodium borohydride reaction with water in neutral medium. Suggest the mechanism of the lactone disruption.

**2**. Why does addition of the acid at the final stage of the synthesis lead to the product precipitation?

**3**. Consider an alkylaldehyde and a dialkyl ketone. Which carbonyl group is more readily reduced with sodium borohydride? Justify your answer.

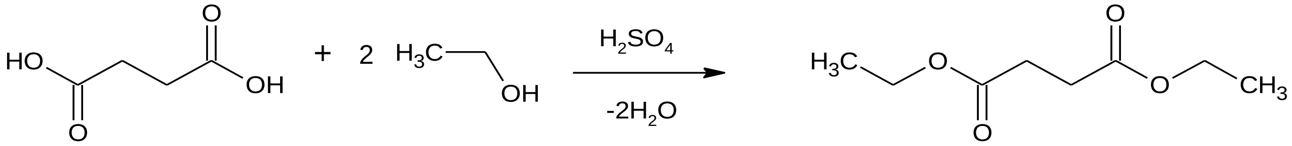
**4**. The reaction considered in this Problem serves as an example of the selective reduction of a keto group in the presence of a carboxyl one. Propose a way how a carboxyl group can be selectively reduced in the presence a carbonyl group.

**5**. A compound with the molecular formula $C_{17}H_{25}NO_2$ is produced when the starting compound is treated with cyclohexylamine (in equimolar amount to ketoacid) in methanol in the presence of catalytic amounts of a strong acid followed by the addition of sodium borohydride. Suggest the structures of the final and intermediate products as well as the mechanism of the first stage of the reaction.

## Problem 32. Synthesis of diethyl ester of succinic acid

Esters are widespread in nature. In particular, these compounds are responsible for pleasant aromas of flowers, fruits and berries. Low molecular weight esters, flammable liquids with low boiling points, are applied as solvents for varnishes and paints, flavoring additives in food industry, etc. Esters of higher monocarboxylic acids and higher alcohols are referred to as waxes. Fats and vegetable oils, vitally important storage compounds, are esters of polyhydric alcohol glycerol and higher carboxylic acids.

Several synthetic schemes are available for ester preparation. The acid catalyzed esterification of a carboxylic acid and an alcohol is among the most used in laboratory practice. Since the reaction is reversible, special attention should be given to shifting the equilibrium towards the ester formation. This can be achieved by either introduction of dehydrating agents or removal of the products (ester and/or water) from the reaction mixture. In the case of starting compounds with relatively low boiling points azeotropic removal of water is possible. In this work you will follow the latter approach to ester synthesis.



**Chemicals and reagents:**

- Succinic acid, 18 g
- Ethanol (absolute), 55 mL
- Toluene (dry), 24 mL
- Sulfuric acid (concentrated), 0.5 mL
- Potassium carbonate (calcined), 25 g

| Substance | Name | State | GHS Hazard Statement |
|---|---|---|---|
| $C_4H_6O_4$ | Succinic acid | solid | H319 |
| $C_2H_5OH$ | Ethanol | liquid | H315, H320, H335, H401 |
| $C_7H_8$ | Toluene | liquid | H225, H304, H336, H361, H373, H401 |
| $H_2SO_4$ | Sulfuric acid | aqueous solution | H302, H314, H332, H351 |
| $K_2CO_3$ | Potassium carbonate | Solid | H315, H319, H335, H336 |

