Theoretical Exam

For marking:

Student name:					code:			
Problem #								
1	2	3	4	5	6			

April 22, 2022
Vilnius, Lithuania

Periodic table legend:

- Atomic number
- Atomic weight
- Atomic symbol
- Covalent radius, Å

Example:
1 / 1.00794 / H / 0.28

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 / 1.00794 / H / 0.28																	2 / 4.00260 / He / 1.40
2	3 / 6.941 / Li	4 / 9.01218 / Be											5 / 10.811 / B / 0.89	6 / 12.011 / C / 0.77	7 / 14.0067 / N / 0.70	8 / 15.9994 / O / 0.66	9 / 18.9984 / F / 0.64	10 / 20.1797 / Ne / 1.50
3	11 / 22.98998 / Na	12 / 24.3050 / Mg											13 / 26.9815 / Al / 1.17	14 / 28.0855 / Si / 1.10	15 / 30.9738 / P / 1.04	16 / 32.066 / S	17 / 35.4527 / Cl / 0.99	18 / 39.948 / Ar / 1.80
4	19 / 39.0983 / K	20 / 40.078 / Ca	21 / 44.9559 / Sc	22 / 47.867 / Ti / 1.46	23 / 50.9415 / V / 1.33	24 / 51.9961 / Cr / 1.25	25 / 54.9381 / Mn / 1.37	26 / 55.845 / Fe / 1.24	27 / 58.9332 / Co / 1.25	28 / 58.6934 / Ni / 1.24	29 / 63.546 / Cu / 1.28	30 / 65.39 / Zn / 1.33	31 / 69.723 / Ga / 1.35	32 / 72.61 / Ge / 1.22	33 / 74.9216 / As / 1.20	34 / 78.96 / Se / 1.18	35 / 79.904 / Br / 1.14	36 / 83.80 / Kr / 1.90
5	37 / 85.4678 / Rb	38 / 87.62 / Sr	39 / 88.9059 / Y	40 / 91.224 / Zr / 1.60	41 / 92.9064 / Nb / 1.43	42 / 95.94 / Mo / 1.37	43 / (97.905) / Tc / 1.36	44 / 101.07 / Ru / 1.34	45 / 102.906 / Rh / 1.34	46 / 106.42 / Pd / 1.37	47 / 107.868 / Ag / 1.44	48 / 112.41 / Cd / 1.49	49 / 114.818 / In / 1.67	50 / 118.710 / Sn / 1.40	51 / 121.760 / Sb / 1.45	52 / 127.60 / Te / 1.37	53 / 126.904 / I / 1.33	54 / 131.29 / Xe / 2.10
6	55 / 132.905 / Cs	56 / 137.327 / Ba	57-71 / La-Lu	72 / 178.49 / Hf / 1.59	73 / 180.948 / Ta / 1.43	74 / 183.84 / W / 1.37	75 / 186.207 / Re / 1.37	76 / 190.23 / Os / 1.35	77 / 192.217 / Ir / 1.36	78 / 195.08 / Pt / 1.38	79 / 196.967 / Au / 1.44	80 / 200.59 / Hg / 1.50	81 / 204.383 / Tl / 1.70	82 / 207.2 / Pb / 1.76	83 / 208.980 / Bi / 1.55	84 / (208.98) / Po / 1.67	85 / (210) / At	86 / (222.02) / Rn / 2.20
7	87 / (223) / Fr	88 / (226.03) / Ra / 2.25	89-103 / Ac-Lr	104 / (261.11) / Rf	105 / (262.11) / Db	106 / (263.12) / Sg	107 / (262.12) / Bh	108 / (265) / Hs	109 / (266) / Mt	110 / (271) / Ds	111 / (272) / Rg	112 / (285) / Cn	113 / (284) / Nh	114 / (289) / Fl	115 / (288) / Mc	116 / (293) / Lv	117 / (294) / Ts	118 / (294) / Og

Lanthanides:

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
138.906 / La / 1.87	140.115 / Ce / 1.83	140.908 / Pr / 1.82	144.24 / Nd / 1.81	(144.91) / Pm / 1.83	150.36 / Sm / 1.80	151.965 / Eu / 2.04	157.25 / Gd / 1.79	158.925 / Tb / 1.76	162.50 / Dy / 1.75	164.930 / Ho / 1.74	167.26 / Er / 1.73	168.934 / Tm / 1.72	173.04 / Yb / 1.94	174.04 / Lu / 1.72

Actinides:

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
(227.03) / Ac / 1.88	232.038 / Th / 1.80	231.036 / Pa / 1.56	238.029 / U / 1.38	(237.05) / Np / 1.55	(244) / Pu / 1.59	(243.06) / Am / 1.73	(247.07) / Cm / 1.74	(247.07) / Bk / 1.72	(251.08) / Cf / 1.99	(252.08) / Es / 2.03	(257.10) / Fm	(258.10) / Md	(259.1) / No	(260.1) / Lr

Constants and Formulae

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

Boltzmann constant, $k_B = 1.3807 \times 10^{-23}$ J K^{-1}

Universal gas constant, $R = 8.3145$ J K^{-1} mol^{-1} = 0.08205 atm L K^{-1} mol^{-1}

Speed of light, $c = 2.9979 \times 10^8$ m s^{-1}

Planck's constant, $h = 6.6261 \times 10^{-34}$ J s

Faraday constant, $F = 9.64853399 \times 10^4$ C

Mass of electron, $m_e = 9.10938215 \times 10^{-31}$ kg

Standard pressure, $P = 1$ bar $= 10^5$ Pa

Atmospheric pressure, $P_{atm} = 1.01325 \times 10^5$ Pa = 760 mmHg = 760 torr

Zero of the Celsius scale, 273.15 K

1 picometer (pm) $= 10^{-12}$ m;   1 Å $= 10^{-10}$ m; nanometer (nm) $= 10^{-9}$ m

1 eV $= 1.6 \times 10^{-19}$ J

1 amu $= 1.66053904 \times 10^{-27}$ kg

Ideal gas equation: $PV = nRT$

Enthalpy: $H = U - PV$

Gibbs free energy: $G = H - TS$ $\Delta G = \Delta G^o + RT \ln Q$

$$\Delta G^o = -RT \ln K = -nFE^o_{cell}$$

Entropy change: $\Delta S = \dfrac{q_{rev}}{T}$, where q_{rev} is heat for the reversible process

$$\Delta S = nR \ln \frac{V_2}{V_1}$$ (for isothermal expansion of an ideal gas)

Nernst equation: $E = E^O + \dfrac{RT}{nF} \ln \dfrac{C_{ox}}{C_{red}}$

Energy of a photon: $E = \dfrac{hc}{\lambda}$ Lambert-Beer law: $A = \log \dfrac{I_0}{I} = \varepsilon b C$

Integrated rate law

Zero order $[A] = [A]_0 - kt$ First order $\ln [A] = \ln [A]_0 - kt$

Second order $\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$

Arrhenius equation

$$k = Ae^{-E_a / RT}$$

$$\text{Code} \quad \boxed{}\boxed{}\boxed{}$$

General Directions

- Write your student code on each page.

- You have 5 hours to work on the exam problems. **Begin** only when the **START** command is given.

- You must **stop** working when the **STOP** command is given.

- The official English version of this examination is available on request only for clarification.

Problem 1. Some chemistry of element X

9 points

Element **X** is very important to industry, where it is primarily used to manufacture semiconductor electronic devices and as an additive to lead alloys. Not long ago, different compounds of **X** were also used as pesticides and even as green pigments in paint, but these practices had to be abandoned due to the toxicity of **X**. Various minerals of this element are present in the Earth's crust and the majority of them are found in China. One such mineral is tennantite, which consists of three elements - Cu, **X** and **Y**. Elements **X** and **Y** can be found in groups 15 and 16 of the periodic table, respectively.

1) Identify the elements **X**, **Y** and determine the chemical formula of tennantite. Crystallographic data for the tennatite unit cell: lattice parameter $a = 10.186$ Å, number of formula units per unit cell $Z = 2$, density $\rho = 4.6479$ g cm^{-3}. Assume that the unit cell is cubic. Elemental composition by mass: $w_{Cu} = 51.56\%$, $w_X = 20.26\%$, $w_Y = 28.18\%$. (6 points)

X -

Y -

The chemical formula of tennantite is   .

Let us consider the production of **X**-containing compounds starting from this mineral.

