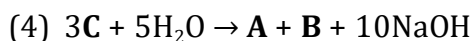
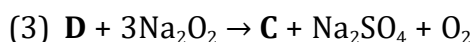
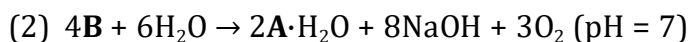
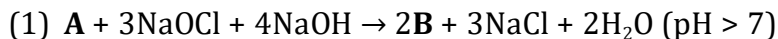


16th BChO, 2008, Vilnius, Lithuania

Problem 1 – ABC, CRYSTAL – A mysterious substance

Part I.

Compound **A** is an oxide and compound **D** is a salt (sulfate). Using chemical equations and data given below, identify compounds **A–D**. Support your answers with calculations.



The color of the solution, containing compound **B**, is deep red-purple. If 0.10 g of compound **C** is dissolved in 100 cm³ distilled water, the pH of the solution becomes 12.2 (**B** fully dissociates).

a) Write chemical formulas for compounds **A–D**.

Part II.

Wustite is a mineral form of iron(II) oxide. It is a non-stoichiometric compound as it is always Fe-deficient and is formulated as Fe_{1-x}O (0.04 < x < 0.11). To counter the charge imbalance caused by Fe²⁺ vacancies, some Fe³⁺ ions are present in the lattice.

b) How many Fe³⁺ ions are needed to counter one Fe²⁺ ion vacancy?

c) Express the ratio $n(\text{Fe}^{3+})/n(\text{Fe}^{2+})$ as a function of x.

Iron atoms in wustite form a face-centered-cubic lattice. The oxygen atoms occupy octahedral gaps between iron atoms.

d) Calculate the lattice constant and the distance between the two closest iron atoms (in Å) in wustite (Fe_{0.925}O, density 6.02 g cm⁻³).

e) Calculate the distance between the two closest oxygen atoms in wustite.

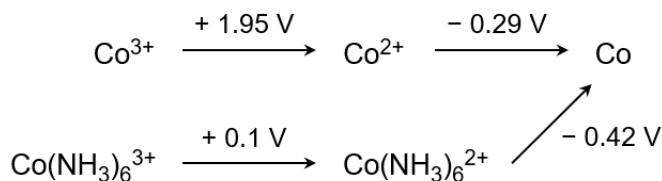
f) Express density as a function of x, assuming that the lattice parameter does not change in the given interval of x.

Problem 2 – ELECTRO, STRUCT – Cobalt-Chameleon

Cobalt is one of the most well-known metals. Since ancient times, cobalt salts have been used to color glass and make enamels. Various cobalt compounds were found in sculptures of ancient Egypt, Persian jewelry, and among the remains of the city of Pompey.

For more than 100 years, scientists have been interested in complex cobalt salts, in which the oxidation state of the metal is +3 rather than the more common +2.

a) Using the given Latimer diagram of cobalt, prove mathematically whether it is possible for cobalt(II) to undergo disproportionation in acidic media. Explain why the more stable oxidation state for complex cobalt ions is +3, whereas for classical cobalt ions it is +2.



At the end of the 19th century, investigations of cobalt complexes with amines gained high popularity, for example, compounds with a general formula $[\text{Co}(\text{NH}_3)_{6-x}\text{Cl}_x]\text{Cl}_{3-x}$, where x is a small natural number.

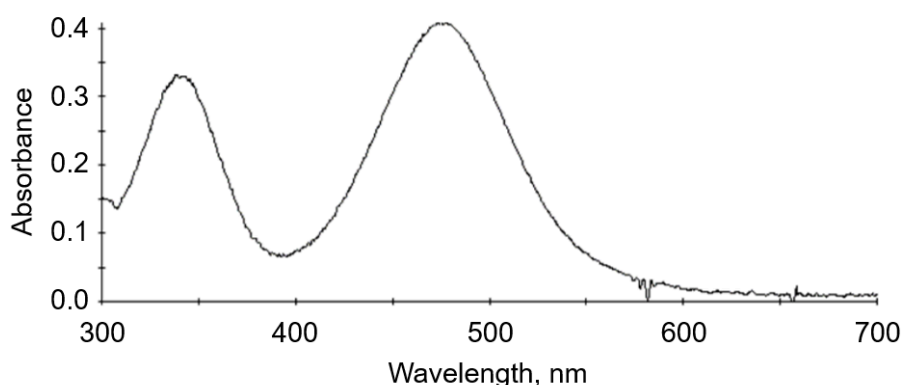
- b) Write all possible isomers for compounds with this general formula, assuming that the coordination number of cobalt is 6 and the oxidation state is +3.
- c) The stability of complex ions can be evaluated based on electrochemical measurements. Using the given data, calculate the stability constants for cobalt(II) and cobalt(III) complexes with amines.

