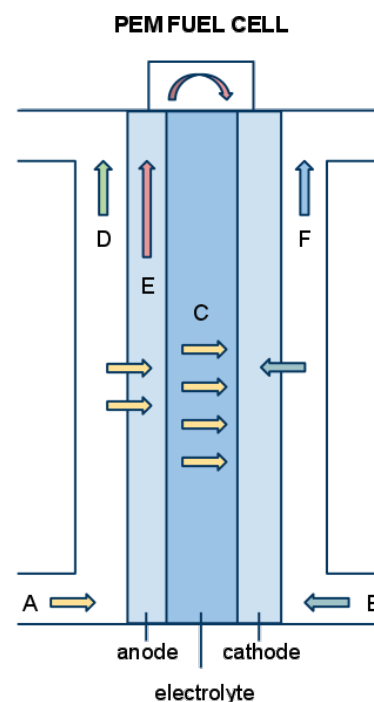


Problem 1 – APPLIED, THERMO – Ethanol as a source of energy

Since ancient times, ethanol has been used for lamp oil and cooking, along with plant and animal oils. Nowadays, the vast majority of ethanol is used as fuel and is produced on a large scale by fermentation, in which certain species of yeast metabolize sugar producing ethanol. It can be said that sunlight is used to run the engine of a vehicle, as a simple sugar is created in the plant by photosynthesis, and during ethanol combustion, carbon dioxide and water are produced with a release of energy.

- a) Write chemical equations for sugar synthesis, ethanol production and combustion.

Early in 1860, Nikolaus August Otto used ethyl alcohol as fuel for an internal combustion engine. Today, ethanol may be used as a fuel to power both direct-ethanol fuel cells (DEFC) and combustion engines. One of the first DEFC, for which a schematic diagram is given above, was introduced in the ShellEco-Marathon in 2007.



- b) Identify chemical species A–F in the figure.

- c) From thermodynamic data, calculate DEFC maximal energy conversion efficiency ratio: $\eta = \Delta_r G^\circ / \Delta_r H^\circ$ (25 °C).

Compounds	O ₂	H ₂	CO ₂	H ₂ O	C ₂ H ₅ OH	C ₆ H ₁₂ O ₆
$\Delta_r H^\circ$, kJ mol ⁻¹	0	0	-394	-286	-278	-1273
S° , J mol ⁻¹ K ⁻¹	205	131	214	70	161	212

- d) For comparison, calculate the efficiency of the combustion engine running on Otto cycle using the equation for maximal efficiency: $\eta = 1 - 1/r^{(\gamma-1)}$, where $\gamma = C_p/C_v \approx 1.4$, r is compression ratio which equals 9 and 12.5 for ethanol and gasoline, respectively. Assume that only half of the efficiency is achieved in practice.

There are several unsolved issues concerning DEFC, thus, in closer perspective, it is more promising to convert ethanol into hydrogen in order to use the latter in a typical hydrogen fuel cell.

- e) Using the given data, calculate the maximal energy conversion efficiency ratio ($\eta = \Delta_r G^\circ / \Delta_r H^\circ$) of the hydrogen fuel cell.

To be more realistic, it should be considered that in order to move a vehicle, the electric energy must be converted into mechanical energy. Let's assume that the conversion efficiency of subsystems is: 90% for inverter, 90% for motor, and 90% for gas compressor. The overall conversion efficiency ratio may be compared to the energy conversion efficiency ratio of a combustion engine in which chemical energy is directly converted to mechanical energy.

- f) Estimate the overall efficiency of a hydrogen vehicle.
- g) Name one to two main advantages of using i) ethanol over gasoline fuel in internal combustion engine; ii) fuel cell over internal combustion engine.

Problem 2 – CALC, KINETICS, STRUCT – Synthesis and aquation of fluoropentaaquachromium(III) ion

5.0 cm³ 2.0 M chromium(III) perchlorate and 5.0 cm³ 2.0 M potassium fluoride were brought together; the solution was boiled under reflux for 3 hours and cooled to 0 °C, and the precipitate **X** was removed. The density of all solutions is 1.1 g cm⁻³. In the water solution, the chromium(III) perchlorate is presented as aquachromium cation with a coordination number equal to six.

a) Write the formula for aquachromium cation and precipitate **X**.