Tennantite

Tennantite

$\downarrow \Delta$

A

$\downarrow O_2$

I ← $\xrightarrow{HgO/H_2O}$ **H** ← $\xrightarrow{CH_3CO_2K}$ **B** $\xrightarrow{HF}$ **C** $\xrightarrow{SbF_5}$ **D**

C $\xrightarrow{CsF}$ **E**

$\downarrow HCl$

J ← $\xleftarrow[cat.]{C_2H_2}$ **F**

$\downarrow NaBH_4$

K ← $\xleftarrow{Ga(CH_3)_3}$ **G**
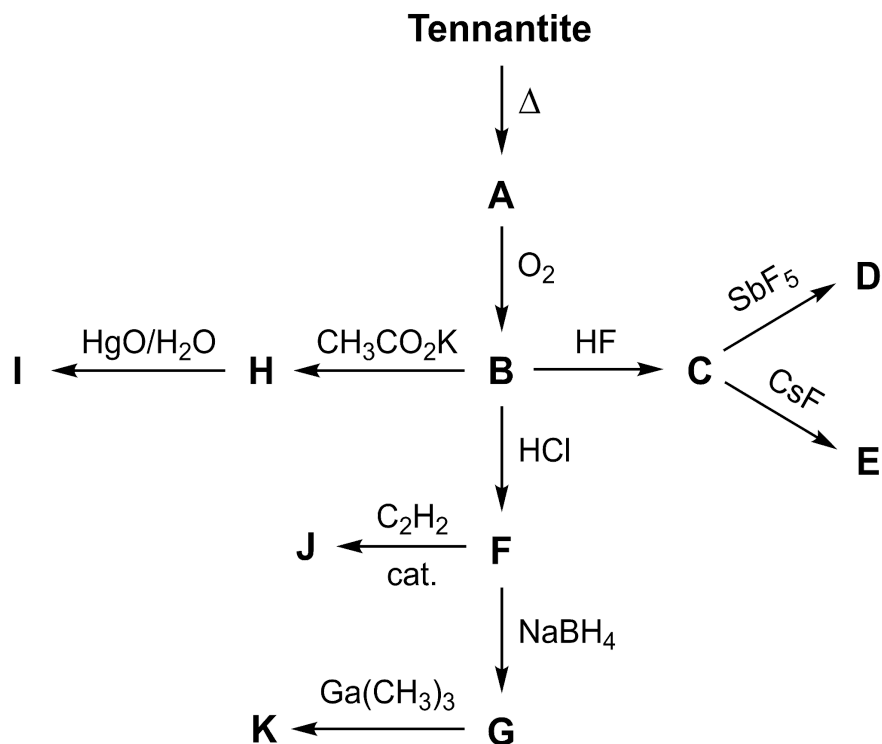
Thermal decomposition of tennantite leads to another mineral **A** with a highly symmetric structure, which consists of **X** and **Y** only. During the reaction, Cu_2Y and vapours of **Y** are formed as by-products. Further oxidation of **A** leads to oxide **B** ($w_X = 75.7$ %), which is a starting material for synthesis of almost all **X**-containing compounds. Compound **C** reacts with SbF_5 in a 1:1 ratio to give salt **D** with an **X**-containing cation and Sb-containing anion. **J**, the *anti*-addition product of **F** to acetylene, is an organo-**X** compound known as Lewisite that has been manufactured for use in chemical weapons. In the reaction **F**→**G**, sodium borohydride acts as a hydride donor. **K** is a semiconductor. **H** ($w_C = 21.26$ %, $w_H = 5.35$ %, $w_X = 66.31$ %, $w_O = 7.08$ %) is otherwise known as cacodyl oxide to obtain which potassium acetate has to react with **B**. During the course of the reaction, evolution of a gas is observed and a potassium salt is formed as a by-product. 2 equivalents of the cacodylic acid **I** are obtained by oxidising 1 equivalent of **H**.

2) a) Identify the <u>formulas</u> of **A-G** and **K** (9 points)

A	B	C
D	E	F
G	K	*Space for corrections*

b) draw the <u>structures</u> of compounds **H-J**. (6 points)

H	I	J

3) Write down balanced equations for all aforementioned reactions. (11 points)

Reaction	Balanced reaction equation
Tennantite → A	
A → B	
B → C	
C → D	
C → E	
B → F	
F → G	
F → J	
G → K	
B → H	
H → I	

Similarly to heavy metal poisoning, patients having been in contact with **J** can be given chelation therapy. A famous example of a covalent drug used specifically in the case of Lewisite poisoning is 2,3-dimercaptopropan-1-ol, also known as British anti-Lewisite (**BAL**).

4) Draw the structures of **BAL** and the product formed in its reaction with **J**. Molar mass of the product is $M = 258.62$ g mol^{-1}. (3 points)

BAL	BAL-Lewisite adduct

5) Using VSEPR theory, determine the geometries of the cation and anion of **D**. (2 points)

Geometry of the anion of compound **D** is
Geometry of the cation of compound **D** is

Nuclear magnetic resonance (NMR) spectroscopy is useful beyond organic chemistry and can also be used in the study of inorganic species, although this can sometimes be more complicated due to line-broadening effects of quadrupolar nuclei (i.e nuclei with a spin quantum number I greater than ½). Just like for protons ($I = ½$) in ^{1}H NMR spectra of organic molecules, the number of lines in a multiplet can be predicted for any other NMR-active nucleus using the equation: $2nI + 1$, where n is the number of coupling nuclei. The natural abundances of ^{19}F ($I = 1/2$) and **X** ($I = 3/2$) are 100%. Two NMR-active nuclei of antimony exist: ^{121}Sb ($I = 5/2$) and ^{123}Sb ($I = 7/2$). The natural abundances of ^{121}Sb and ^{123}Sb are 57.25% and 42.75%, respectively. In the following questions, assume that any anisotropies resulting from cation-anion interactions average out over the experiment time course and only through-bond couplings are observed.

6) For solution-state NMR spectra of **D**, predict the number of resonances and their theoretical splitting patterns in the **a)** ^{121}Sb NMR spectrum, **b) X** NMR spectrum and **c)** ^{19}F NMR spectrum. In your assignments, include the ratios of peak intensities for any multiplets as predicted by Pascal's triangle. *NB! There is no need to include integrals or any approximate chemical shifts.* (8 points)

Nucleus	No. of resonances in the NMR spectrum	Multiplicities and peak intensity ratios
^{121}Sb		
X		
^{19}F		

Problem 2. Thermodynamics of electrochemical CO_2 capture

10 points

The electrochemical CO_2 capture is a promising technique for direct air capture, allowing to capture CO_2 from the atmosphere and then release it in pure concentrated form for further application. In this task, we will look at the electrochemical (Part I) and thermodynamical (Part II) basis for the capture process.

Even though the text from Part I is relevant to Part II, Part II can be attempted without any results from Part I.
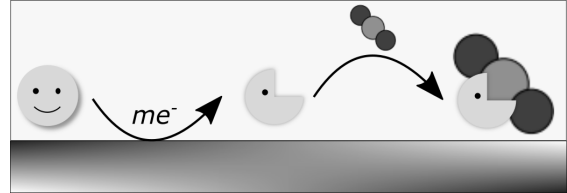
Part I - EMCS in the solution

One of the simplest systems is the electrochemically mediated complexation separation (EMCS), where the redox-active adsorbent is activated for the CO_2 capture at the cathode, while at the anode it is deactivated and releases CO_2. A more specific case is the EMCS in the solution, where the adsorbate is dissolved directly in the solution.

In the capture process, the first step is an electrochemical reaction

$$A(aq) + me^- \rightleftharpoons A^{m-}(aq)$$
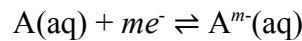
1. Using the Nernst equation **write** an expression for the reduction half-cell potential E.

Further the reduced A^{m-} is capturing CO_2

$$A^{m-}(aq) + mCO_2(g) \rightleftharpoons A(CO_2)_m{}^{m-}(aq)$$
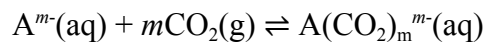
2. **Write** an expression for the equilibrium constant K for the given reaction, assuming the reference pressure P_0 to be 1.

For convenience we can define *total adsorbent concentration - A_0* :

$$A_0 = [A] + [A^{m-}] + [A(CO_2)_m{}^{m-}]$$

And *activated fraction $x_{A'}$* :

$$x_{A'} = ([A^{m-}] + [A(CO_2)_m{}^{m-}])/A_0$$

We are now equipped to separate expression for half-cell potential E into terms related to activated fraction and CO_2 pressure:

$$E = E^0 + RT/mF \cdot f_1(x_{A'}) + RT/mF \cdot f_2(KP_{CO2}{}^m)$$

3. **Find** expressions for $f_1(x_{A'})$ and $f_2(KP_{CO2}{}^m)$.

Now if we define E_0 to be potential when no CO_2 is present ($P_{CO2} = 0$), we can consider *deviation potential* E^{dev} observed at different P_{CO2}:

$$E^{dev} = E(P_{CO2}) - E_0$$

4. **Write** an expression for E^{dev} in this case.
(*In case you could not do the previous question, provide the answer using* $f_1(x_{A'})$ *and* $f_2(KP_{CO2}{}^m)$)

Part II - Thermodynamical analysis (

To calculate the work needed to perform the capture-release cycle we have to consider a diagram analogous to that of the *p-V* diagram known from classical thermodynamics. However, in this case, we consider a diagram E^{dev} vs. α (state of charge, which describes the relative amount of reduced species).

To construct this diagram, we must first understand the relation between total CO_2 content (x_{CO2}, normalised with respect to A initial concentration) and partial pressure of CO_2 (P_{CO2}), which is given by the relation:

$$x_{CO2} = \alpha \cdot KP_{CO2}/(1+KP_{CO2}) + k'_{h, CO2}P_{CO2}$$

The first term in the sum describes CO_2 which is bound to the reduced form of A, where α is the *state of charge*, which in the ECMS case coincides with the activated fraction $x_{A'}$ defined before. The second term, however, describes the part of CO_2 that is dissolved in the solution, where $k'_{h, CO2}$ is normalised Henry constant.