At the beginning of the 20th century, complexes of cobalt with organic molecules were widely investigated, for example, the well-known cobalt complex with ethylenediamine (en).

- d) Write the formula of this compound, provide the structures of all possible isomers and explain the difference in physical properties of these isomers. What type of ligands does ethylene diamine belong to? In this regard, what is its difference from ammonia and chloride anion?

It is well-known that d -orbitals can be split into numerous sublevels by the ligand field.

- e) Provide a diagram of split d -orbitals of the cobalt in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ complex. For every energy level, give the index of the d -orbital from which the new orbital was formed. Explain your choice.
- f) Based on the spectrum provided below, calculate the energy difference between d -orbitals.



Problem 3 – KINETICS – Negative activation energy!?

According to the results of the investigation, the direct reaction $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ has a negative apparent activation energy.

	$[\text{NO}], [\text{M}]$	$[\text{O}_2], [\text{M}]$	$r = d[\text{NO}]/dt, [\text{M s}^{-1}]$
1	0.010	0.010	$2.5 \cdot 10^{-5}$
2	0.020	0.010	$1.0 \cdot 10^{-4}$
3	0.010	0.020	$5.0 \cdot 10^{-5}$

- a) Determine the partial reaction orders based on the data given in the table.
- b) Calculate the rate constant k .

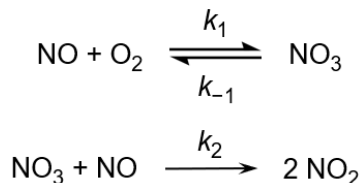
The rate constant (k') of the reverse reaction at 327 °C and 372 °C is 83.9 and 407 $\text{M}^{-1} \text{s}^{-1}$.

- c) Calculate the activation energy of the reverse reaction (E_a').
- d) Calculate the reaction enthalpy ΔH_r according to the data given in the table.

	NO	NO ₂
ΔH_f [kJ mol ⁻¹ K ⁻¹]	90.29	33.10

- e) Sketch the reaction energy diagram in the coordinates energy vs reaction coordinate, and mark E_a , E_a' , ΔH_r on it.

Based on experimental data, the following reaction mechanism was suggested:



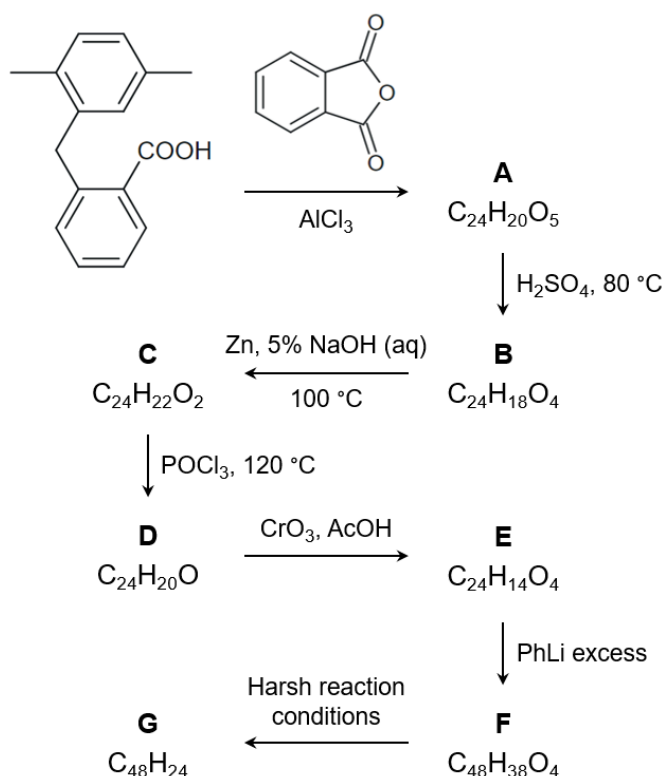
- f) Derive the rate equation.
- g) Decide whether the suggested mechanism supports kinetic and thermodynamic data. Explain why the value of the apparent activation energy is less than zero and the dependence of the rate constant of a direct reaction on temperature