During reflux, the water in the inner sphere of the complex is replaced by anion.

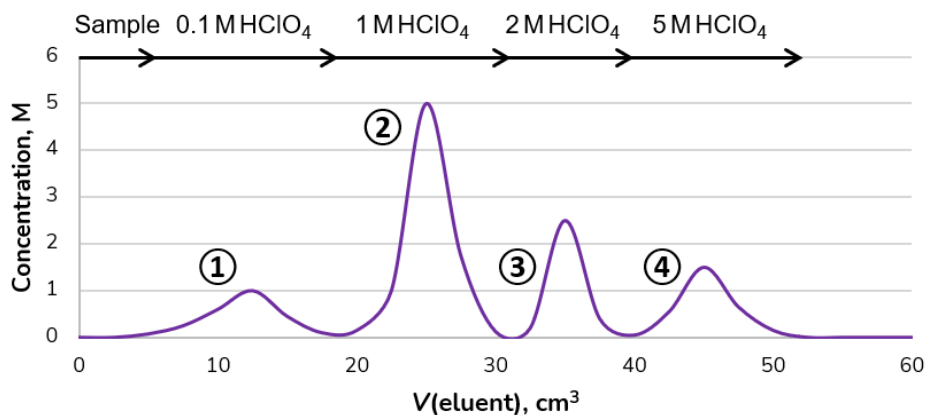
b) Write the equation of reaction.

The solubility product of the salt **X** is $K_{sp} = 2.9 \cdot 10^{-3}$ at 0 °C, but it is possible to dissolve 10.9 g of the salt in 50 g water at 100 °C ($\rho = 1.1 \text{ g cm}^{-3}$).

c) Calculate how many grams of salt **X** precipitated during the cooling process.

The reaction mixture contained various complexes of chromium. Cation-exchange (contains R-SO₃H groups) separation allowed isolation of hexaaquachromium(III) ions, fluoropentaaquachromium(III) ions, difluorotetraaquachromium(III) ions and hydrolytic dimers of chromium. During the elution process, the sample was first taken into the column and afterwards the ions were eluted out using HClO₄ with varying concentrations.

d) Identify which species the peaks correspond to on the chromatogram. Which compound would come out of the column during the process of taking the sample into the column?



The contents of chromium and fluoride in purified fluoropentaaquachromium(III) ions were established. 10.0 cm³ of the sample was first decomposed using the alkaline solution of hydrogen peroxide. The fluoride ion is liberated and the oxidation state of chromium changes from III to VI. After that, the sample was divided into two equal parts. The first part was acidified using concentrated HCl and then 3 g KI was added. After 5 min, the solution was titrated using 18.5 cm³ 0.0975 M Na₂S₂O₃. The endpoint was determined using the starch solution. The second part was analyzed using the fluoride ion selective electrode which was calibrated using solutions with known concentration of F⁻. The equation of the calibration curve was $E = 183 \text{ mV} - 56 \text{ mV} \cdot \log[F^-]$. The reading of the voltmeter was 252.6 mV and the final volume of the solution was 10 cm³ after adjusting the pH of the solution to six.

e) Write all the equations of chemical reactions in the analysis process and calculate the ratio of $n(F)/n(Cr)$ in the sample.

The pseudo first order rate coefficient of aquation of fluoropentaaquachromium(III) ion $[\text{Cr}(\text{H}_2\text{O})_5\text{F}]^{2+} + \text{H}^+ + \text{H}_2\text{O} = [\text{Cr}(\text{H}_2\text{O})_6]^{3+} + \text{HF}$ ($\Delta H_r = -5.41 \text{ kJ mol}^{-1}$) is

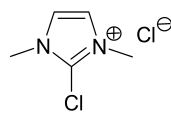
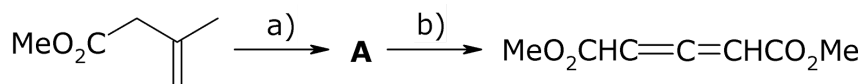
$$k = \frac{2.303 \left([\text{CrF}^{2+}]_0 - [\text{CrF}^{2+}]_\infty \right)}{t \left([\text{CrF}^{2+}]_0 + [\text{CrF}^{2+}]_\infty \right)} \log \frac{[\text{CrF}^{2+}]_0^2 - [\text{CrF}^{2+}] [\text{CrF}^{2+}]_\infty}{[\text{CrF}^{2+}]_0 \left([\text{CrF}^{2+}] - [\text{CrF}^{2+}]_\infty \right)}$$