In a specific example, let's assume that $K=500$, $P_{CO2} = 1$ bar and $k'_{h, CO2} = 0.05$ bar^{-1}.

5. **Calculate** the total CO_2 content x_{CO2} for cases α=0.25 and α=0.75.

During the CO_2 adsorption and desorption cycle, there are three types of thermodynamic pathways possible:

- Constant state of charge - CO_2 is adsorbed or released from A with no electrochemical reaction happening.
- Constant total CO_2 concentration - During the reduction/oxidation process the CO_2 in the solution adsorbs to the reduced species/adsorbed CO_2 is released into the solution, while the total CO_2 concentration remains constant.
- Constant CO_2 partial pressure - the external pressure is kept constant, therefore while the capture/release happens the total CO_2 concentration and state of charge change, while the partial pressure is constant.

The following plot shows the diagram of E^{dev} vs. α. Solid lines indicate constant total CO_2 concentration (x_{CO2} is constant), and dashed lines indicate constant CO_2 partial pressure (P_{CO2} is constant). The labelled points **A-F** show special points during the capture-release cycle, which will be described later. Note, that
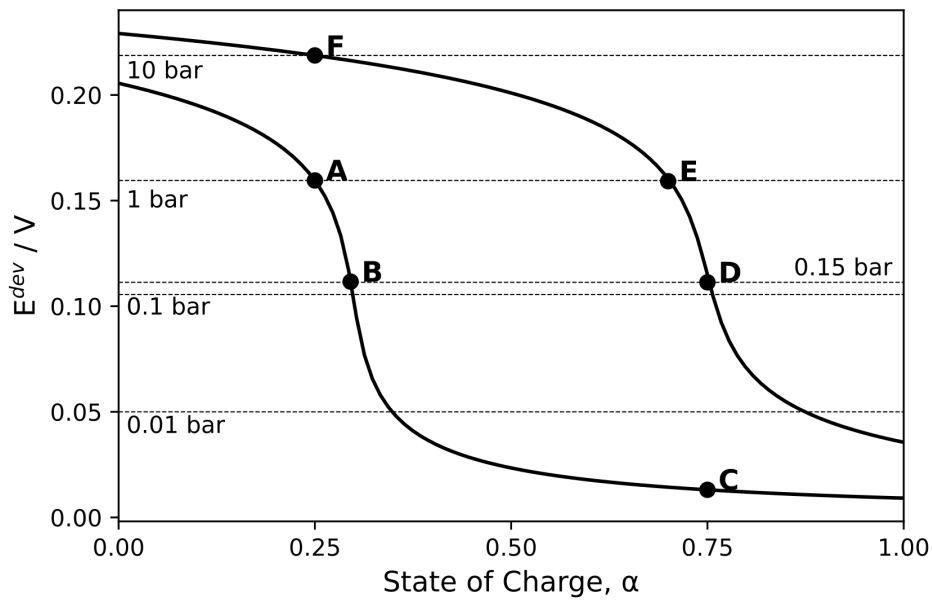
you have already calculated the x_{CO_2} for points **A** and **E** in question 5 (or, if you haven't, the precise values are not of particular interest).

6. **Calculate** the partial pressure P_{CO2} at point C.
(In case you could not calculate x_{CO2} in the previous question, use a value $x_{CO2} = 0.35$)

The release-capture system can be considered in two extremes. In both cases, the initial state of charge is 0.25, during adsorption, the partial pressure of the feed stream is 0.15 bar, and adsorption continues until the state of charge is 0.75. At the release stage, the CO_2 is released in a pure stream with a partial pressure of 1 bar.

Four-stage system:
1. As the absorbent is activated, *i.e.,* the state of charge increases, while the total CO_2 concentration remains constant.
2. The activated absorbent is contacted with the feed gas until the partial pressure of the feed gas is reached.
3. The absorbent is deactivated as the state of charge decreases. In the end, the free CO2 in the solution is at a partial pressure of 10 bar.
4. CO_2 is removed by desorption as a gas in the flash tank at a pressure of 1 bar

Two-stage system:
1. The adsorbent is activated and CO_2 is captured at the same time.
2. The adsorbent is deactivated and CO_2 is released at the same time.

7. **Assign** all the described steps with points shown in the E^{dev} vs. α diagram.
(*In the form:* 1. X to Y)

Four-stage system:
    1.
    2.
    3.
    4.
Two-stage system:
    1.
    2.

The work required to perform the capture-release cycle is described as the area enclosed by the cycle in the E^{dev} vs. α diagram.

8. **Tick** the correct answer, consistent with your answer to the previous part.

☐ - Four-stage system requires less work.
☐ - Two-stage system requires less work.

Problem 3. Solution ≠ liquid

12 points

We are used to use term "solution" in the context of liquid materials. But solid solutions also exist. In solid solutions different atoms or ions form compounds with different stoichiometric composition, but the crystal lattice remains the same.

Ferrochrome has empirical formula Fe_xCr_{1-x} (x − non-integer value). Both iron and chromium form body-centered cubic (BCC) crystal lattice, therefore their solid solution has the same lattice if a certain amount of iron atoms are substituted by chromium atoms in nodes of crystal lattice.

One ferrochrome cubic cell and five planar projections, perpendicular to z axis, are shown in Fig. 1.
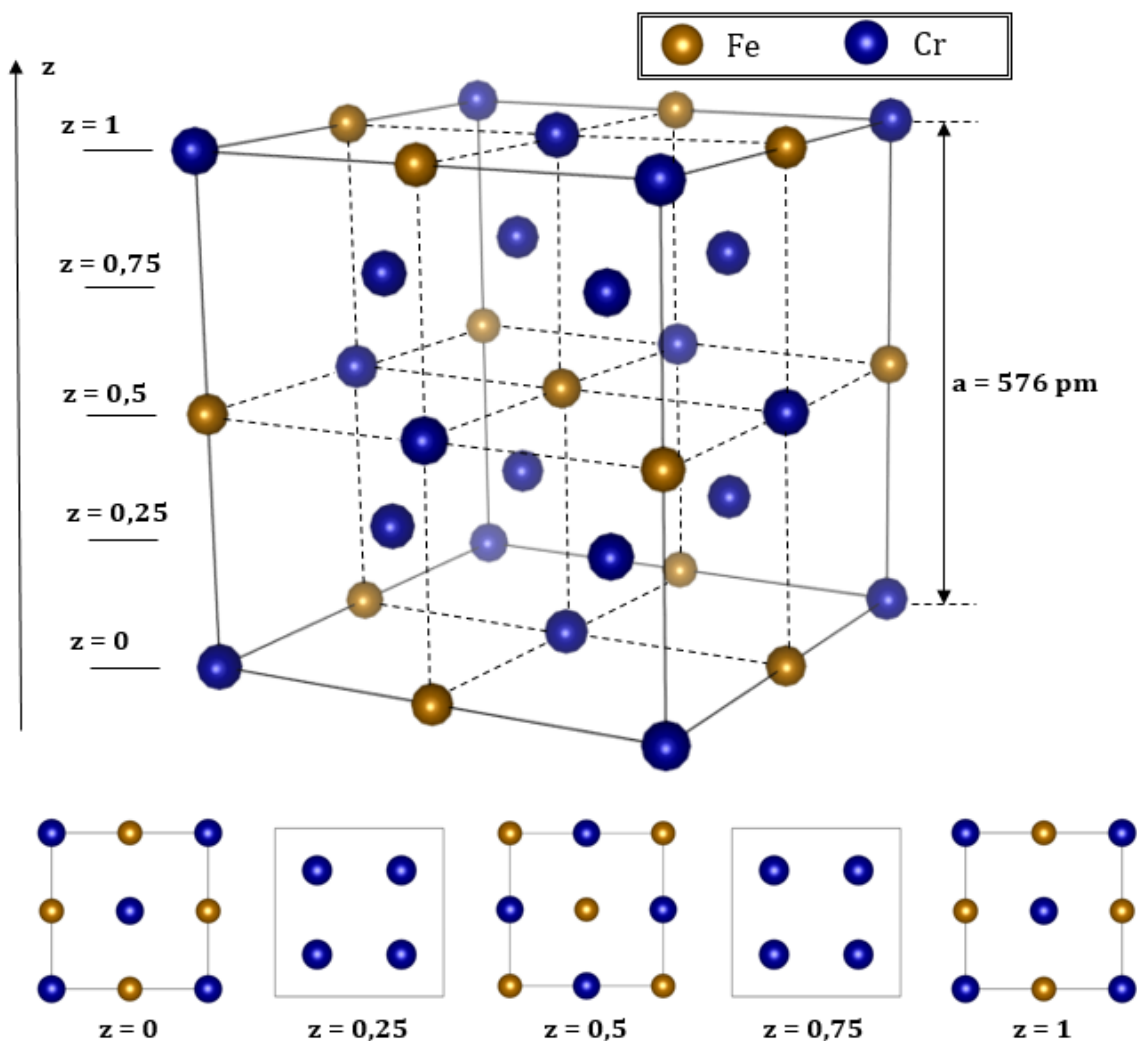
Fig. 1 Cubic cell of ferrochrome and its five planar projections along z axis.