Problem 4 – SYNTH – An elegant compound of the last century

The target compound **G** in this problem is a polycyclic aromatic hydrocarbon. It was first synthesized in 1964 by Professor Erich Clar at the University of Glasgow. At the time of the synthesis, this type of compound was associated with the investigation of theoretical problems of aromaticity. In modern times, with the rapid developments in the field of nanoscience, these compounds find their use as novel materials used as liquid crystals and synthetic “metals”.

Draw the structural formulas of compounds **A–G** in the scheme provided below. Pay particular attention to the following notes:

- (1) Dicarboxylic acid **A** is the major isomer of all the possible products in this acylation reaction.
- (2) In compound **B**, there is only one new ring formed.
- (3) Compound **D** is pentacyclic.
- (4) The ¹H NMR spectrum of compound **E** has three sets of signals with relative intensities of 1 : 1 : 3.
- (5) The last chemical transformation is lousy in terms of chemical yield but it does provide an elegant structure **G**.



Problem 5 – APPLIED, ELECTRO, THERMO – Li-ion battery

Video cameras, smartphones, laptops, etc, require a portable power source – batteries. The ideal battery is reliable, lightweight, long-lasting, stable, and environmentally safe. A battery consists of anode, cathode, and electrolyte.

Metal	Li	Ca	Al	Cd
ρ [g cm ⁻³]	0.53	1.54	2.70	8.64
E° [V]	-3.04	-2.87	-1.66	-0.40

The table provides density and standard potential for metals that are usually used as anodes.

- Write the half-reactions of these metals.
- Calculate the electrochemical capacity of these metals. The electrochemical capacity is defined as the maximal quantity of electric charge produced per 1 g of metal (A h g⁻¹).
- Which metal is most suitable for the battery anode? Provide two reasons.

The standard reduction potential of water is -0.83 V.

- Write the reduction reaction of water.
- Which of the listed metals react with water at room temperature? Write the reaction equations and explain the answer.
- Calculate the equilibrium constant for the reaction between water and lithium. Is the process spontaneous? Provide an explanation.

The ions solvate in the electrolyte during the oxidation of the metal. The formed solution must be a good electrolyte. Lithium hexafluorophosphate(V) is added to the solvent to increase its electrical conductivity.

- Which of the solvents: (a) water, (b) ethanol, (c) dimethyl sulfoxide, (d) hexane is the most suitable for a lithium battery? Provide an explanation.

Compounds	Bi ₂ O ₃	FeS ₂	LiCl	Li ₂ O	Li ₂ S	CuCl ₂
ΔG_f°	-493	-160	-384	-562	-439	-382

- Draw the spatial structures of dimethyl sulfoxide and lithium hexafluorophosphate(V) using the VSEPR model. Write the hybridization and partial charge of S and P atoms.

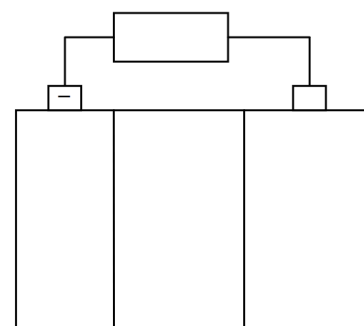
Sulfides, oxides and halogenides are used as materials for cathodes.

- Write the equation of the total reaction in the lithium battery if the cathode is (a) Bi₂O₃, (b) FeS₂, (c) CuCl₂ and the metal will be released as an element. For which battery (a-c) is the maximum non-expansion work of the reaction largest?

FeS₂ was used as the cathode of the lithium battery and the electrolyte was LiPF₆ solvated in dimethyl sulfoxide.