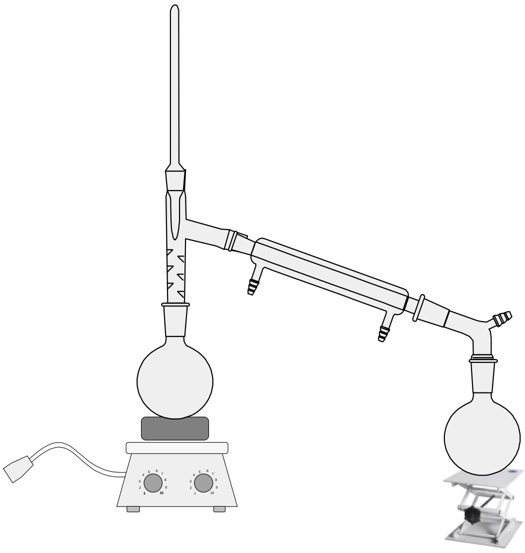
**Equipment and glassware:**

- Graduated cylinders, 5 and 50 mL
- Round-bottom flask, 250 mL
- Long Vigreux distilling column with a downward condenser
- Vacuum adapter
- Hoses for the condenser
- Glass capillaries or boiling granules
- Receiver flask, 100 mL
- Thermometer with a tapered joint
- Magnetic stirrer with heating or hot plate
- Claisen flask (150 mL) with a downward condenser
- Capillary for Claisen flask
- Filter paper or fritted glass filter
- Beaker, 100 mL
- Three-way vacuum adapter
- Receiver, 50 mL (3 ea.)
- Water-jet air pump
- Manometer
- Analytical balances (± 0.001 g)
- Refractometer
- Teflon sleeves for tapered joints or vacuum grease
- Spatula
- Pressure nomogram

## Procedure

### A. Assembly of the apparatus

Assemble the apparatus as shown in the hereunder picture. Equip every joint with the Teflon sleeve or apply vacuum grease.



**Note**: the tip of the thermometer should be positioned slightly below the outlet to the condenser.

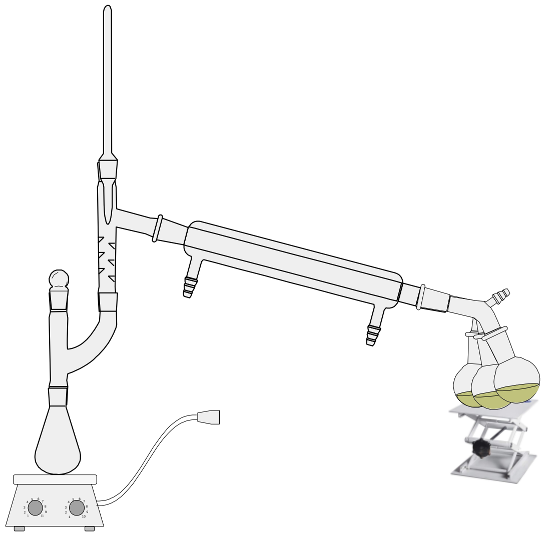
### B. Preparation of the reagents and synthesis of the product

Weigh out and admeasure the required amounts of succinic acid (18 g), absolute ethanol (55 mL), toluene (24 mL), and concentrated sulfuric acid (0.5 mL). Place all the materials into the 250 mL round-bottom flask.

Heat the reaction mixture constantly monitoring the temperature. The fraction with the azeotropic mixture of the alcohol, water and toluene should start distilling off at 74-80°C. Collect the distillate in the 100 mL receiver flask and terminate distillation (turn off the heater plate and disconnect the receiver flask with the collected distillate). Add 25 g of calcined $K_2CO_3$ to the receiver flask to dry the distillate. Shake the flask and leave it for 1 h. Then separate the liquid from the desiccant by filtration through any filter enlisted in the "Equipment and glassware" section. Place the dried distillate back to the reaction mixture in the round-bottom flask, switch on heating and collect once again the fraction with the azeotropic mixture of the alcohol, water and toluene distilled off at 80°C.

### C. Vacuum distillation of the residue

Label and take weights of all empty 50 mL receiver flasks. Transfer the residue from the round-bottom flask to the Claisen flask and add glass capillaries or boiling granules. Assemble the apparatus for vacuum distillation as shown in the hereunder picture. Equip every joint with the Teflon sleeve or apply vacuum grease. Connect the vacuum line to the vacuum adapter.



Distill the residue under vacuum using the water-jet pump. Collect the fractions into the receiver flasks. Maintain the rate of distillation of about 1-2 drops of the distillate per second. Once the temperature reaches 103°C (as read on the thermometer) at 15 mm Hg, collect about 10 drops in the first receiver flask and change it to the second one by turning the adaptor. Collect the fraction up to 107°C at 15 mm Hg. Then change to the third receiver flask and switch off the heating. Let the apparatus cool down before disconnecting the vacuum line and letting air in.

Note. Use the pressure nomogram to recalculate the temperatures if you observe pressure other than 15 mm Hg.

Record the pressure and the temperature of distillation.

**Attention!**

**Never use flat-bottomed flasks as receivers!**

**Always wear protective glasses or mask when doing vacuum distillation!**

## D. Analysis of the product

Weigh the receiver flask with the required fraction and find the mass of the product. Calculate the yield.