1. Assuming that the cubic cell given in Fig. 1 corresponds to the composition of whole material, calculate the x value in empirical formula Fe_xCr_{1-x}.

2. The lattice parameter of the cell given in Fig. 1 is 576 picometers. Calculate the density of ferrochrome. Express the answer in g·cm^{-3} dimensions.

3. The experimental ferrochrome density value differs by 5 % compared with the result you've calculated in question 2. Which of the following statements can explain such a difference? *Circle correct answer letter(s)*

a)	Additional Fe or Cr atoms can be intercalated in octahedral or tetrahedral voids of the lattice
b)	Formation of vacancies in nodes of crystal lattice
c)	Because of random distribution of Fe and Cr atoms in the lattice one cubic cell does not ideally correspond to the actual composition of material
d)	Chemical interactions between Fe and Cr cause the significant change of metallic radii of Fe and Cr atoms
e)	In solid solutions lattice parameter values fluctuates significantly

Ionic solid solutions can be obtained by combining two or more ionic compounds. Substituting cations or anions of different charges in the lattice gives rise to peculiar physical properties of such material.

Forsterite is a mineral which has empirical formula Mg_2SiO_4. Silicon is covalently bound to oxygen atoms and magnesium ions occupy octahedral holes in orthorhombic lattice. Reaction between forsterite and lanthanum (III) oxide yields $La_xMg_ySiO_4$ solid solution and one more byproduct, which contains no lanthanum.

4. Write chemical formula of byproduct.

5. Express index y as a function of x.

6. When La^{3+} ions substitute Mg^{2+} ions, a certain concentration of vacancies are formed. Vacancies influence electrical conductivity of ionic solid solution. Which electric charge transfer mechanism occurs in $La_xMg_ySiO_4$ solid solution? ***Circle one correct answer letter.***

a)	Mg^{2+} migrates to the vacancy, a new vacancy is formed in Mg^{2+} node
b)	La^{3+} migrates to the vacancy, a new vacancy is formed in La^{3+} node
c)	Si^{4+} migrates to the vacancy, a new vacancy is formed in Si^{4+} node
d)	O^{2-} migrates to the vacancy, a new vacancy is formed in O^{2-} node
e)	Mg^{2+} or La^{3+} migrates to the vacancy, a new vacancy is formed in Mg^{2+} or La^{3+} node
f)	Mg^{2+}, La^{3+} or Si^{4+} migrates to the vacancy, a new vacancy is formed in Mg^{2+}, La^{3+} or Si^{4+} node
g)	Mg^{2+}, La^{3+}, Si^{4+} or O^{2-} migrates to the vacancy, a new vacancy is formed in Mg^{2+}, La^{3+}, Si^{4+} or O^{2-} node
h)	Free electrons migrate from vacancy to vacancy

7. By performing electrical conductivity measurements it was calculated that concentration of vacancies in lanthanum-doped forsterite is $6.2 \cdot 10^{17}$ cm^{-3}. Density of the material is 3.223 g·cm^{-3}. One unit cell contains one silicon and four oxygen atoms. Calculate index x in formula $La_xMg_ySiO_4$ by assuming that all vacancies are formed because of La^{3+}–Mg^{2+} exchange.

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Cations can intercalate in ionic compounds via different mechanisms. For example, ferrous oxide FeO can react with lithium oxide Li_2O to yield a solid solution $Li_xFe_{1-x}O$. During the reaction, a fraction of iron atoms oxidize to +3 oxidation state. One of the simplest methods to analyze the composition of such solid solution is electrochemical Fe^{3+}/Fe^{2+} ratio determination. We denote the ratio $r = \frac{n(Fe^{3+})}{n(Fe^{2+})}$, where $n(Fe^{3+})$ ir $n(Fe^{2+})$ are molar amounts of Fe^{3+} and Fe^{2+} respectively. Reciprocal values of empirical formula index x and ratio r are related linearly (a and b – integer numbers):

$$\frac{1}{x} = a\cdot\frac{1}{r} + b$$

8. Calculate values a and b.

When $Li_xFe_{1-x}O$ is dissolved in non-oxidizing acid, an excess of sodium cyanide is added to bind all iron atoms to $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ complex ions. Two electrodes are immersed in this solution: a working Pt electrode and reference $AgCl|Ag, Cl^-$ electrode, filled with saturated KCl solution. 0.092 V potential difference is measured at the starting moment of experiment, then an increase of $[Fe(CN)_6]^{4-}$ concentration was observed. Redox potentials at 298 K and 1 bar are:

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) \quad E = E°\left(Ag, Cl^-\right) - \frac{RT}{F}\ln ln\left[Cl^-\right]_{saturated} = + 0.197\,V$$

$$\left[Fe(CN)_6\right]^{3-}(aq) + e^- \rightarrow \left[Fe(CN)_6\right]^{4-}(aq) \quad E° = + 0.370\,V$$
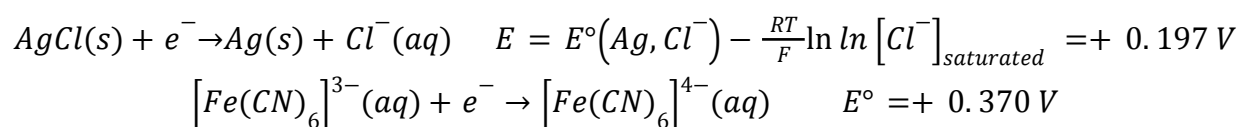
9. Calculate the ratio r and index x from electrochemical measurement data.
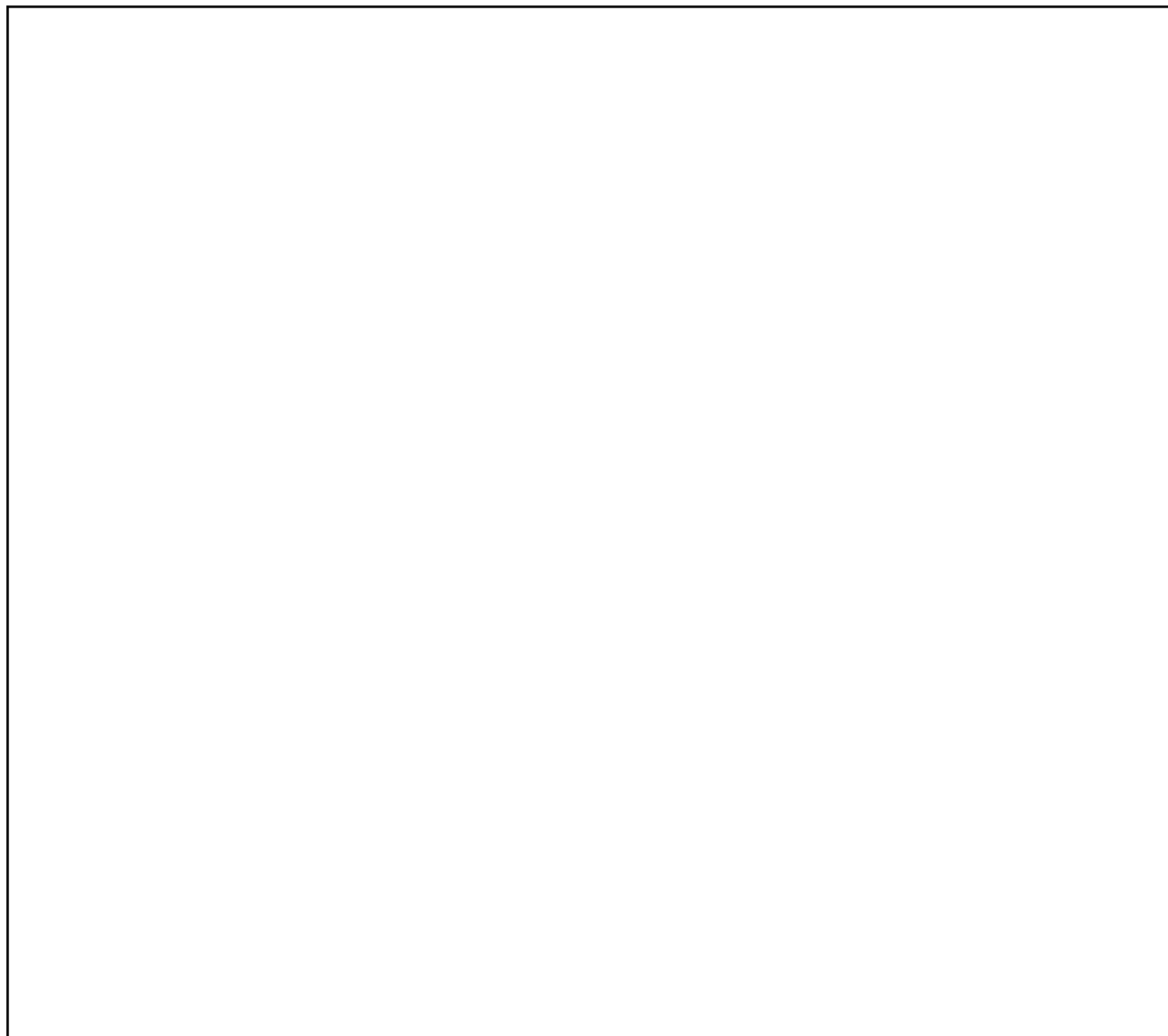
Organic solid solutions are attractive because of their optical properties. For instance, p-bromobenzaldehyde derivatives weakly phosphoresce (emit light) in crystalline state. But if p-bromobenzaldehyde derivative (**A**) is co-crystallized with 1,4-dibromobenzene (**B**), a solid phosphorescent solution forms. **B** molecules interrupt interactions between **A** molecules and does not allow for vibrational relaxation of excited **A** molecules. This solid solution has primitive orthorhombic structure, where nodes can be occupied by either **A** or **B** (Fig. 2 (a)).