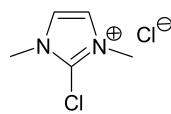
where $[\text{CrF}^{2+}]_0 = 5.28 \cdot 10^{-3} \text{ M}$ is the starting concentration and $[\text{CrF}^{2+}]_\infty$ is equilibrium concentration of the complex ion.

- f) Calculate the time t (h) needed to aquate 70% of the complex ion at 77.2°C if the concentration of hydrogen ions is 0.414 M , the rate constant is $4.40 \cdot 10^{-6} \text{ s}^{-1}$ and the equilibrium constant of the reaction is 0.048 . The water is in excess and not included in the equilibrium constant.
- g) Calculate $\text{p}K_a(\text{HF})$ at 25°C if the equilibrium constant of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + \text{F}^- \rightleftharpoons [\text{Cr}(\text{H}_2\text{O})_5\text{F}]^{2+} + \text{H}_2\text{O}$ reaction is $K = 2.1 \cdot 10^4$.

Problem 3 – STEREO – Asymmetry without asymmetric center

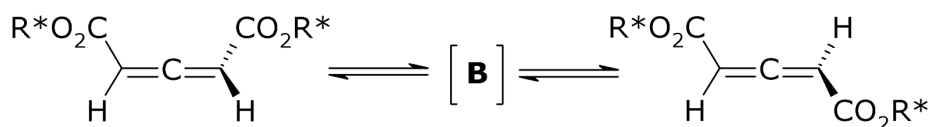
Allenes are not only versatile starting materials in organic synthesis but also present an interesting case of molecular chirality. Since it is quite difficult to synthesize allenes in a stereoselective manner, they are first obtained as a racemic mixture and then resolved into individual enantiomers. One of the ways of synthesizing allenes is depicted below.



(1) $i\text{-Pr}_2\text{NLi}$, THF; then the addition of $(\text{CH}_3\text{O})_2\text{O}$; (2) , Et_3N , CH_2Cl_2 .

- a) Identify symmetric structure **A**. Keep in mind that this reaction is not very efficient and **A** is only one of few possible products in this reaction.
- b) Provide the mechanism for the conversion of **A** into an allene.

One of the methods to produce allenes in pure enantiomeric form is dynamic resolution of racemic mixtures. The method takes advantage of quick epimerization and the low solubility of one of the stereoisomers. Epimerization means interconversion of one enantiomer into another proceeding through a common intermediate **B** (see the scheme below). Since all of the compounds are in equilibrium, the position of the equilibrium is shifted in the direction of the less soluble stereoisomer, which is then collected as a precipitate.



Reaction conditions: room temperature, Et_3N (0.05 eq), pentane; R^* is (–)-menthyl.

- c) Draw structural formula of **B**.

In order to establish the absolute configuration of the allene **X** obtained by dynamic resolution, one can follow a method developed by Agosta in 1964. To better understand the essence of the method let us consider all transformations performed on both enantiomers.

The allene ester is first hydrolyzed to dicarboxylic acid and then in Diels-Alder reaction with cyclopentadiene is transformed into a mixture of separable products.

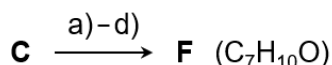
- d)** Provide structures for all possible adducts with cyclopentadiene that could be formed from each allene enantiomer (C_{1-4} from one allene enantiomer and C_{5-8} from the other).

Each of the individual compounds C_{1-8} is then subjected to 2 test reactions: a) iodolactonization (I_2 , $NaHCO_3$) and b) cyclic anhydride formation (acetic anhydride).



- e)** In your list of adducts, identify which structures C_{1-8} are capable of giving desired products in both test reactions. Draw an equation for one iodolactonization reaction (**D**) and one cyclic anhydride formation (**E**).