Determine the refractive index $n_D^{20}$ of the product using the refractometer. If you perform the measurement at a different temperature, reduce the obtained value to 20 °C.

**Questions**

**1.** What is the role of toluene in the above process?

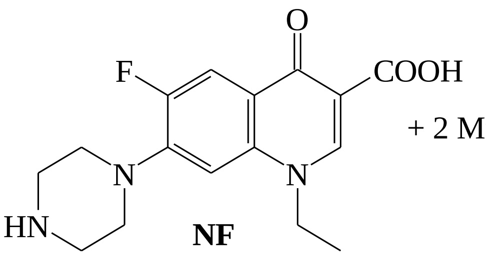
**2.** Write down the reaction mechanism.

**3.** Suppose $^{18}$O-labeled ethyl alcohol and $^{18}$O-labeled *tert*-butyl alcohols are involved into the reactions instead of unlabeled ethyl alcohol. Which compound(s) will be the $^{18}$O atom found in when the reactions with the labeled alcohols are complete? Prove your choice.

## Problem 33. Kinetic studies of Norfloxacin oxidation with permanganate in alkaline medium

Norfloxacin [1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid] is a synthetic fluoroquinolone antibacterial agent of broad spectrum characterized by high activity against many gram-positive and gram-negative bacteria. As a result of constantly increasing administration, fluoroquinolones are expected to enter environment via waste waters. These substances are capable of bringing serious harm to aquatic life even if present in marginal concentrations mainly by giving rise to drug-resistant bacteria. Development of advanced oxidation processes leading to transformation of fluoroquinolones in water is an important task of contemporary chemistry.

Recently it was found that Norfloxacin (NF) can be oxidized by potassium permanganate in alkaline medium according to the following reaction:



**NF**

$$+ 2\,MnO_4^- + 2\,OH^- \;=\; \mathbf{A} \;+ 2\,MnO_4^{2-} + H_2O$$

**Product of oxidation**

According to the mass action law, the reaction rate can be expressed as:

$$r = k[\mathrm{NF}]^{\nu_1}[\mathrm{MnO_4^-}]^{\nu_2}[\mathrm{OH^-}]^{\nu_3}$$

where [NF], $[MnO_4^-]$, $[OH^-]$ are the concentrations of Norfloxacin, permanganate and alkali, respectively, and $\nu_1$, $\nu_2$, $\nu_3$ are reaction orders with respect to the corresponding reagents.

In this task you will determine the reaction orders with respect to the involved reagents following the reaction progress photometrically at 525 nm, the wavelength of maximum absorbance of permanganate.

**Chemicals and reagents:**

- Potassium permanganate
- Sodium hydroxide
- Sodium perchlorate
- Norfloxacin

| **Substance** | **Name** | **State** | **GHS Hazard Statement** |
|---|---|---|---|
| $KMnO_4$ | Potassium permanganate | aqueous solution | H272, H302, H400, H410 |
| NaOH | Sodium hydroxide | aqueous solution | H314 |
| $NaClO_4$ | Sodium perchlorate | aqueous solution | H271 |
| $C_{16}H_{18}FN_3O_3$ | Norfloxacin | aqueous solution | Not classified |

**Equipment and glassware:**

- Analytical balance (± 0.0001 g)
- Visible spectrophotometer (or photometer with fixed wavelength of 525 nm) equipped with thermostated cell holder
- Spectrophotometer cells with 3.5 cm optical path length (you will need to recalculate concentrations of the reagents if you use cells with different optical path length)
- Tissue to clear cell surfaces
- Thermostat
- PC (or other computing techniques) with Microsoft Excel software (English version)
- Volumetric flasks, 100 mL (4 ea.)
- Graduated cylinder, 100 mL
- Volumetric pipettes, 1, 2, 5, and 10 mL
- Pipette filler
- Spatula

### Procedure

### A. Preparation of stock solutions

Read the Procedure to the end and calculate the concentrations of stock solutions of potassium permanganate, sodium hydroxide, sodium perchlorate, and Norfloxacin that will allow easy preparation of the reaction mixtures to be analyzed. Prepare the stock solutions of potassium permanganate, sodium hydroxide and sodium perchlorate in the volumetric flasks according to standard procedures. Norfloxacin suffers from poor solubility in water at neutral pH values, thus first dissolve it in a small amount (about 6 mL) of 0.3 M alkali (in the volumetric flask) and then add water to attain the required concentration. Do not forget to account for the amount of alkali introduced with the Norfloxacin solution when preparing the reaction mixtures. Close the flasks containing the stock solutions with stoppers and place them into the thermostat pre-adjusted to 25 $^{o}$C.

