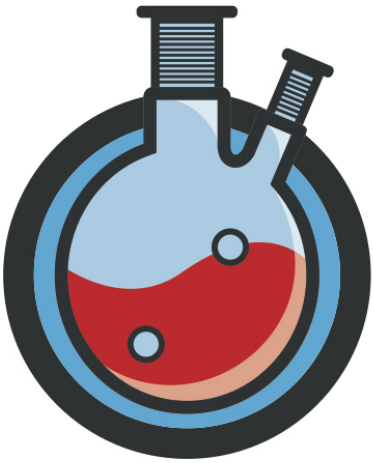

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OLIMPIADI DELLA CHIMICA

SwissChO 2022 - Theoretical Final Exam

Instructions

- Write your name on each page and number these.
- You have three hours to solve the problems. Wait for the **START** signal before you begin.
- Use a new page for each problem.
- Write all necessary calculations legibly.
- Put your pages into the provided envelope at the end of the exam. Do not seal the envelope.
- Finish your work immediately when the **STOP** signal is given.
- Leave your seat only when allowed to do so.
- Only **answers written on the answer sheets** can be considered.
- This exam has 27 pages.

Viel Erfolg!

Bonne chance!

Buona fortuna!

Good luck!

CONSTANTS AND FORMULAE

Avogadro constant	$N_A = 6.022 \cdot 10^{23}\ \mathrm{mol^{-1}}$	Ideal gas law	$pV = nRT$
Universal gas constant	$R = 8.314\,\mathrm{J\ mol^{-1}\ K^{-1}}$	Gibbs energy	$G = H - TS$
Faraday constant	$F = 96\,485\,\mathrm{C\ mol^{-1}}$	$\Delta_r G^0 = -RT \cdot \ln(K) = -nFE^0_{\text{cell}}$	
Planck constant	$h = 6.626 \cdot 10^{-34}\ \mathrm{J\ s}$	Nernst equation	$E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln\left(\frac{c_{\text{ox}}}{c_{\text{red}}}\right)$
Speed of light	$c = 2.998 \cdot 10^8\ \mathrm{m\ s^{-1}}$	Energy of a photon	$E = \frac{h \cdot c}{\lambda}$
Temperature	$0\,^\circ\mathrm{C} = 273.15\,\mathrm{K}$	Lambert-Beer law	$A = \log\left(\frac{I_0}{I}\right) = \epsilon \cdot c \cdot L$

For the calculation of equilibrium constants all concentrations, refer to the standard concentration $1\,\mathrm{mol\ dm^{-3}} = 1\,\mathrm{mol\ L^{-1}}$. If not stated otherwise in a task, consider all gases ideal throughout this test.

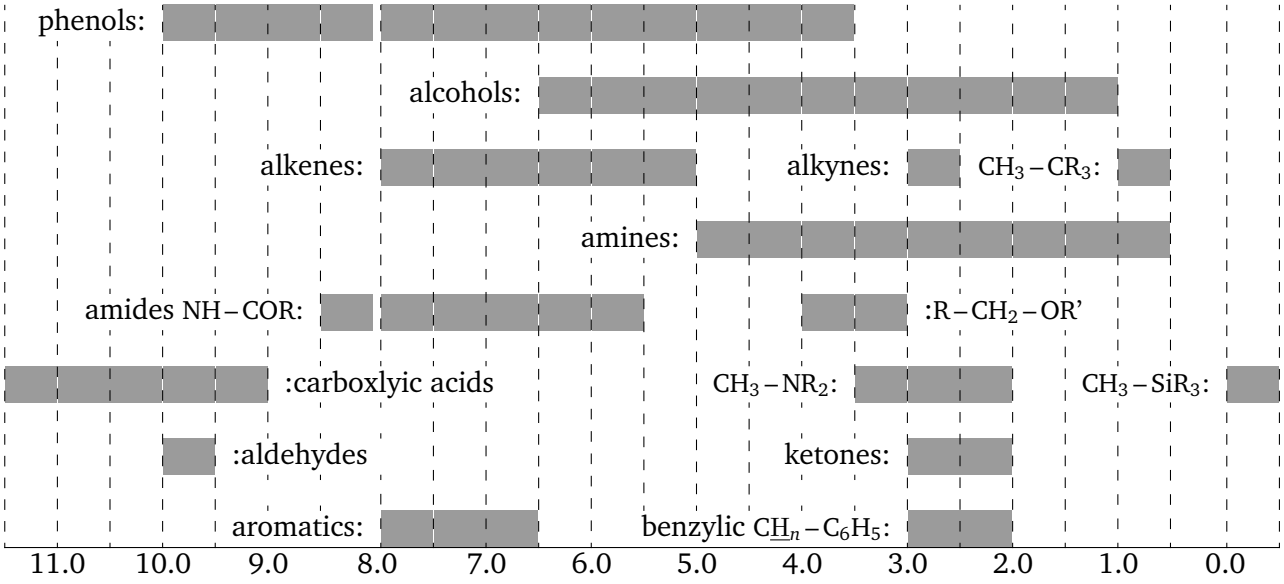
Periodic Table of Elements

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57–71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [212]
87 Fr [223]	88 Ra [226]	89–103	104 Rf [267]	105 Db [268]	106 Sg [269]	107 Bh [270]	108 Hs [270]	109 Mt [278]	110 Ds [281]	111 Rg [282]	112 Cn [285]	113 Nh [286]	114 Fl [289]	115 Mc [290]	116 Lv [293]	117 Ts [294]	118 Og [294]

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 140.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac [227]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [266]

^{1}H Nuclear Magnetic Resonance Spectroscopy

Chemical Shifts (in ppm / TMS)



H – H Coupling Constatns (in Hz)

Connectivity	**Specification**	$\lvert J_{ab}\rvert$
$R_2CH_a-H_b$	-	$4-20$
$R_2CH_a-CR_2H_b$	freely rotating ax-ax in C_6H_{12} ax-eq in C_6H_{12} eq-eq in C_6H_{12}	$6-8$ $10-12$ $3-5$ $2-3$
$R_2CH_a-CR_2-CR_2H_b$	freely rotating rigid	<0.1 $1-8$
$RCH_a=CRH_b$	*cis* *trans*	$7-12$ $12-18$
$R_2C=CH_aH_b$	-	$0.5-3$
$H_a(CO)-CR_2H_b$	-	$1-3$
$RH_aC=CR-CR_2H_b$	-	$0.5-2.5$