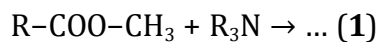
- Write the shorthand notation of the lithium battery. Write the cathodic half-reaction and calculate its standard potential.
- Rewrite on the block diagram of the lithium battery: Li, FeS₂, lithium hexafluorophosphate(V), „+“, dimethyl sulfoxide, anode (A), cathode (K), electrolyte and engine. Mark the direction of the movement of electrons in the outer circuit.

- Which material should be in excess in the lithium battery? Why?



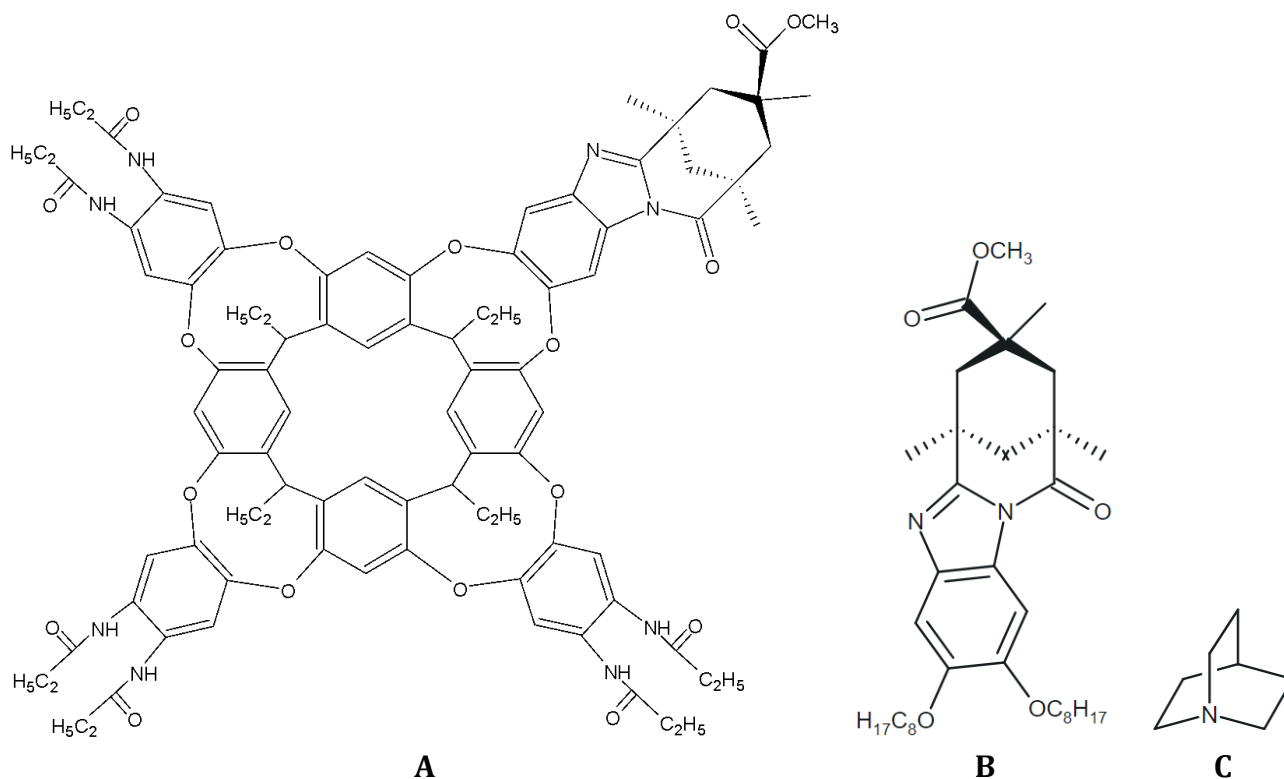
Problem 6 – CALC, MECH, STEREO – Supramolecular basket

It is well known that carboxylic acid methyl esters react with tertiary amines:

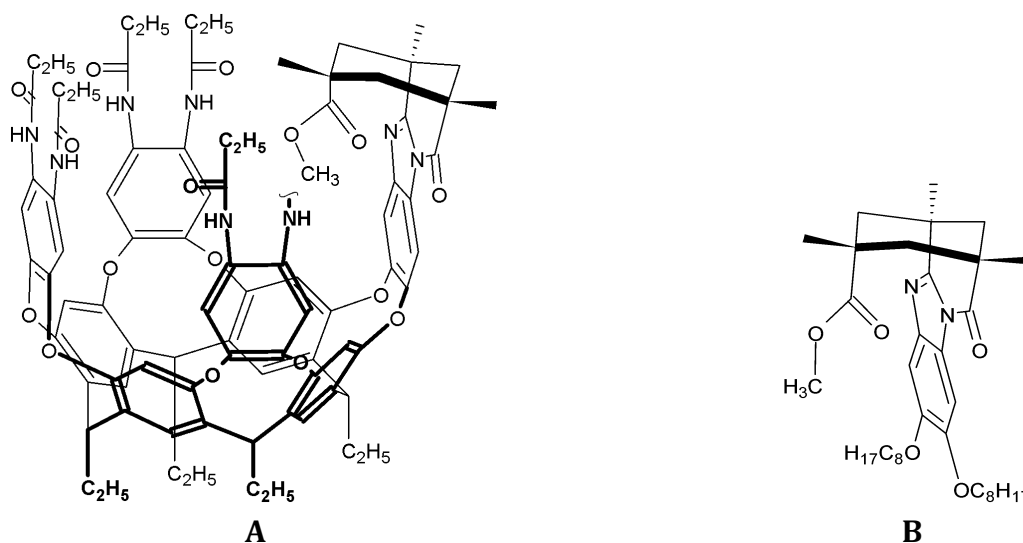


- a) Write the reaction products and the mechanism.
- b) The reaction is generally slow, taking hours to days. Why does **reaction 1** proceed faster in polar solvents like dimethylformamide than in non-polar ones like heptane?

Compounds **A** and **B** are esters, which react with quinuclidine **C** in the same manner as is shown in **reaction 1**. Despite the fact that atoms near ester groups in compounds **A** and **B** are exactly the same, the quinuclidine reaction with ester **A** in mesitylene (1,3,5-trimethylbenzene) completes in 3 minutes, however, the reaction of compound **B** and quinuclidine at the same conditions is so slow that it is practically not observed.

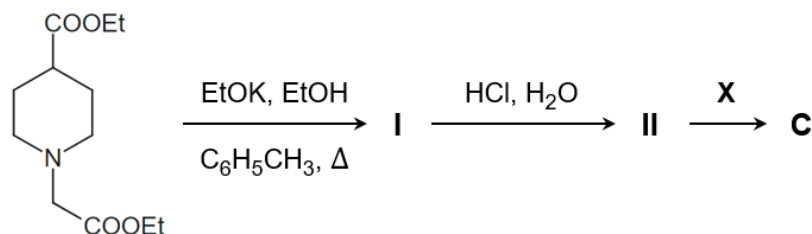


The three-dimensional structures of compounds **A** and **B** are as follows:



- c) Explain why ester **A** in mesitylene does not have a plain structure but has a cavitated shape.

- d) Complete the synthesis of quinuclidine identifying intermediate products **I** and **II**, write the mechanism of the formation of compound **I**, and give the reagent **X** in the last step. Draw the three-dimensional shape of quinuclidine **C**. Identify chiral atoms in structures **II** and **C**.



- e) Draw the three-dimensional structure of the transition complex of the reaction between ester **A** and quinuclidine and write a reaction product. (Draw schematically, don't waste your time keeping exact proportions and drawing every bond and atom. Show only the general shape of molecules, their location and the position of ester methyl and carboxyl atoms with respect to the quinuclidine nitrogen atom).
- f) It is calculated that the volume of the ester's **A** cavity is $160 \text{ \AA}^3$. Consider the shape of the cavity as a sphere, all the bonds in a quinuclidine molecule are $1.2 \text{ \AA}$ and the radius of a hydrogen atom is $1.2 \text{ \AA}$. Estimate approximately the size of the quinuclidine molecule and calculate how many quinuclidine molecules can fit into the cavity of one "basket" of ester **A**.
- g) Calculate the quinuclidine concentration (M) in a cavity.
- h) When quinuclidine is mixed with ester **A** in chloroform (trichloromethane), the reaction is as slow as the reaction of quinuclidine with ester **B**. Explain this result.