**Note**. Norfloxacin is commercially available as a pure reagent. Also, it can be found as an ingredient in medicines. In the latter case, it is recommended to check that the other ingredients do not interfere with Norfloxacin when it is being oxidized by potassium permanganate.

### B. General design of the task

The experimental work consists of three parts as can be seen from the hereunder table:

- Part 1: $KMnO_4$ concentration is varied, concentrations of all other reagents being constant (lines 1 to 5);
- Part 2: Norfloxacin (NF) concentration is varied, concentrations of all other reagents being constant (lines 6 to 10);
- Part 3: NaOH concentration is varied, concentrations of all other reagents being constant (lines 11 to 16).

| | $[MnO_4^-]\cdot10^4$ M | $[NF]\cdot10^3$ M | $[OH^-]\cdot10^2$ M | $[ClO_4^-]\cdot10^2$ M | $k_{obs}$ |
|---|---|---|---|---|---|
| 1 | 0.4 | 1.0 | 5.0 | 5.0 | |
| 2 | 0.8 | 1.0 | 5.0 | 5.0 | |
| 3 | 1.0 | 1.0 | 5.0 | 5.0 | |
| 4 | 2.0 | 1.0 | 5.0 | 5.0 | |
| 5 | 4.0 | 1.0 | 5.0 | 5.0 | |
| 6 | 1.0 | 0.8 | 5.0 | 5.0 | |
| 7 | 1.0 | 1.0 | 5.0 | 5.0 | |
| 8 | 1.0 | 4.0 | 5.0 | 5.0 | |
| 9 | 1.0 | 6.0 | 5.0 | 5.0 | |
| 10 | 1.0 | 8.0 | 5.0 | 5.0 | |
| 11 | 1.0 | 1.0 | 1.0 | 5.0 | |
| 12 | 1.0 | 1.0 | 2.0 | 5.0 | |
| 13 | 1.0 | 1.0 | 5.0 | 5.0 | |
| 14 | 1.0 | 1.0 | 6.0 | 5.0 | |
| 15 | 1.0 | 1.0 | 8.0 | 5.0 | |
| 16 | 1.0 | 1.0 | 10.0 | 5.0 | |

## C. Determination of the reaction orders

1) Adjust the temperature of the thermostated cell unit to 25 °C.

2) Place the flasks with the stock solutions in the thermostat and let the solutions attain the desired temperature. Check the temperatures inside the flasks from time to time with the thermometer. Always carefully wash the thermometer with water before placing it in the next flask.

3) When ready with the temperature of the solutions, use the spectrophotometer cell to prepare the mixture containing $KMnO_4$, NaOH, and $NaClO_4$ in concentrations as indicated in the corresponding line in the Table. Add the Norfloxacin solution last (note that its introduction initiates the reaction) and promptly place the cell into the thermostated cell holder.

**Note**. If a thermostated cell holder is not available, fulfill the task at room temperature having in mind that temperature alterations will produce only slight effect on the results of kinetic studies.

4) Immediately start recording the absorbance at the wavelength of 525 nm. Continue measuring till the absorbance remains constant ($A_\infty$).

5) Plot the obtained data as the dependence of $\log(A_t - A_\infty)$ on time ($A_t$ is the reaction mixture absorbance at time $t$).

6) Carefully wash the cell with plenty of water, dry the cell and wipe the walls with clean tissue.