ax = axial, eq = equatorial

IR Spectroscopy Table

Vibrational Mode	σ / **cm**$^{-1}$	**Intensity**
alcohol O–H (stretching)	$3600 - 3200$	strong
carboxylic acid O–H (stretching)	$3600 - 2500$	strong
amine; amide N–H (stretching)	$3500 - 3350$	strong
alkyne ≡C–H (stretching)	3300	strong
alkene =C–H (stretching)	$3100 - 3000$	weak
alkane –C–H (stretching)	$2950 - 2840$	weak
aldehyde –(CO)–H (stretching)	$2900 - 2800$	weak
nitrile C≡N (stretching)	2250	strong
alkyne C≡C (stretching)	$2260 - 2100$	variable
aldehyde C=O (stretching)	$1740 - 1720$	strong
anhydride C=O (stretching 1)	$1840 - 1800$	weak
anhydride C=O (stretching 2)	$1780 - 1740$	strong
ester C=O (stretching)	$1750 - 1720$	strong
ketone C=O (stretching)	$1750 - 1710$	strong
amide C=O (stretching)	$1700 - 1500$	strong
alkene C=C (stretching)	$1680 - 1600$	weak
aromatic C=C (stretching)	$1600 - 1400$	weak
amine N–H (bending)	$1800 - 1600$	medium
aliphatic CH_2 (bending)	$1480 - 1440$	medium
aliphatic CH_3 (bending 1)	$1470 - 1440$	medium
aliphatic CH_3 (bending 2)	$1390 - 1360$	medium
ester; ether C–O–C (stretching)	$1250 - 1050$	strong
alcohol C–OH (stretching)	$1200 - 1020$	strong
nitro NO_2 (stretching 1)	$1600 - 1500$	strong
nitro NO_2 (stretching 2)	$1400 - 1300$	strong
sulfonate S=O (stretching 1)	$1400 - 1200$	strong
sulfonate S=O (stretching 2)	$1100 - 1000$	strong
halide C–F (stretching)	$1400 - 1000$	strong
halide C–Cl (stretching)	$800 - 600$	strong
halide C–Br (stretching)	$600 - 500$	strong
halide C–I (stretching)	500	strong

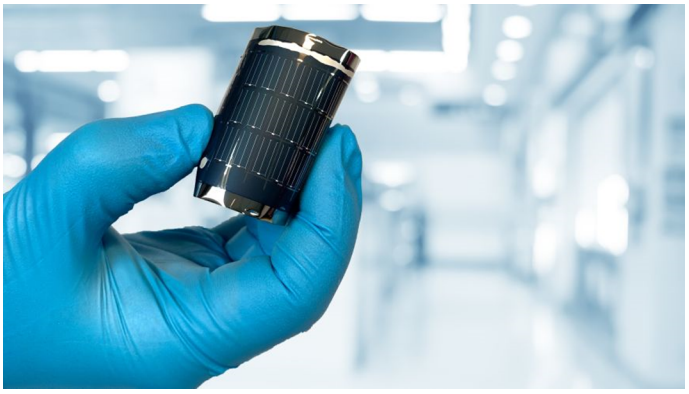
SCORE SHEET **NOT TO BE FILLED IN BY PARTICIPANTS**

Name of participant: _____

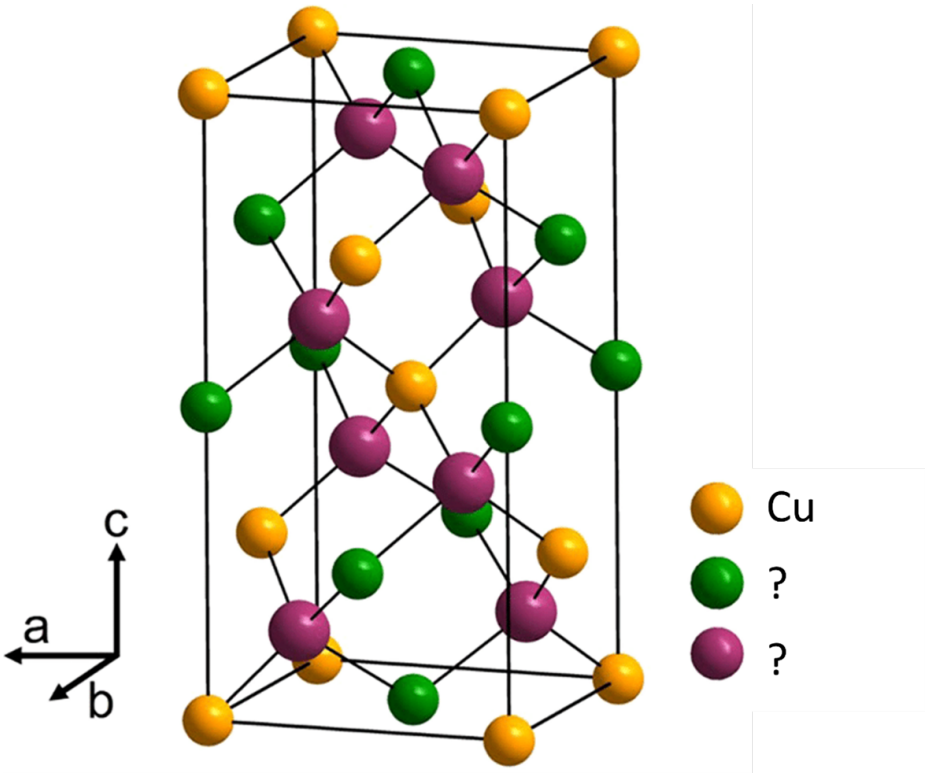
Problem	Title	Maximum Points	Achieved Points
1	Crystalline Solar Cells	11.0	
2	Formation of Tartar in Wine	14.0	
3	Fuel of an Apogee Engine	16.5	
4	Electrochemistry of Gold	14.0	
5	Kinetic Studies of the Formation of Nitryl Fluoride	12.5	
6	Crystal Field Theory and Complex Chemistry	11.0	
7	Stereo- and Biochemistry of Lactic Acid	15.0	
8	Structural Analysis	20.0	
9	Functional Group Interconversion	18.0	
10	Total Synthesis of Platensimycin from (S)-Carvone	14.0	
Total		146.0	

PROBLEM 1 - CRYSTALLINE SOLAR CELLS — 11.0 POINTS

Copper-indium-selenide crystals ($CuInSe_2$) are semiconductors and strongly absorb sunlight. Therefore, $CuInSe_2$ crystals have been studied for application in solar cells. Compared to other semiconductor materials, a much thinner $CuInSe_2$ film for light absorption is required because $CuInSe_2$ has a very high absorption coefficient. This also means $CuInSe_2$-based solar cells are thin enough to be flexible. The record in efficiency for this type of solar cells is held by the Swiss Federal Laboratories for Materials Science and Technology (EMPA). In autumn 2021, the EMPA has claimed a 21.4 % efficiency to convert sunlight into electric power of this type of solar cell.



In the figure below the tetragonal unit cell of the $CuInSe_2$ crystal is depicted. The crystal structure type is like two zincblende unit cells (face-centered-cubic) stacked above each other. The angles of the unit cell are all $\alpha = \beta = \gamma = 90°$. The lattice constants are a = b = 5.8 Å and c = 11.6 Å.