The compound(s) **C** that gives positive results in both test reactions is (are) then degraded according to the following scheme: a) Pd/C , H_2 ; b) CH_2N_2 ; c) O_3 ; d) HCl , reflux.



In summary, the explicit assignment of the absolute configuration by the method of Agosta is based on the fact that one enantiomer of **F** can only be produced from (*R*)-allene, while the opposite enantiomer of **F** stems only from the (*S*)-allene.

- f)** In the aforementioned case of dynamic resolution of allenes, the degradation yields exclusively (1*S*,4*R*)-**F** stereoisomer. Draw the structure of **F**.
- g)** Based on the structure of compound (1*S*,4*R*)-**F** and the identification method by Agosta, suggest the structure of allene **X** which was obtained by dynamic resolution.

Problem 4 – ABC, CRYSTAL, EQUIL – Environmental hazards

Around World War II, the Jinzu River in Toyama prefecture, Japan, was contaminated with element X_1 compounds and nowadays, Japan is still one of the top three producers of this element. Element X_1 accumulates in rice and can cause Itai-Itai disease in humans; it also replaces calcium in bones. This element is produced from compound **A** which is its only mineral of practical importance. Compound **A** is also a direct band gap semiconductor and has many applications, for example, in light detectors and as thermally stable pigments.

Binary compound **A** also contains nonmetallic element Y_1 and this compound forms minerals greenockite (first discovered in Scotland and named after the landowner Lord Greenock) and hawleyite. The first mineral has a hexagonal structure, while the second mineral has a cubic structure. The mass fraction of X_1 in compound **A** is 77.6%.

Element X_1 can be obtained from **A** by roasting it in air. Obtained oxide is treated with sulfur trioxide to form X_1 sulfate which is dissolved in water and electrolyzed.

- a)** Determine element X_1 .
- b)** Write equations for all mentioned reactions taking place in element production.
- c)** Calculate the mass of metal X_1 which can be obtained by electrolysis of 0.15 M metal sulfate solution with a 0.50 A current that is one hour long.
- d)** Write an electron formula for element X_1 ions in sulfate solution, knowing that there are no *f* electrons in this ion.

- e) The table with lattice parameters for greenockite and hawleyite is shown below. Calculate Z value (number of “molecules” in a unit cell) for hawleyite and the density for greenockite.

Parameter	Greenockite	Hawleyite
System	hexagonal	cubic
Parameters	$a = b = 3.82 \text{ \AA}$ $c = 6.26 \text{ \AA}, \gamma = 120^\circ$	$a = 5.818 \text{ \AA}$
Z	2	?
Density	?	4.87 g cm^{-3}

Practically important is also compound **B** which is used for the production of solar energy panels and which contains nonmetallic element Y_2 . The mass fraction of element X_1 in compound **B** is less than 50% and it is known that element Y_2 is in the same group as element Y_1 but electronegativity for element Y_2 is smaller than for Y_1 .

- f) Determine element Y_2 .

Usually, element X_1 is found together with element X_2 which is placed in the same group in the periodic table. Binary compound of element X_2 with Y_1 crystallizes in cubic face-centered crystals (FCC) with parameter $a = 5.406 \text{ \AA}$. The density of this compound is 4.09 g cm^{-3} .

- g) Determine element X_2 , show your calculations.

- h) Order all possible binary compounds from elements X_1 , X_2 , Y_1 and Y_2 in order of increasing covalent bond content and decreasing ionic bond content.

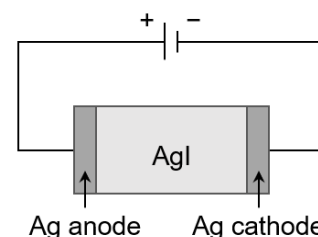
Elements X_1 and X_2 can also be separated due to different solubilities of their hydroxides. Hydroxides and carbonates are the forms of X_1 compounds which are now found in the Jinzu River bed (X_1 concentration approx. 2 ppm).