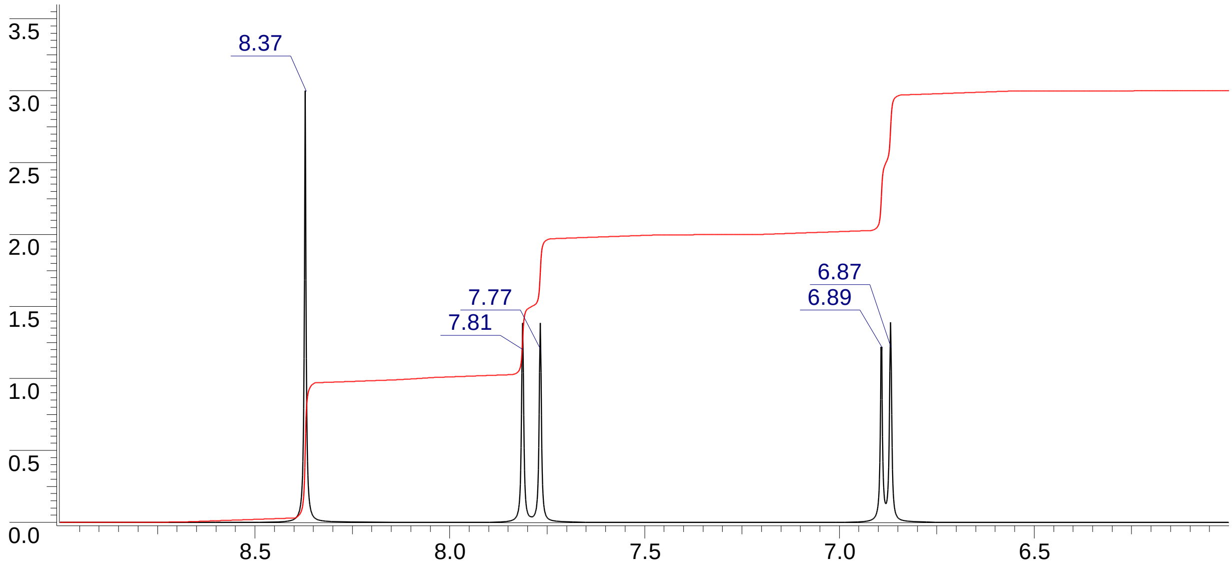
7) Use the initial straight part of the curve to calculate the observed rate constant of Norfloxacin oxidation. Write down the value in the Table.

8) Repeat steps 3-7 for all the lines of the Table.

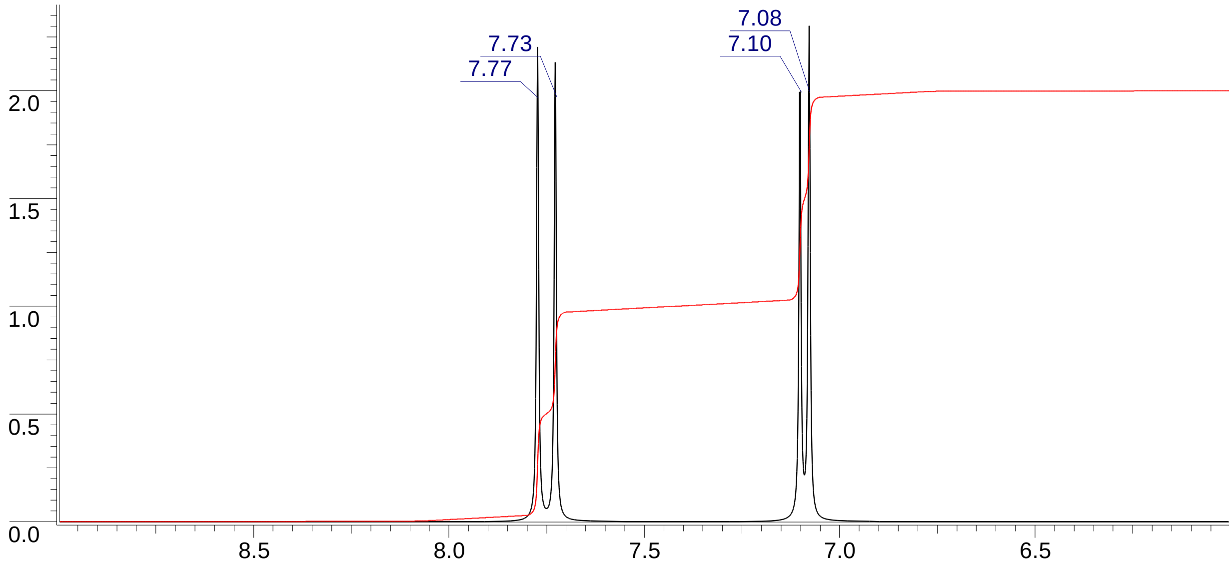
## D. Questions and Data Analysis

**1a.** Propose the structure of the oxidized product **A** based on data given below:

- mass spectrum of the product **A** have peaks with m/z = 335, 321, and 64;
- NMR spectra (aromatic region) of Norfloxacin and the product **A** are as follows:



$^1$H NMR spectrum (300 MHz, 5% NaOD/D$_2$O, aromatic region) of Norfloxacin



$^1$H NMR spectrum (300 MHz, 5% NaOD/D$_2$O, aromatic region) of the product **A**.