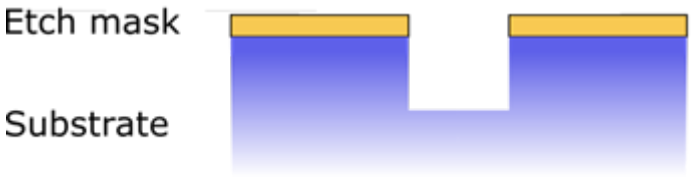
1.1 The orange atom is copper. Which of the atoms (purple or green) is indium, which of the atoms (purple or green) is selenium?

1.2 How many $CuInSe_2$ units make up a unit cell?

1.3 Calculate the density of $CuInSe_2$ in $g\,cm^{-3}$.

1.4 Copper, indium, and selenium are applied to a surface by a method called "low temperature vapour deposition". To perform this method, you need to know how much copper is needed in the final product. Calculate the copper content as weight percentage in $CuInSe_2$.

After the $CuInSe_2$ substrate is applied as an even fine layer, you wish to take it away in certain spots. Therefore, you use a method called "etching". A mask is applied onto the $CuInSe_2$ surface and harsh reagents are applied to remove the $CuInSe_2$ crystals from the desired places.

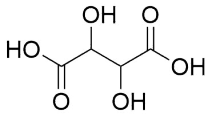


1.5 Write down the balanced equation when $CuInSe_2$ is dissolved by etching solution (sulfuric acid, H_2SO_4, and hydrogen peroxide, H_2O_2). As products, H_2SeO_4, $In_2(SO_4)_3$, $CuSO_4$, and H_2O are observed.

PROBLEM 2 - FORMATION OF TARTAR IN WINE 14.0 POINTS

After a long time in storage, crystals can start to form in wine caskets. Depending on the presence of colouring anthocyanins, these can be yellowish in white wine and pinkish in red wine. Famous German writer J.W. Goethe already documented this, and 100 years ago the chemical engineer W. Klapproth investigated the solubility of this mineral called "Weinstein" (literally, wine rock) or tartar. This tartar is the potassium salt of tartaric acid, a slightly tart tasting salt naturally occurring in grapes. Klapproth performed his investigations in pure water, which of course does not reflect the fact that wine contains a moderate amount of alcohol. Furthermore, he was not aware that the tartaric acid-alcohol-water system is made more difficult due to three facts: 1) solubility of tartrates in alcohol-water mixtures is lower than in pure water, 2) the solubility depends strongly on the temperature, and 3) tartaric acid can form other salts, e.g. with calcium.

Table 2: Overview of possible substances involved. Solubility is given in pure water at 20 °C.

Trivial name	Formal name	Sum formula	Solubility [$g\,L^{-1}$]	Chemical structure
Tartaric acid	2,3-Dihydroxy-butanedioic acid	$C_4H_6O_6$	1394	
Tartar	Potassium hydrogen tartrate	$C_4H_5KO_6$	4.2	
Lime tartar	Calcium tartrate	$C_4H_4CaO_6$	1.2	

2.1 Tartaric acid has two stereogenic centres. However, in grape juice only the *R,R*-form occurs naturally. Draw all possible stereoisomers of tartaric acid, determine if they are chiral, and assign their absolute configurations.

2.2 Tartaric acid is very soluble in water, as you can see from the table above. Give two reasons why this is the case.

2.3 In which pH range will the formation of the classical tartar occur preferentially? And at what pH value exactly? Explain and draw a diagram showing the condition for the formation of tartar as a function of pH.

2.4 In a white wine, the total tartaric acid content is 5.64 $g\,L^{-1}$ and the pH is 3.4. Which forms of tartaric acid are present in which molar concentrations? You can give the ratios rounded to integer values for simplicity.

2.5 The potassium content in grape juice varies depending on the soil conditions. In our white wine from **2.4** it is determined to be 210 mg L^{-1}. What concentration in mol L^{-1} does this correspond to?

If the solubility of tartrate in a solution of 12 % ethanol in water at 15 °C is 2.25 gL^{-1}, does the tartrate present in our white wine precipitate at this temperature? As a simplification, consider tartar as an insoluble salt and try to determine the solubility product at 15 °C.

2.6 Now consider the following solubility table. At what temperature does tartrate precipitate?

Table 3: Solubility of tartrate in g L^{-1} in alcohol-water model solutions. ABV: alcohol by volume.

Temperature (°C)	0 % ABV	10 % ABV	11 % ABV	12 % ABV	13 % ABV
-4	2.00	1.05	0.98	0.91	0.86
0	2.25	1.26	1.17	1.11	1.04
5	2.66	1.58	1.49	1.40	1.32
10	3.42	2.02	1.91	1.81	1.71
15	4.17	2.45	2.35	2.25	2.13
20	4.92	3.08	2.92	2.77	2.63

PROBLEM 3 - FUEL OF AN APOGEE ENGINE — 16.5 POINTS

In order to bring a satellite into a stable orbit after shooting up from an initial parabolic flight curve or to bring it into a higher orbit, a special propulsion technique is used: the apogee engine. In this process, two propellants are mixed and allowed to ignite in a combustion chamber. The thrust from the nozzle propels the remote-controlled satellite. Often the components are so reactive that simple contact in the combustion chamber is sufficient! This is the case in this example, where, as often used, methylhydrazine (CH_6N_2, liquid in the fuel tank) and dinitrogen tetroxide N_2O_4 (in fuel tank also liquid) are used as fuels without adding any other component.

You can find the thermodynamic data of all possible involved compounds in the following table:

Table 4: Thermodynamic data of the compounds at 300 K and 100 Pa.

Compound	ΔH_f^0 (g) [$kJ\,mol^{-1}$]	S^0 (g) [$J\,K^{-1}\,mol^{-1}$]	ΔH ($l \rightarrow g$) [$kJ\,mol^{-1}$]	C_p [$J\,kg^{-1}\,K^{-1}$]
CH_6N_2	54.2	250	40.3	1.410
N_2O_4	9.0	304	2.0	0.785
H_2O	-242	189	44.0	1.858
N_2	0.0	192		1.039
CO_2	-393	214		0.817

3.1 Dinitrogen tetroxide, a dimer of nitrogen dioxide (NO_2) is an extremely reactive substance, yet it is in equilibrium with nitrogen dioxide even at room temperature. How is this possible? Draw the skeletal formulae of the (asymmetrical) methylhydrazine molecule and the (symmetrical) dinitrogen tetroxide, and explain why N_2O_4 is highly reactive and at the same time stable enough as to not disintegrate immediately.

3.2 Write down the balanced equation for the reaction between methylhydrazine and dinitrogen tetroxide. Calculate the required mass ratio for an optimal stoichiometric mixture of the two compounds.

3.3 Determine the molar reaction enthalpy for one of the two reactants and also per gram of fuel mixture (use your result from **3.2**) at standard mixture.