A simple kinetic model can be used to estimate phosphorescence intensity I of the material:

$$I = \frac{CN \cdot k_{ph}}{k_{ph} \bullet r_0^2 + k_{vib} \bullet \sum_i \left(CN_i^2 \bullet r_i^2 \right)}$$

CN – coordination number, defining average count of **A** molecules around selected **A** molecule. k_{ph} and k_{vib} are phosphorescence and vibrational relaxation rate constants, r_0 is a constant and CN_i are average counts of **A** molecules, that are at a specific r_i distance from selected **A** molecule. r_0 and r_i must be

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expressed in angstrems (Å) and CN, CN_i and r_i values should be considered only for the first coordination shell (nearest atoms, Fig. 2 (b)).
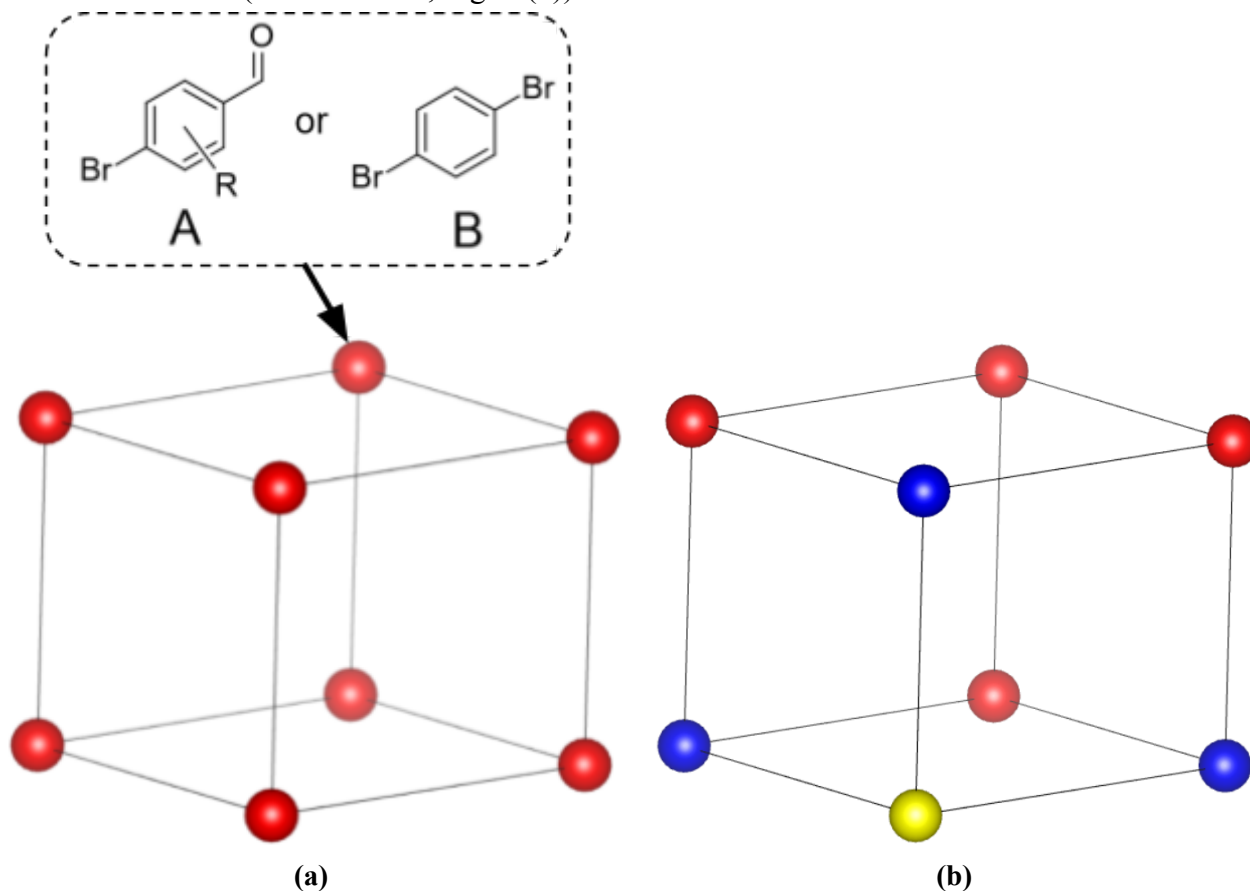

Fig. 2 (a) Primitive orthorhombic cell with parameters a, b, c and nodal positions marked as red balls; (b) if yellow molecule is the selected one, blue molecules are in the first coordination shell.

10. Show that for orthorhombic lattice with different unit cell lengths a, b, c phosphorescence intensity can be calculated using formula below.

$$I = \frac{9 \cdot CN \cdot k_{ph}}{9 \cdot k_{ph} \bullet r_0^2 + k_{vib} \bullet CN^2 \bullet (a^2 + b^2 + c^2)}$$

11. Solid solution **X** is prepared by co-crystallising **A** and **B** in ratio $n(A): n(B) = 1: 1$. Solid solution **Y** is prepared by co-crystallising **A** and **B** in ratio $n(A): n(B) = 2: 1$. **X** phosphoresce 1.25 times more intensely than **Y**. Calculate the length of the diagonal of orthorhombic unit cell, if $\frac{k_{ph}}{k_{vib}} \approx 10^{-4}$ and $r_0 \approx 710$ Å.
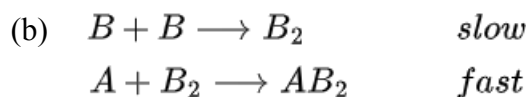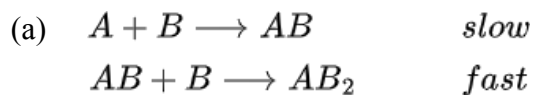
Problem 4. Kinetics

9 points

The following reaction that proceeds via an unknown mechanism:

$$A + 2B \longrightarrow AB_2 \qquad (0)$$

1. Assume that reaction (0) proceeds in a second-order fashion in relation to [B].
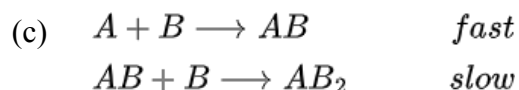
1. 1. <u>Select</u> ALL appropriate mechanisms which are consistent with the assumption given in **1.**
Note: notations "slow" and "fast" show that a said reaction step is proceeding in a slow and fast manner, respectively.

(a) $A + B \longrightarrow AB$ *slow*
   $AB + B \longrightarrow AB_2$ *fast*

(b) $B + B \longrightarrow B_2$ *slow*
   $A + B_2 \longrightarrow AB_2$ *fast*

(c) $A + B \longrightarrow AB$ *fast*

     $AB + B \longrightarrow AB_2$ *slow*

(d) $A + A \longrightarrow A_2$ *slow*

     $B + B \longrightarrow B_2$ *slow*

     $A_2 + B_2 \longrightarrow AB_2 + A$ *fast*
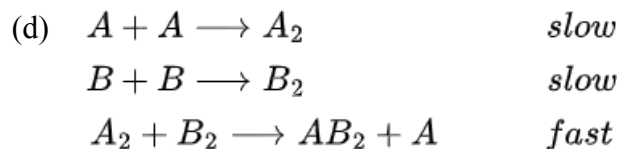
☐ Mechanism (a)

☐ Mechanism (b)

☐ Mechanism (c)

☐ Mechanism (d)

---

1. 2. **Select** ALL graphs that could depict the relationship between $[B]$ and both t, time, or r, rate of reaction (0), and are consistent with the assumption given in **1.** Assume a constant state for $[A]$.