**1b.** Explain the $^1$H NMR spectral pattern of Norfloxacin in the aromatic region.

**2.** Propose coordinates allowing determination of the reaction order with respect to a reagent.

**3.** Using the found values of $k_{obs}$ and compositions of the mixtures, sketch the necessary plots and determine the reaction orders with respect to permanganate, Norfloxacin, and alkali.

**Note**. You are expected to fulfill this item by using the English version of Microsoft Excel software.

**4.** Write down the expression for calculation of the rate of Norfloxacin oxidation with permanganate.

The mechanism of Norfloxacin oxidation by alkaline manganese(VII) is given hereunder (**B** and **C** are intermediates of the process).

$$MnO_4^- + OH^- \overset{K_1}{\rightleftharpoons} [MnO_4OH]^{2-}$$

$$NF + [MnO_4OH]^{2-} \overset{K_2}{\rightleftharpoons} \mathbf{B}$$

$$\mathbf{B} \xrightarrow[\text{slow}]{k_1} \mathbf{C} + MnO_4^{2-} + H_2O$$

$$\mathbf{C} + [MnO_4OH]^{2-} \xrightarrow[\text{fast}]{k_2} \mathbf{A} + MnO_4^{2-}$$

**5a.** Propose the structures of **B** and **C**. Note that **C** is a radical.

**5b.** Propose the expression for the rate of Norfloxacin oxidation with permanganate according to the above scheme.

## Problem 34. Temperature dependence of the reaction rate of disproportionation

Autocatalytic reaction is a chemical process in which at least one of the reactants turns out to be also a product. The rate equations for autocatalytic reactions are fundamentally nonlinear. Oxidation of oxalic acid with permanganate is one of famous examples of such reactions. When no manganese(II) ions are added into the system, the reaction initially proceeds slowly. Still, at a particular moment the rate gradually increases because the product autocatalyzes the reaction. Addition of a few crystals of $MnSO_4$ greatly accelerates the reduction of purple permanganate affording a grayish-brown complex ion **A**. This complex ion is characterized by an extremely low stability in water and practically immediately starts decomposing via disproportionation giving colorless products.

The progress of the disproportionation reaction can be followed photometrically at the wavelength of 405 nm corresponding to the maximum absorbance of the trioxalomanganesate ion. Since potassium permanganate is rapidly and quantitatively consumed in the reaction and all the rest substances found in the reaction mixture are colorless, the measured value of the absorbance ($A$) is proportional to the complex ion concentration ($c$) according to Beer-Lambert-Bouguer law:

$$A = \varepsilon c l$$

where $\varepsilon$ is the molar extinction coefficient and $l$ is the optical path length.

**Chemicals and reagents:**

- Potassium permanganate
- Manganese(II) sulfate
- Oxalic acid

| Substance | Name | State | GHS Hazard Statement |
|---|---|---|---|
| $KMnO_4$ | Potassium permanganate | aqueous solution | H272, H302, H400, H410 |
| $MnSO_4$ | Manganese(II) sulfate | aqueous solution | H373, H411 |
| $C_2H_2O_4$ | Oxalic acid | aqueous solution | H314, H318 |

**Equipment and glassware:**

- Analytical balance (± 0.0001 g)
- Visible spectrophotometer (or photometer with fixed wavelength of 405 nm) equipped with thermostated cell holder
- Spectrophotometer cells
- Tissue to clear cell surfaces
- Thermostat
- Thermometer
- PC (or other computing techniques) with Microsoft Excel software (English version)
- Volumetric flask, 100 mL, with a tight stopper (4 ea.)
- Graduated cylinder, 100 mL
- Volumetric pipettes, 5 and 10 mL
- Pipette filler
- Spatula

## Procedure

### A. Preparation of stock solutions

Read the Procedure to the end and calculate the concentrations of stock solutions of potassium permanganate, manganese(II) sulfate, and oxalic acid that will allow easy preparation of the reaction mixture to be analyzed. Prepare the stock solutions of potassium permanganate, manganese(II) sulfate, and oxalic acid in the volumetric flasks according to standard procedures.