3.4 The actual driving force is the free enthalpy. For this, however, the thermodynamic data of the substances would have to be available at the conditions in the nozzle; whereby the rocket technicians assume a temperature in the combustion chamber of about 3'400 K. So therefore, you have to convert: Adapt your heat of reaction from **3.3** to the conditions.

3.5 Determine the driving force for the estimated temperature. Choose a reference (per mol or per gram) in such a way that you can quickly give answers to loading questions from technology! (If you do not know the procedure, then determine the driving force as a rough approximation at room temperature 300 K).

The telecommunications satellite Hotbird 7A with a mass of m = 4100 kg is lifted by means of the last stage of a launch rocket via a low earth orbit - LEO at an altitude of 200 km to a geostationary orbit GEO with an orbital radius of 4223 km, where it arrives without the last stage of the carrier rocket. In order to swing into GEO at this altitude, the satellite's apogee motor must be fired for the first time to provide an acceleration from about 1995 $\mathrm{m\,s^{-1}}$ to 3071 $\mathrm{m\,s^{-1}}$. The rate of kinetic energy can be used in order to determine the energy needed.

The fuel on board must not only be sufficient for this ignition, but also for further course corrections.

3.6 What amount of propellant is needed to achieve the acceleration for the geostationary orbit GEO? How large should the amount of propellant be if you take into account that, as an approximation, about half of your calculated propellant mass must also be accelerated as well and a surplus of 15 % must be available for future orbit corrections?

PROBLEM 4 - ELECTROCHEMISTRY OF GOLD — 14.0 POINTS

Gold is well known as a noble metal. However, some gold compounds exist, such as the chloride coordination compounds $[AuCl_4]^-$ and $[AuCl_2]^-$.

4.1 What are the oxidation states of gold in $[AuCl_4]^-$, $[AuCl]_2{}^-$, and elementary Au?

4.2 Write down the half-cell reactions and the full redox reaction of the disproportionation reaction of $[AuCl_2]^-$.

4.3 Using the Latimer diagram at pH = 0 below, calculate if $[AuCl_2]^-$ would be stable to disproportionation.

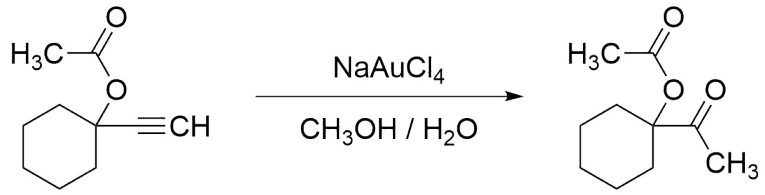
$$[AuCl_4]^- \xrightarrow{0.926\ V} [AuCl_2]^- \xrightarrow{1.154\ V} Au$$

4.4 What is the electrochemical potential of the reaction going from $[AuCl_4]^-$ directly to Au?

4.5 Is it possible to oxidise gold powder using pure oxygen? Provide a balanced redox equation. Assume that the partial pressure of oxygen is $p(O_2) = 1$ atm and the gold is in aqueous solution in the presence of chloride ions. The electrode potential of the oxygen half-cell is given as $E^0{}_{O_2,H^+/H_2O} = 1.229\,V$.

4.6 At what pH interval is it possible to oxidise gold powder by hydrogen peroxide (H_2O_2, $E^0{}_{H_2O_2,H^+/H_2O} = 1.763\,V$) in the presence of chloride ions? Assume that the concentrations of all ions in the solution except H^+ are 1 $mol\,L^{-1}$ and that the potential $E^0{}_{[AuCl_2]^-/Au}$ doesn't change its value with varying pH.

4.7 Gold salts, like $NaAuCl_4$ are used as catalysts in the oxidation of alkynes to methyl ketones. They can also be used in the formation of terminal amides. How would you change the reactant below to obtain an amide in stead of a methyl ketone? Draw the revised reactant.



PROBLEM 5 - KINETIC STUDIES OF THE FORMATION OF NITRYL FLUORIDE 12.5 POINTS

Nitryl fluoride can be formed through the reaction of fluorine gas with nitrogen dioxide according to the following steps:

$$\mathrm{NO_2^\bullet\,(g) + F_2\,(g) \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} NO_2F\,(g) + F^\bullet\,(g)} \tag{1}$$

$$\mathrm{NO_2^\bullet\,(g) + F^\bullet\,(g) \xrightarrow{k_2} NO_2F\,(g)} \tag{2}$$

5.1 Formulate the overall stoichiometric equation for the formation of nitryl fluoride from steps (1) and (2) above.

5.2 Write down the rate law for the formation of nitryl fluoride in this form:

$$\frac{\mathrm{d}\,[\mathrm{NO_2F}]}{\mathrm{d}t} = \ldots$$

5.3 Which of the species in steps (1) and (2) is highly reactive and therefore never present in a high concentration (name only one)?

5.4 For the appropriate species, use a steady-state approximation to determine the concentration of this species.

5.5 With your results from **5.3**, write down the simplified rate law for the formation of nitryl fluoride.

5.6 Under the assumption that $k_2 \gg k_1$ and k_{-1}, simplify the expression from **5.4**. The resulting equation is:

$$\frac{\mathrm{d}\,[\mathrm{NO_2F}]}{\mathrm{d}t} = 2 \cdot k_1\,[\mathrm{NO_2}]\,[\mathrm{F_2}] - \frac{k_{-1} \cdot k_1\,[\mathrm{F_2}]\,[\mathrm{NO_2F}]}{k_2}$$

5.7 At very low concentrations of nitryl fluoride i.e., at the start of the reaction, the rate law gets very simple:

$$\frac{\mathrm{d}\,[\mathrm{NO_2F}]}{\mathrm{d}t} = 2 \cdot k_1\,[\mathrm{F_2}]\,[\mathrm{NO_2}] \tag{3}$$

Why is this the case?

5.8 From your result in **5.5**, show in a few steps how you get the simple rate law (3).

In order to determine k_1, the initial reaction rate v_0 was determined for different concentrations of fluorine and nitrogen dioxide.

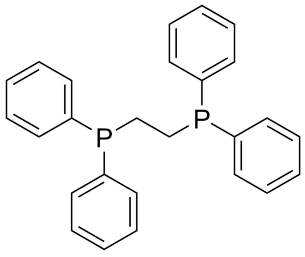
Initial reaction rate v_0 [$\mathrm{mol\,m^{-3}\,s^{-1}}$]	$[F_2]$ [$\mathrm{mol\,m^{-3}}$]	$[NO_2]$ [$\mathrm{mol\,m^{-3}}$]
0.004	$5.2889 \cdot 10^{-6}$	$5.2889 \cdot 10^{-6}$
0.008	$5.3000 \cdot 10^{-7}$	$1.0555 \cdot 10^{-4}$
0.006	$9.3100 \cdot 10^{-6}$	$4.5068 \cdot 10^{-6}$
0.002	$4.5454 \cdot 10^{-4}$	$3.0770 \cdot 10^{-8}$

5.9 Considering all the data points, determine the rate constant k_1 with the corresponding units.

5.10 After some time, the rate law from task **5.7** is no longer valid. Why is that? *Hint*: Think about which reactions take place.