- i) Which element (X_1 or X_2) hydroxide has better solubility in alkaline solutions? Explain it using the atomic structure of elements.
- j) Calculate the solubility (M) of both compounds in water at pH = 10.0. Consider the formation of a complex ion. All necessary data are given in the following table:

	pK_{sp}	pK_1	$pK_{1,2}$	$pK_{1,2,3}$	$pK_{1,2,3,4}$
I	14.14	4.17	8.33	9.02	8.62
II	16.5	4.40	11.30	14.14	17.66

Problem 5 – CALC, CRYSTAL, ELECTRO – Half solid half melted

In 1914, Tubandt and Lorenz showed that solid silver iodide above 147°C transforms into $\alpha\text{-AgI}$ modification that is a good electrical conductor. A temperature of 147°C may be considered as the melting point for silver ion sublattice. The remaining iodide ion sublattice is stable until 557°C . It was determined that iodide ions form body-centered cubic (BCC) sublattice with lattice constant (lattice parameter) $5.04 \cdot 10^{-10} \text{ m}$. Tubandt's electrochemical cell is shown in the following scheme.



In this cell, silver electrodes 0.1000 g each were placed in contact with both sides of solid AgI pellet. Then, electric current of 35.2 mA flowed for 15.5 min . After that, silver electrodes were taken off the pellet and placed into two labeled 100.0 cm^3 volumetric flasks (label “Solution A” for anode and “Solution B” for cathode). Excess of dilute $\text{HNO}_3 (\text{aq})$ was added into both flasks. After the dissolution of metallic electrodes both volumetric flasks were filled with distilled

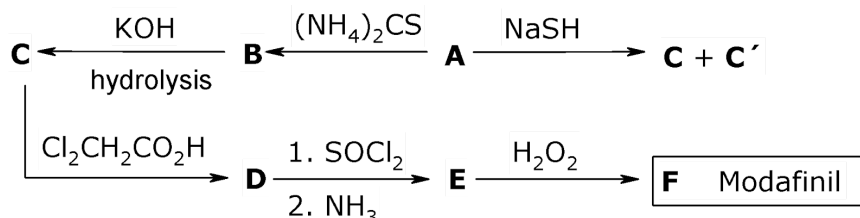
water till the calibration mark. Solution A and Solution B were used for titration of 10.00 cm³ samples of 0.0113 mol dm⁻³ NaCl solution that contains a small amount of K₂CrO₄. The endpoint for these titrations was the appearance of brick-red precipitate.

- Write half-reactions that represent what was happening at the anode and at the cathode during the electric current flow.
- Write the chemical equation describing the action of dilute HNO₃ onto electrodes.
- Write a formula for the brick-red compound that precipitates at the titration endpoint.
- Calculate the ratio $V(\text{Solution A})/V(\text{Solution B})$ (ratio of volumes of respective solutions that were used up for the titration of samples of NaCl solution).
- Determine the radius of iodide ion in the BCC sublattice.
- Calculate the density of solid AgI conductor.
- AgI is a light-sensitive compound suitable for photography. After the development of a black and white photo, the image should be "fixed" by dissolving away all the remaining silver iodide (or other silver salts). Sodium thiosulfate Na₂S₂O₃ is a suitable fixing agent. In reaction with silver iodide, it produces a compound that contains 26.9% of silver by mass. Write a chemical equation that shows what is happening during the "fixing" photo.

Problem 6 – SPECTRA, SYNTH – Modafinil – work without sleep?

Modafinil was originally created to treat narcolepsy (a condition when a person falls asleep at inappropriate times), but it spread widely among students and businessmen. Although a productive day after a sleepless night sounds unbelievable, it is not the only effect of modafinil; it also acts as an antidepressant and improves memory in some cases. Modafinil has a considerably smaller list of side effects than caffeine but due to its unknown long-term effects, it remains a prescription drug.

An industrial synthesis scheme of Modafinil is presented below. In the ¹H NMR spectrum of compound **A**, there is one singlet (6.0 ppm) and ten times more intensive multiplet (7.3 ppm). In its mass spectrum, two peaks of equal intensity for the molecular ion are observed at 246 and 248 *m/z*. After treating compound **A** with sodium hydrosulfide, a side product **C'** was detected, therefore, to avoid its formation, one additional step was introduced in the synthesis.



- Draw the structural formulas of all letter-named compounds.
- Sketch a mechanism for the reaction **D** → **E**.

Modafinil is actually a mixture of two enantiomers, where only the *R*-isomer shows the indicated biological activity.

- Draw the structural formula of Modafinil's active enantiomer.