(a) $[B]$ vs t (b) $ln[B]$ vs t (c) $\frac{1}{[B]}$ vs t (d) r vs $[B]$ (e) r vs $[B]$ (f) r vs $[B]^2$
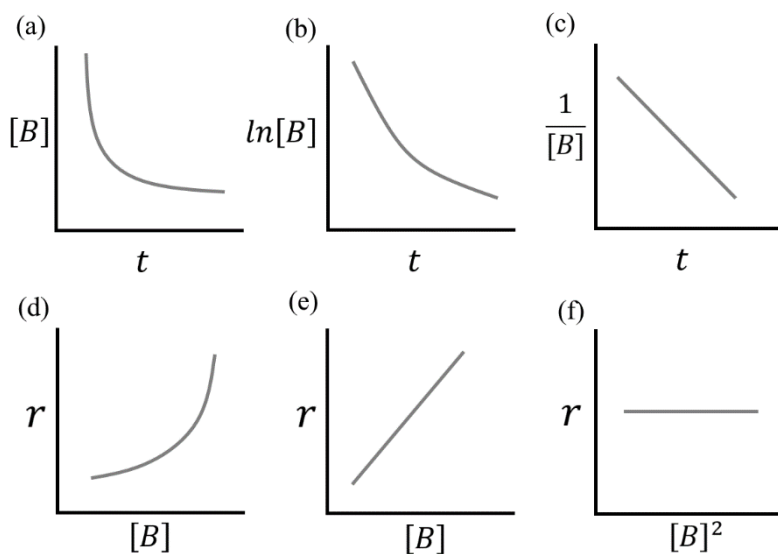
☐ Graph (a)   ☐ Graph (d)

☐ Graph (b)   ☐ Graph (e)

☐ Graph (c)   ☐ Graph (f)

In reality, reaction (0) proceeds via the mechanism given below:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB \qquad (1)$$

$$AB + B \overset{k_2}{\longrightarrow} AB_2 \qquad (2)$$
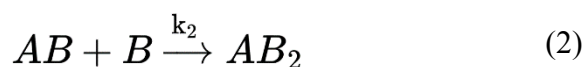
2. For each condition listed below, **determine** whether the rate-limiting step of the mechanism presented above is step (1), step (2) or neither. Assume that $[A]$ and $[B]$ are much greater than $[AB]$ and $[AB_2]$.

2. 1. $k_1 \gg k_{-1}; \; k_2 \gg k_1$

2. 2. $k_1 \gg k_{-1}; \; k_2 \ll k_1$

2. 3. $k_1 \gg k_{-1}; \; k_2 \cong k_1$

2. 4. $k_1 \cong k_{-1}; \; k_2 \ll k_1$

Condition **2. 1.**	Step (1) ☐	Step (2) ☐	Neither ☐
Condition **2. 2.**	Step (1) ☐	Step (2) ☐	Neither ☐
Condition **2. 3.**	Step (1) ☐	Step (2) ☐	Neither ☐
Condition **2. 4.**	Step (1) ☐	Step (2) ☐	Neither ☐

Unknown amounts of reagents A and B were added together to a container under conditions that favor reaction (0).

3. At time $t = t_1$, the concentration of intermediate AB has become constant, i.e. $[AB] = [AB]_{const}$, and the concentration of reagent A has reached a certain value, i.e. $[A] = [A]_1$.

3. 1. **Express** the ratio of the rate constants, namely $\frac{k_1}{k_2}$, using terms $[A]_1$ and $[AB]_{const}$. Assume that $k_1, k_2 \gg k_{-1}$.

$$\frac{k_1}{k_2} =$$

4. At time $t = t_2$, and at a different temperature, a certain amount of reagent C was added into the mixture. C interacts with intermediate AB via the following reaction:

$$AB + C \xrightarrow{k_3} ABC \qquad (3)$$

The experimental rate of production of ABC, r, can be expressed as $r = k_{obs} \cdot a$, where k_{obs} is the observed rate constant for the production of ABC, and a is a product of concentration(s) of certain compound(s).

4. 1. Assuming that under given conditions steps (1) and (2) proceed much slower than step (3), **show** that the observed rate constant, k_{obs}, is approximately equal to rate constant k_1.

The temperature of the mixture was <u>increased</u> to a certain value, at which rate constants k_2 and k_3 became equal.

4. 2.   Using signs $>$, $<$ and/or $\cong$, **denote** the relationship between reactions' (2) and (3) Arrhenius pre-factors, A_2 and A_3, and activation energies, E_{a2} and E_{a3}, respectively. Assume that Arrhenius pre-factors and activation energies of these reactions are independent of temperature.

$$A_2 \,\square\, A_3 \qquad\qquad\qquad E_{a2} \,\square\, E_{a3}$$

5.   Certain amounts of B, C and AB were added to a container under conditions that favor <u>only</u> reactions (2) and (3). Assume, that the initial concentration of AB, $[AB]_0$, is much greater than initial concentrations of both B, $[B]_0$, and C, $[C]_0$.

At time $t = t_3$, concentrations of compounds AB_2 and ABC were measured and their values were found to be equal.

5. 1.   **Express** the ratio of initial concentrations of B and C, namely $\frac{[B]_0}{[C]_0}$, in terms of $[AB]_0$, k_2, k_3 and t_3.

$$\frac{[B]_0}{[C]_0} =$$

5. 2. <u>Calculate</u> the ratio of the rates of reactions (2) and (3), namely $\frac{r_2}{r_3}$, at time $t = t_3$, where
$[AB]_0 = 1.20 \cdot 10^{-3} \, mol \cdot L^{-1}$, $k_2 = 1.40 \cdot 10^{-3} \, L \cdot mol^{-1} \bullet s^{-1}$, $k_3 = 5.60 \cdot 10^{-4} \, L \cdot mol^{-1} \bullet s^{-1}$ and
$t_3 = 2.50 \cdot 10^3 \, s$.

34

$$\frac{r_2}{r_3} =$$

Code ☐☐☐

## Problem 5. Total synthesis of (–)-Colombiasin A

10 points

(–)-Colombiasin A is a marine natural product first isolated from a species of coral found off the coast of San Andres island, Colombia. Following the initial reported total synthesis and structural assignment by K. C. Nicolaou and co-workers in 2001, Colombiasin A and structurally closely related compounds have been prepared via numerous different synthetic approaches. Construction of the carbon skeleton poses in this case some rather unique challenges to the synthetic chemist. Most notably, the two adjacent quaternary carbons central to Colombiasin A's carbacycles have been recognised as some of the most challenging aspects of building this natural product.
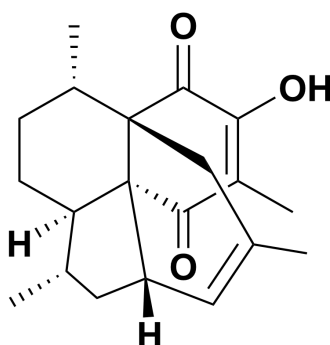
(–)-Colombiasin A

In this task, you will follow the approach of D. C. Harrowven and co-workers, which starts off simple, yet concludes in a spectacular fashion. The synthesis begins from enantiomerically pure dihydrocarvone. In the first half of the sequence, a number of simple transformations eventually lead to an *E/Z* mixture of conjugated diene **E**. The stereochemical configurations of compounds **A** and **B** have been provided in the scheme below. In reaction C → D, a partial reduction occurs over steps 2i)-ii). It is also known that both **C** and **D** contain a secondary hydroxyl group.
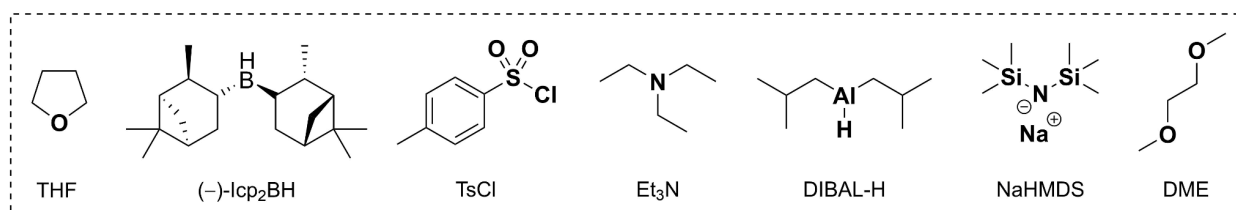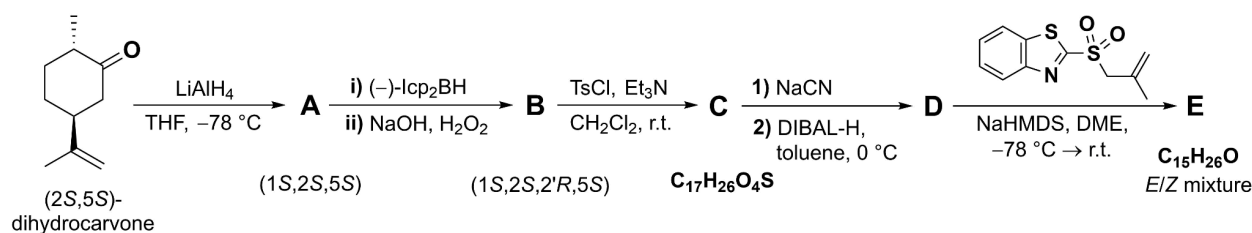
1) Draw the structures of **A-E**, taking stereochemistry into account. (9 points)

A	B	C
D	E	*Space for corrections*

2) From the list below, tick the most suitable solvent for the reaction **C** + NaCN. (2 points)
- *n*-hexane
- toluene
- $NH_3(l)$
- 1,2-dichloroethane (DCE)
- dimethylsulfoxide (DMSO)
- kefir
- 1:1 MeOH/H_2O with 5% v/v H_2SO_4