PROBLEM 6 - CRYSTAL FIELD THEORY AND COMPLEX CHEMISTRY 11.0 POINTS

Chelating ligands play a very important role in complex chemistry since they form very stable complexes, as they bind using more than one atom (hence their name, from Greek "chelé", meaning a crab's claws). One such chelating ligand is dppe (1,2-bis(diphenylphosphaneyl)ethane). The structure of the ligand dppe is given below:



dppe

Consider the following reaction:

$$[\mathrm{Mo(CO)_6}] + 2\,\mathrm{dppe} \longrightarrow [\mathrm{Mo(CO_2)_2(dppe)_2}] + 4\,\mathrm{CO} \tag{1}$$

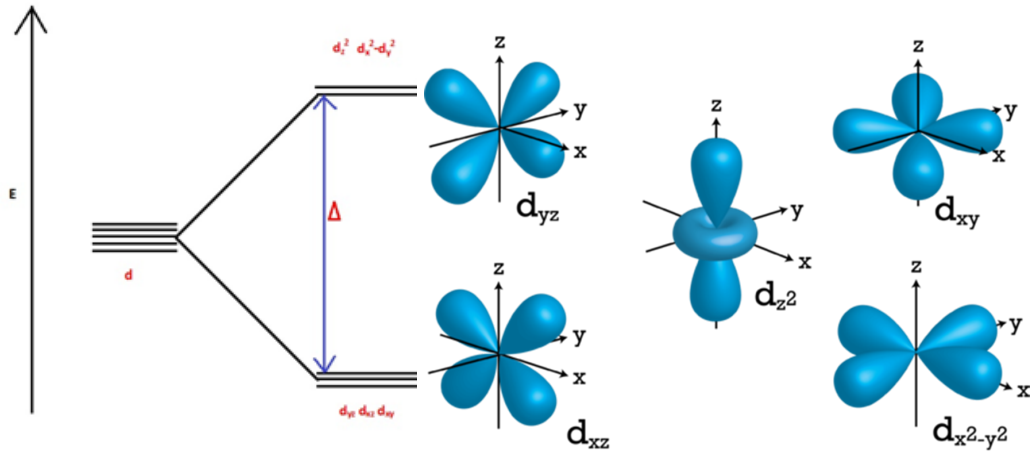
6.1 What is the oxidation state of molybdenum in the complexes above? What is its *d*-electron configuration?

6.2 As mentioned above, chelating ligands form very stable complexes, due to the binding of more than one donor atom. Considering reaction (1), what could be a major thermodynamic driving force for the formation of the product and why (consider the number of products and reactants)?

6.3 Draw all possible stereoisomers of the product. To save you a bit of time, you can draw the dppe ligand as follows:

6.4 What is the relationship between the isomers? Are they diastereo- or enantiomers?

A very valuable model for transition metal complexes is the crystal field theory where the five *d*-orbitals get split up to different energies due to the influence of the ligands. Below, you can see this orbital splitting for an octahedral complex with the shape of the respective *d*-orbitals:



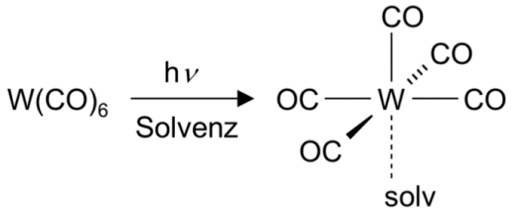
The splitting of the crystal field increases according to the spectrochemical series for the ligands as follows:

$$I^- < Br^- < S^{2-} < SCN^- \approx Cl^- < N_3{}^- < F^- < OH^- < \text{oxalate}^{2-} \approx H_2O < NCS^- < Py \approx NH_3 < NO_2{}^- < PR_3 < P(OR)_3 < CN^- < H^- < CO < NO$$

6.5 Considering the provided spectrochemical series, what spin state do you expect for the complex $[\mathrm{Mo(CO)_2(dppe)_2}]$, high-spin or low-spin and why?

6.6 Draw the orbital diagram for an octahedral complex with the d electrons of the metal centre according to your results from **6.3** and **6.5**. Is the complex para- or diamagnetic?

Tungsten hexacarbonyl, another example of an octahedral carbonyl complex has very interesting properties. Upon exposure to light, one metal-carbon bond is broken and a square-pyramidal complex, stabilised by the solvent, is formed.



Solvenz = dissolution, solv = solvent molecule.

The crystal field splitting for a square-pyramidal complex is slightly different from the one of the octahedral complexes. The d_{z^2} orbital gets stabilised and now lies between the energies of the d_{xy} and the $d_{x^2\text{-}y^2}$ orbitals; furthermore the d_{xz} and the d_{yz} orbitals are also slightly stabilised and now lie energetically below the d_{xy} orbital.

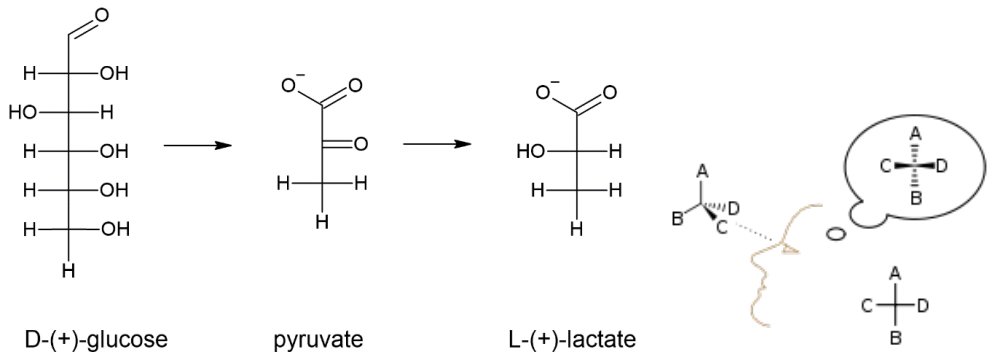
6.7 According to the description above, draw a qualitative crystal field splitting diagram for a square-pyramidal complex and label the orbitals.

6.8 Determine the *d*-electron configuration of the metal centre in $[\mathrm{W(CO)_5}]$ and fill these electrons into the diagram obtained in **6.7**.

6.9 What is the reactivity of the complex? Is it a Lewis acid, a Lewis base, or none of those two? And why?

PROBLEM 7 - STEREO- AND BIOCHEMISTRY OF LACTIC ACID 15.0 POINTS

The human body needs energy to function. An effective means of energy production during short, intense exercise is *anaerobic glycolysis*. Anaerobic glycolysis is the transformation of *glucose* (sugar) via *pyruvate* to *lactate* when limited amounts of oxygen are available. The structures of glucose, pyruvate, and lactate are shown below as Fischer projections.