## B. General design of the task

The reactions are carried out at five different temperatures, always with the same concentrations of the reagents (0.012 M manganese(II) sulfate, 0.085 M oxalic acid, and 0.002 M potassium permanganate). The disproportionation progress is always followed photometrically at the wavelength of 405 nm by detecting the decrease of the complex ion concentration. The reactions are first conducted at a temperature between 20 and 25 $^{o}$C. When changing to new conditions, the temperature is always increased by about 10 $^{o}$C. Carefully fix the actual temperatures studied. This will be of importance in order to get reliable results when analyzing the experimental data.

## C. Determination of the temperature dependence of the reaction rate

1) Prepare the mixture containing $MnSO_4$ and oxalic acid in the required concentrations in the volumetric flask.

2) Adjust the temperature of the thermostated cell unit and that of the thermostat to the required temperature. Place the flasks with the reaction mixture and potassium permanganate stock solution in the thermostat and let the mixture and the solution attain the desired temperature. Check the temperatures inside the flasks from time to time with the thermometer. Always carefully wash the thermometer with water before placing it in the next flask.

3) When ready with temperatures, add the required amount of potassium permanganate stock solution and mix well for 2-3 s. Transfer the mixture promptly to the photometer cell, place the cell into the cell holder and immediately start recording the absorbance.

Note. The thermostated cell holder is desirable, still can be omitted, since the reaction is completed within a short period of time. As a result, the temperature alterations will produce only slight effect on the results of kinetic studies.

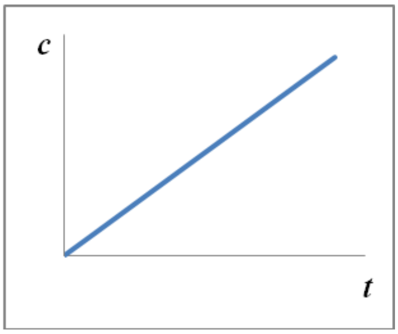
4) Continue recording the absorbance till the reaction mixture turns colorless.

5) Carefully wash the cell with plenty of water, dry the cell and wipe the walls with clean tissue.

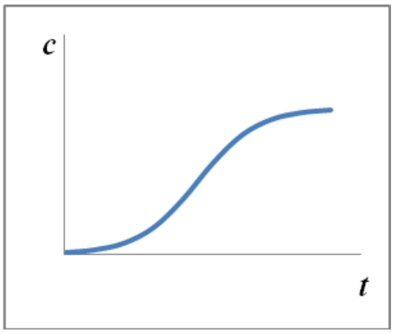
6) Repeat the steps 2-5 for the other four temperatures.

## D. Questions and Data Analysis

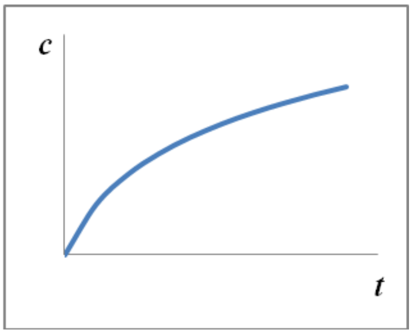
**1.** Choose the plot which corresponds to the autocatalytic reaction (c is the product concentration, and t is time)



**a**



**b**



**c**

**2.** Propose the formula of the ion **A** if it known that its charge is –3 and it contains 17.22% of manganese.

**3.** Write down the equation of the formation of **A**.

**4.** Write down the equation of the disproportionation of **A**.

**5.** Graphically determine the general reaction order by testing the first and second order coordinates and choosing which of these provide for the best fit.

**6.** For each temperature studied, draw a plot in the coordinates chosen in i. 2 and determine the value of the rate constant. Hint: use the initial section of plot.

**7.** Calculate the activation energy of the disproportionation reaction.

**Note**. You are expected to fulfill ii. 5-7 by using the English version of Microsoft Excel software.