3) Sketch the reaction mechanism for transformation **D→E** and clearly indicate the <u>three</u> by-products formed in progress. You may abbreviate parts of molecule(s) irrelevant to this transformation. *Hint: the reaction proceeds via an anionic spirocyclic intermediate. Spiro compounds are molecules, which contain at least two ring systems with only a single common atom.* (8 points)
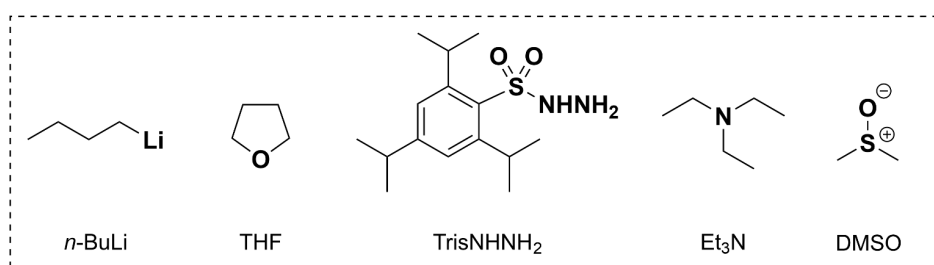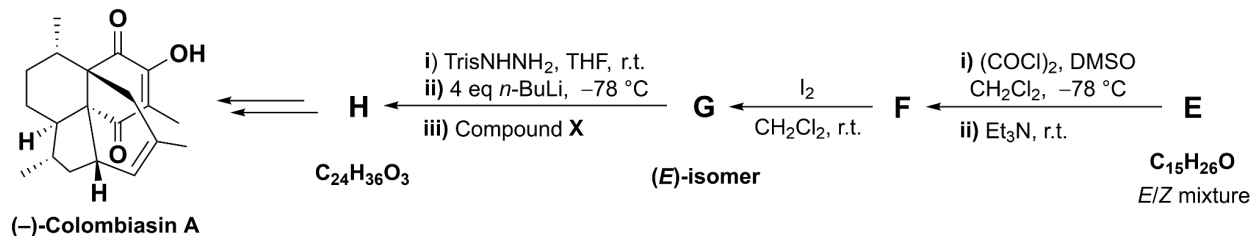
4) Explain briefly, with reference to relevant $^3J_{\text{H-H}}$ coupling constants, how the *E/Z* isomeric ratio of compound **E** could be estimated by ^{1}H NMR spectroscopy. (3 points)

In the next part of the synthesis, the *E/Z* mixture of compound **E** is first oxidised into **F** and subsequently, with the aid of catalytic I_2, converted into stereochemically pure **G**. Compound **G** is then subjected to an interesting sequence of reactions. First, an alkenyllithium species is formed *in situ* from **G** via a Shapiro reaction, which then undergoes a nucleophilic addition to compound **X**. Following aqueous work-up, the α-hydroxy ketone **H** is obtained. *Hint: the first step in the Shapiro reaction is formation of a hydrazone via condensation.*

(–)-Colombiasin A

H
i) TrisNHNH$_2$, THF, r.t.
ii) 4 eq *n*-BuLi, −78 °C
iii) Compound **X**
$C_{24}H_{36}O_3$

G
I_2
CH$_2$Cl$_2$, r.t.
(*E*)-isomer

F
i) (COCl)$_2$, DMSO
CH$_2$Cl$_2$, −78 °C
ii) Et$_3$N, r.t.

E
$C_{15}H_{26}O$
E/Z mixture

n-BuLi   THF   TrisNHNH$_2$ Et$_3$N   DMSO

Information about compound **X**:
- Elemental composition: C - 64.27 %; H - 7.19 %; O - 28.54 %.
- ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.19 (s, 1H), 1.62 (s, 3H) ppm. *NB! The listed integrals are relative not absolute.*
- ^{13}C NMR (75 MHz, CDCl$_3$): δ 199.9, 195.9, 192.8, 182.7, 87.5, 28.7, 9.3 ppm.
- Selected IR spectroscopic data: v_{max} (cm^{-1}) - 1799, 1748, 1584, 1395.

5) Identify the <u>four</u> low molecular weight by-products formed in step **E**→**F**. (2 points)

6) Draw the structures of **F**, **G**, compound **X** and **H**, taking stereochemistry into account where applicable. (8 points)

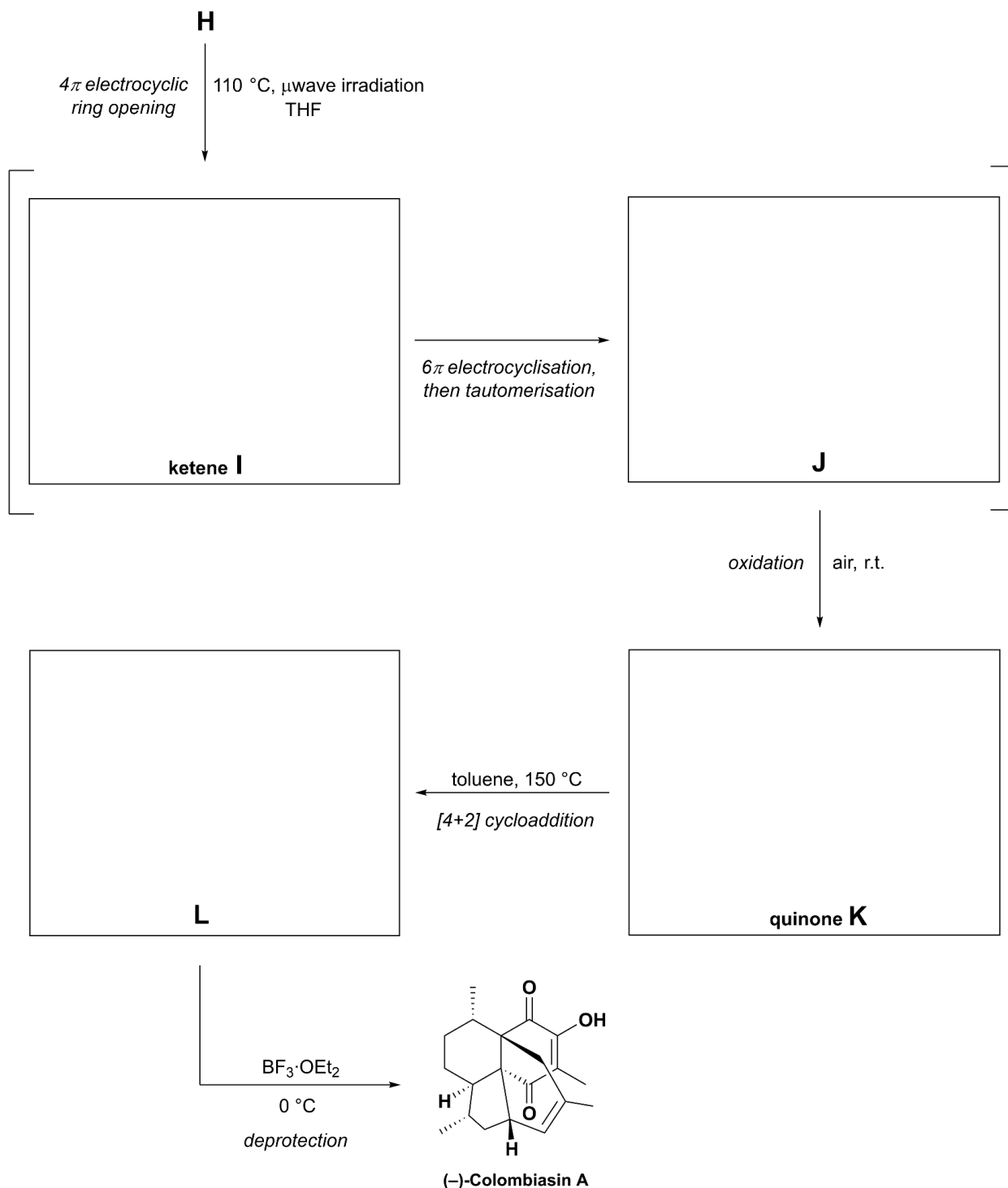| F	G
X	H

Continued on the next page…

The total synthesis of **(−)-Colombiasin A** from dihydrocarvone culminates in an impressive cascade, which proceeds from **H** to **K** via intermediates **I** and **J**. In the very last steps, a [4+2] cycloaddition furnishes the **(−)-Colombiasin A** core and deprotection using BF_3 etherate reveals the target molecule.

H

4π electrocyclic ring opening | 110 °C, μwave irradiation THF

ketene I

6π electrocyclisation, then tautomerisation

J

oxidation | air, r.t.