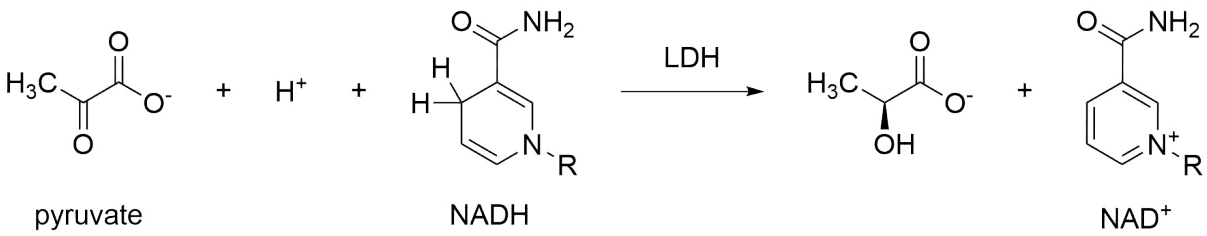
7.1 For D-(+)-glucose, pyruvate, and L-(+)-lactate:

a) Indicate all chiral centres with a star.

b) Assign the absolute configuration (R/S) to all chiral centres based on the Cahn-Ingold-Prelog (CIP) rules.

7.2 Draw the enantiomer of D-(+)-glucose in the Fischer projection.

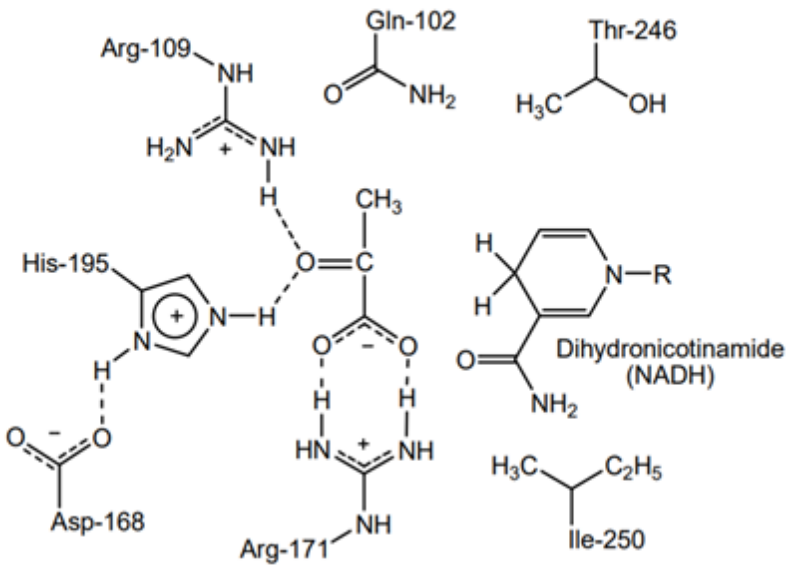
Let's have a closer look at the second step in anaerobic glycolysis i.e., the conversion of pyruvate to lactate:



NADH acts as the reducing agent in this reaction. The reaction is formally the transfer of hydride ion (H^-) from NADH to pyruvate. An enzyme called *lactate dehydrogenase* (*LDH*) catalyses this reaction. An enzyme is protein with a biocatalysis function. It has an active site to bind reactants.

The structure of the substrates pyruvate and NADH bound in the active site of LDH is shown schematically in Scheme 1. Several key amino acid residues in the active site of the enzyme LDH are indicated. They are abbreviated by their three-letter-code, sequence number in LDH and only the side chains of the respective amino acids are shown. The dotted lines between fragments of LDH indicate weak intermolecular interactions among groups in the active site.

Scheme 1



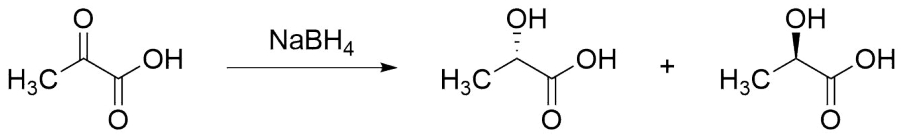
7.3 An achiral compound, pyruvate, is being converted to a chiral compound, L-(+)-lactate. How is it possible that only one enantiomer, the L-(+)-lactate, arises?

7.4 What type of weak intermolecular interaction exists between Arg-109 and the carbonyl group of pyruvate, and between His-195 and the carbonyl group of pyruvate? Why does this interaction occur?

Isoleucin has an alkyl (*sec*-butyl) side chain. The side chain of Ile-250 lies directly below the plane of the dihydronicotinamide ring of NADH (c.f. Scheme 1).

7.5 What type of intermolecular interaction would the sidechain of Ile-250 make with NADH?

You've tried to convert pyruvate to lactic acid in your lab by using the reducing agent $NaBH_4$. You've been successful in your synthesis; however, you obtain both enantiomers of lactic acid in equal amount.



7.6 What is the name of a 50:50 mixture of both enantiomers?

7.7 You wish to separate the two enantiomers and find the following bases in your lab: methylamine, dimethylamine, 1-amino-1-phenylethane, methylphenylamine. Which base is suited for enantiomer separation? How would you proceed?

PROBLEM 8 - STRUCTURAL ANALYSIS — 20.0 POINTS

After staying (yet again) after hours in your laboratory, you come across some your old lab partner's synthesis products. Strangely enough, you find a small vial marked only with the molecular formula of a compound which is still inside it. On the label you find: $\mathbf{C_{15}H_{14}O}$.

Your interest being piqued, you decide to father investigate by running an IR and NMR spectrum of the compound to discover what it is.

8.1 Using the molecular formula, determine the degree of unsaturation of the molecule.

8.2 Using the IR-Spectrum on the next page, identify the structural unit giving the peak with the highest intensity, which is not in the fingerprint area of the spectrum.

8.3 Using both the IR- spectrum and the ^{1}H-NMR spectra of the compound given on the following pages, determine the structural formula of the compound and its IUPAC name.

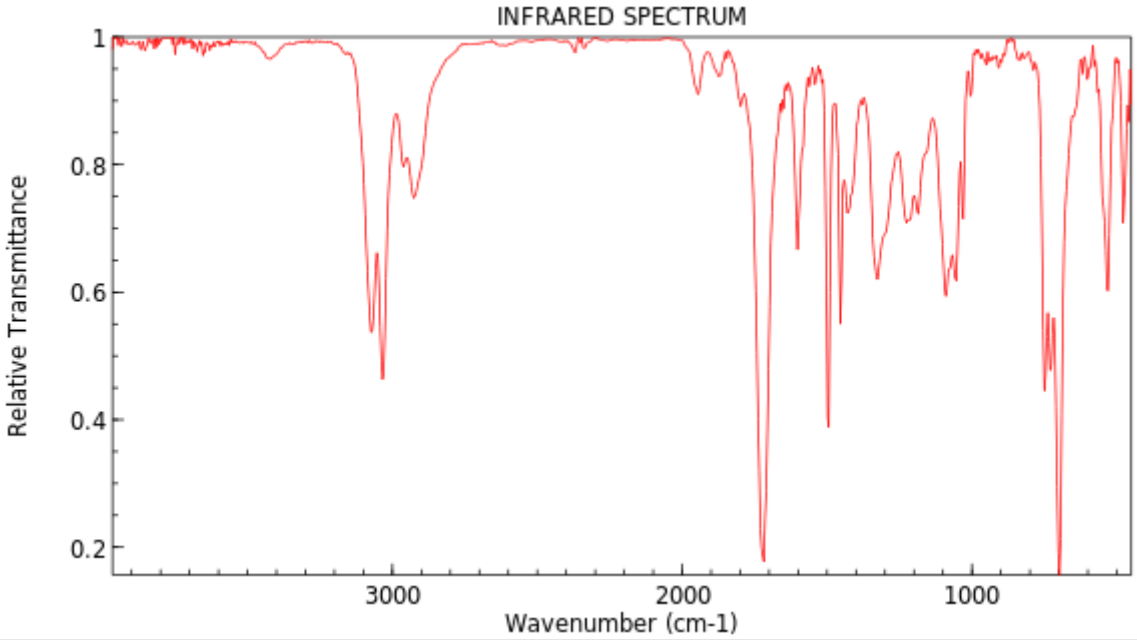
Whilst further rummaging through your partner's lab notes, you come across a paper, detailing which reactions led to the creation of compound $\mathbf{C_{15}H_{14}O}$:

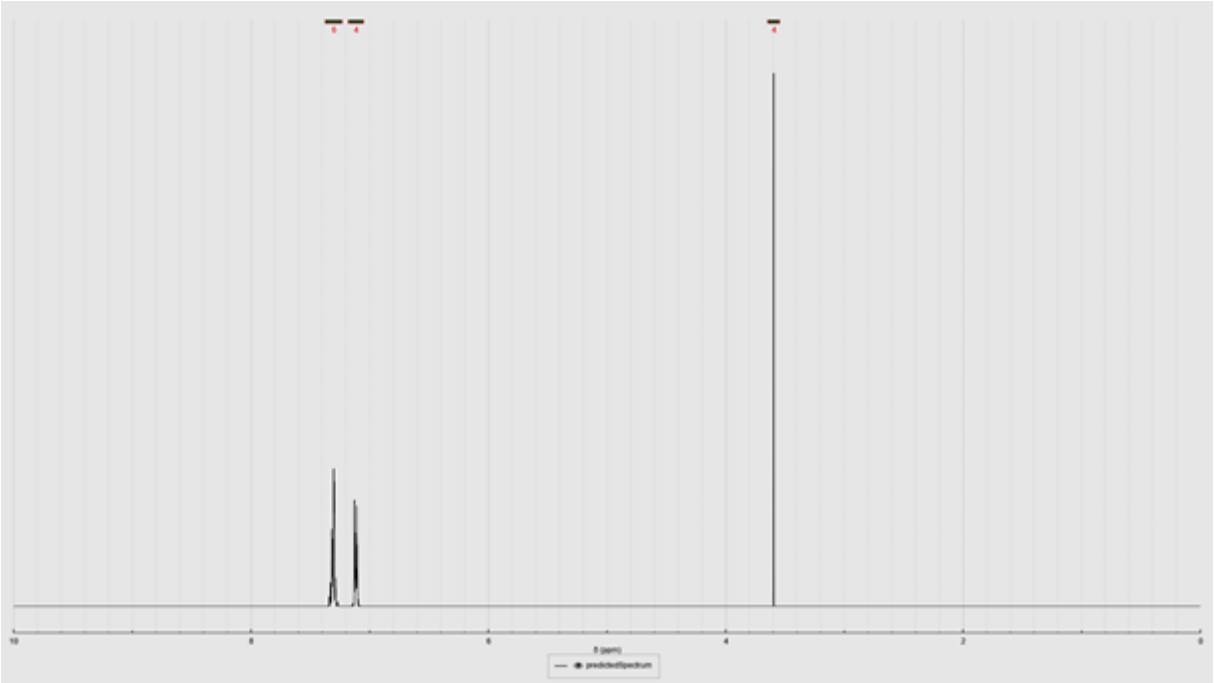
A reaction using BH_3, NaOH and H_2O was performed on compound **X** to create an intermediate molecule with the formula $\mathbf{C_{15}H_{16}O}$. This compound was then oxidised using $Al(O^iPr)_3$ to give the desired compound $\mathbf{C_{15}H_{14}O}$.

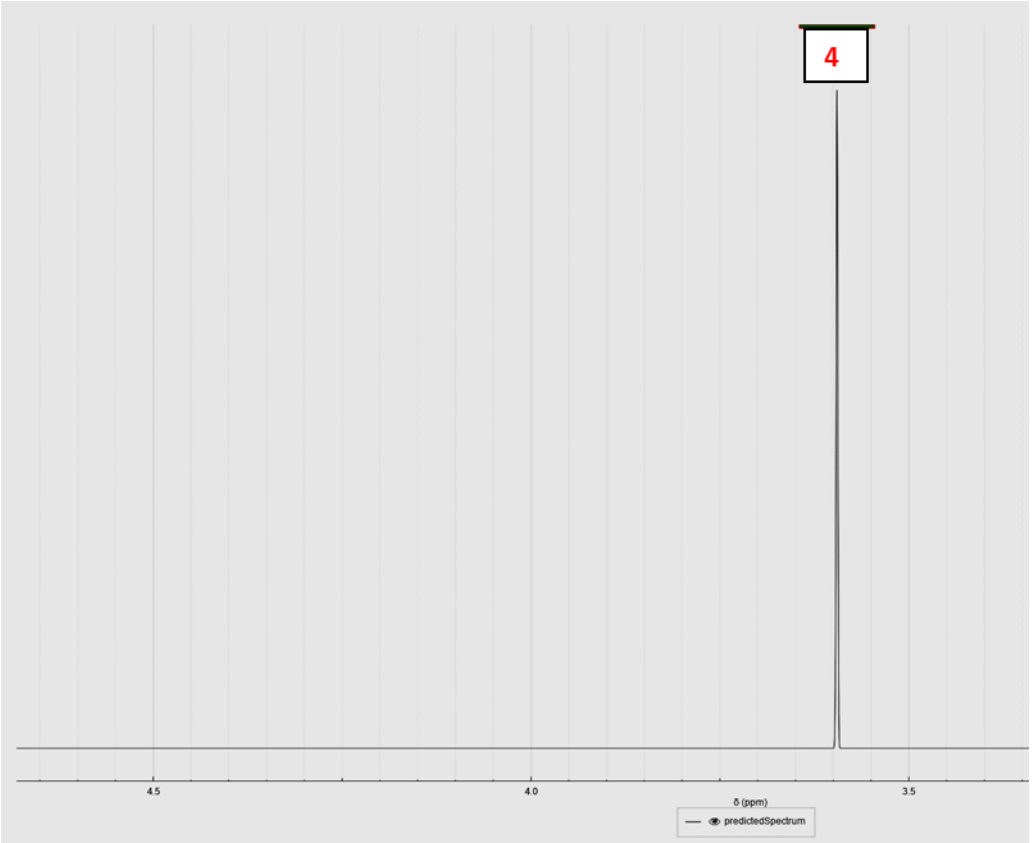
8.4 Give the structural formula of the reaction intermediate $\mathbf{C_{15}H_{16}O}$ and its IUPAC name.