L

toluene, 150 °C

[4+2] cycloaddition

quinone K

$BF_3·OEt_2$

0 °C

deprotection

(−)-Colombiasin A

**7)** Draw the structures of **I-L** in the boxes above, taking stereochemistry into account. (8 points)

Problem 6. Chiral Pool
10 points

Chiral pool is a collection of enantiopure (thus chiral), cheap compounds that could be used as starting materials in synthesis, creating chiral ligands, reagents etc. One of the most popular members of the chiral pool is a terpene Carvone. In this problem we will take a look at a synthesis of sesquiterpene lactone 8-epigosheimin, that utilizes *(S)*-carvone (**A**) as a source of chirality.
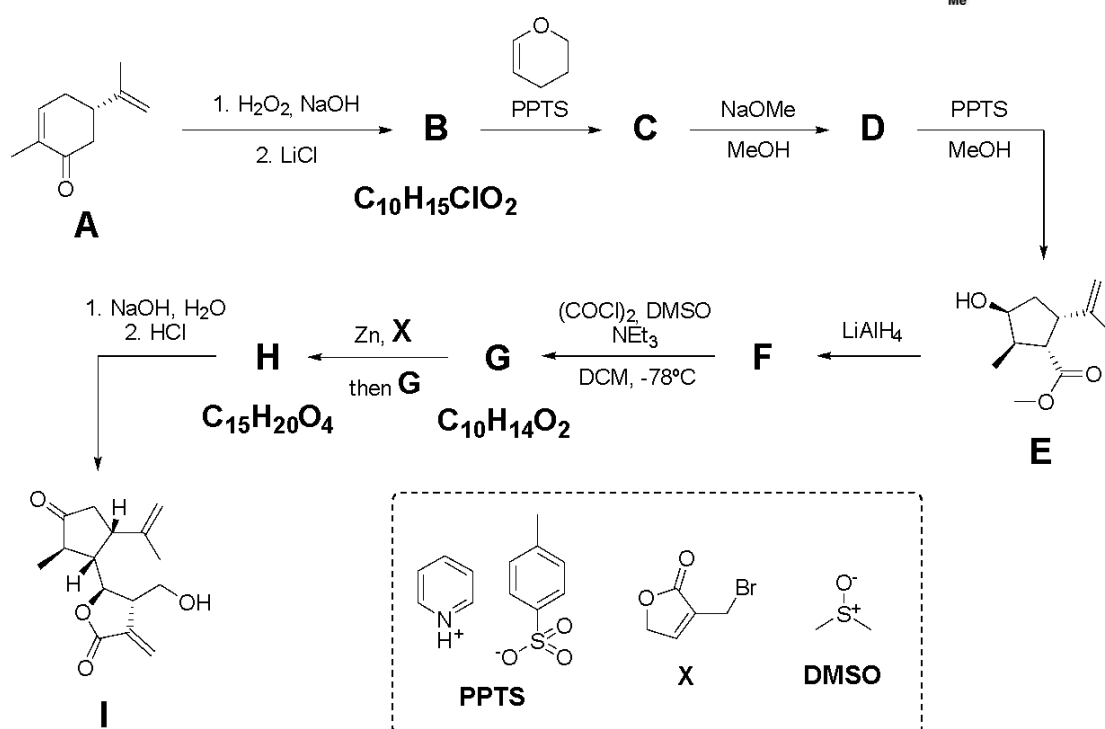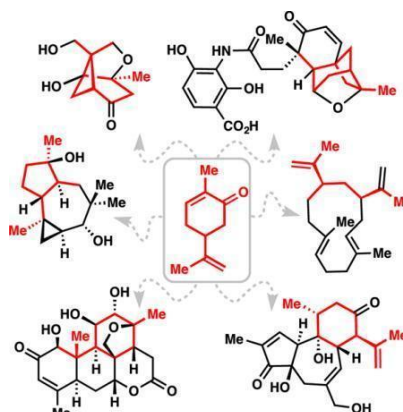
Note, that:

- **PPTS** is a weakly acidic catalyst
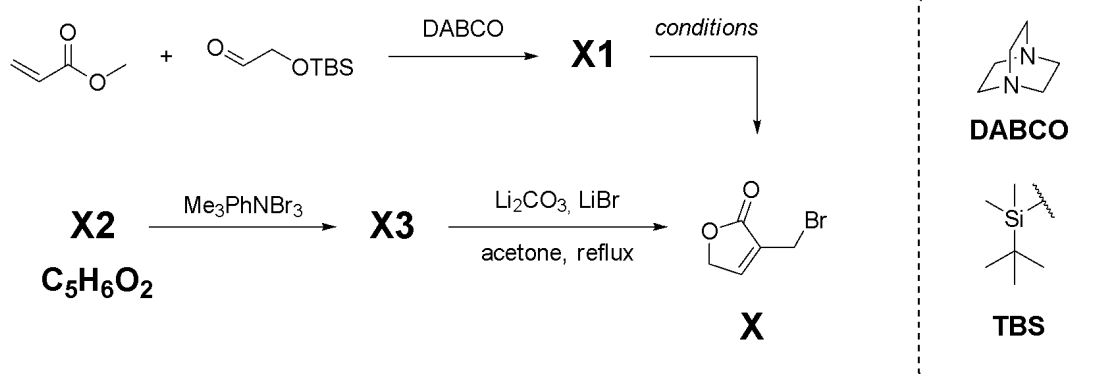- In the reaction **G** → **H**, zinc is required to create an organometallic species

1.Determine the structures of compounds **B – D**, **F – H**. (15 points)

B	F
C	G
D	H

The reagent **X** could be obtained in many ways. In the scheme below, two of the most popular routes are shown.

^{1}H NMR spectra of **X2**: 6.08 (t, J = 3 Hz, 1H), 5.63 (t, J = 3 Hz, 1H), 4.30 (t, J = 7 Hz, 2H), 2.97 (m, 2H).

2.Determine the structures of compounds **X1**, **X2** and **X3**. (6 points)

X1	X2
X3	*You can draw something nice here*

3.Propose a mechanism for the synthesis of **X1**. (3 points)

4.Propose a reagent(-s) to obtain **X** from **X1** in **<u>one step</u>**. (2 points)

The endgame of the synthesis was planned through a Swern oxidation followed by cyclization to obtain the 8-epigosheimin (**K**). During the oxidation, an isomer **J1** was formed instead of the necessary **J2**. Although the endgame was quite short, in order to prove the absolute configuration, a different route was taken (through **L**).

(COCl)$_2$, DMSO
NEt$_3$
DCM, -78°C → **J1**

DMAP   Pyridine   DMP
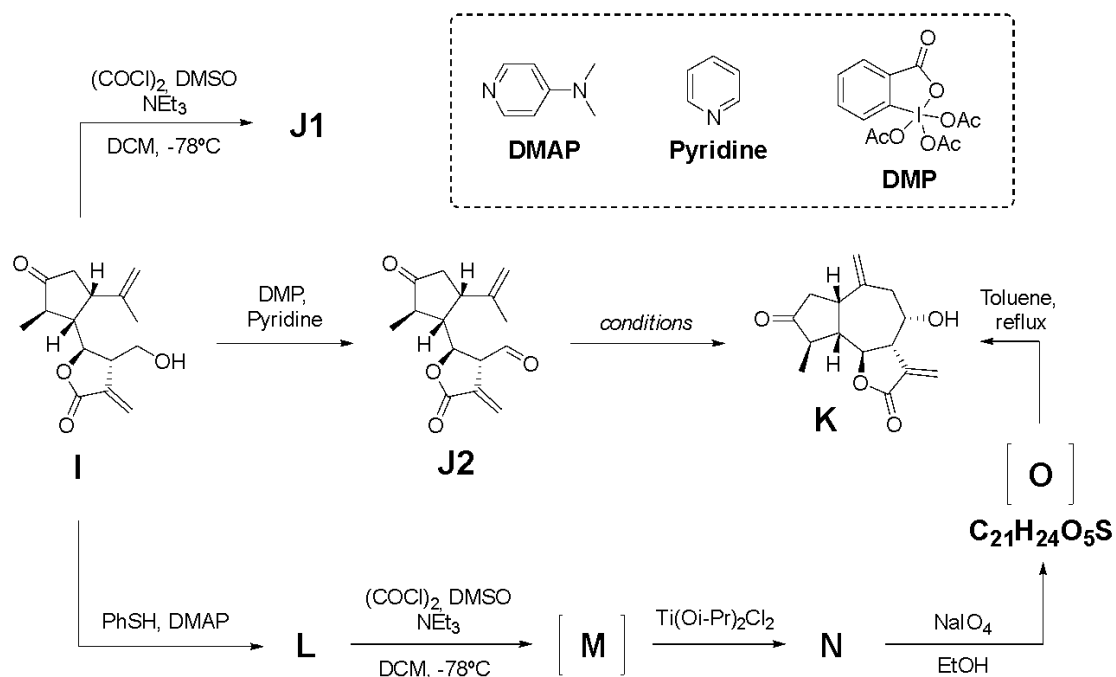
Note, that Ti(IV) salts are strong, oxophilic Lewis acids.

5.Determine the structures of compounds **J1**, **L − O**. (10 points)

J1	N
L	[O]
[M]	*Space for corrections*

6.Choose (from the set of conditions below) the appropriate conditions for the transformation of **J2** to **K**. (2 points)

☐	nBuLi, diethylamine
☐	$MgSO_4$, toluene, reflux
☐	$BF_3 \cdot Et_2O$
☐	NaOH, H_2O_2
☐	$NaClO_2$, NaH_2PO_4, tBuOH/H_2O