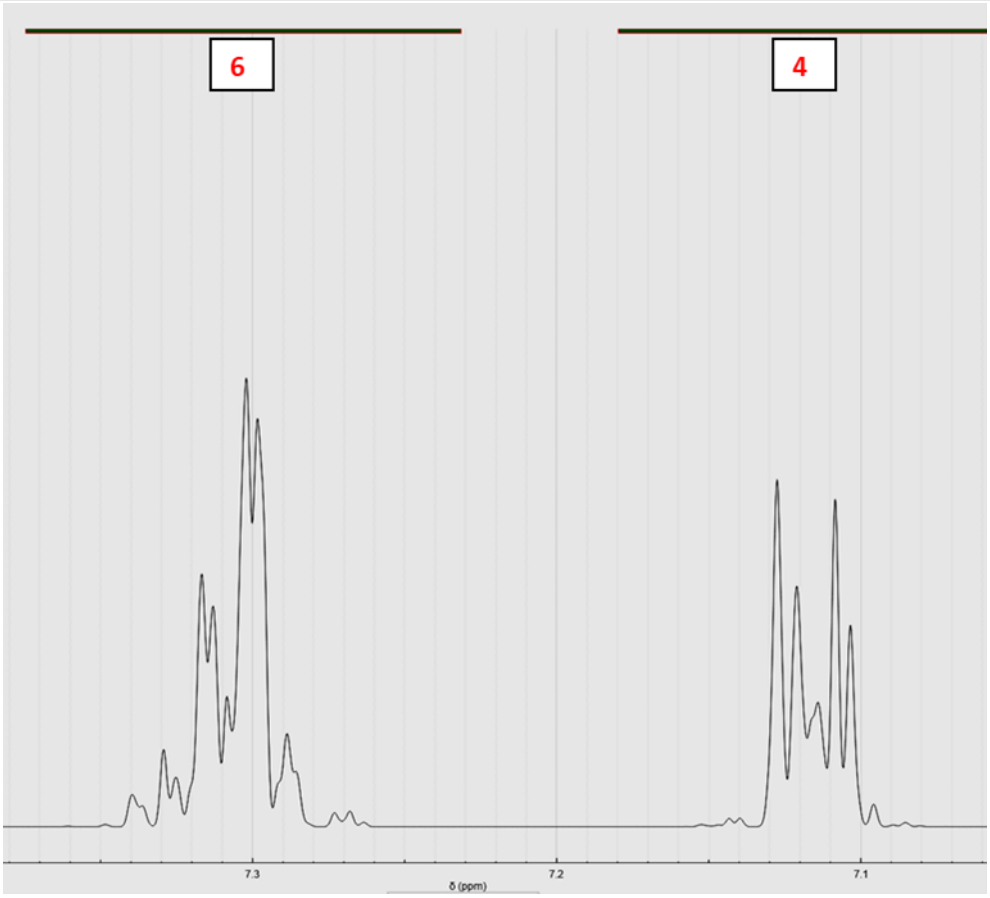
8.5 Give the structural formula of compound **X** and its IUPAC name. Can you name the reaction to get from compound **X** to the intermediate?

8.6 Detail in what way the ^{1}H-NMR spectrum of compound X will be different from $\mathbf{C_{15}H_{14}O}$ in terms of chemical shift and multiplicity.


INFRARED SPECTRUM
Relative Transmittance
1
0.8
0.6
0.4
0.2
3000
2000
1000
Wavenumber (cm-1)

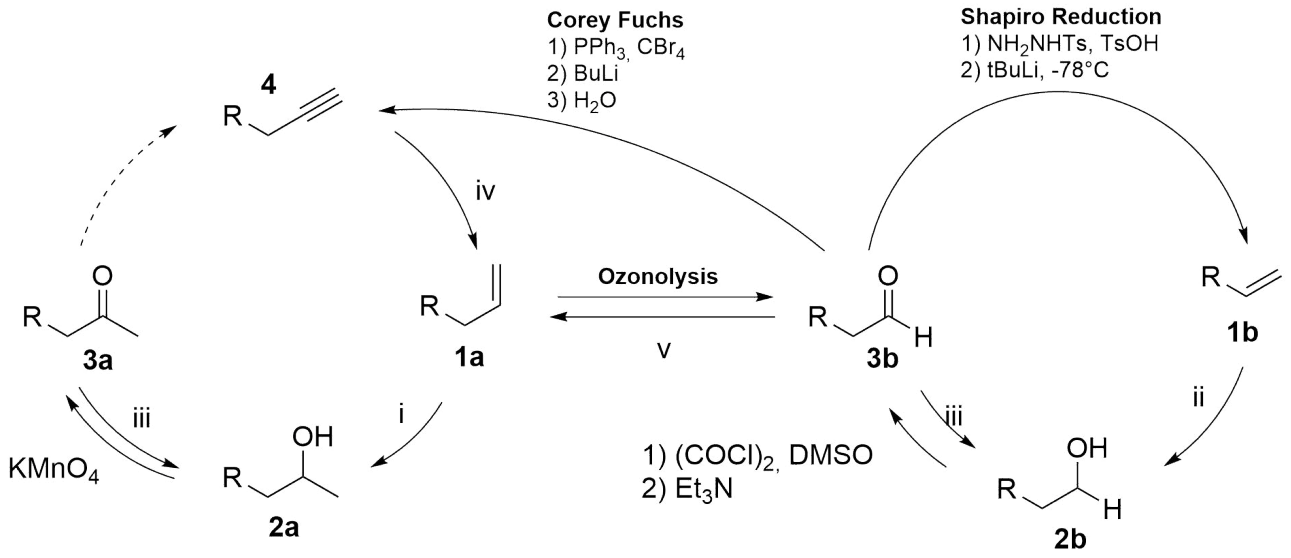



4
4.5
4.0
3.5
δ (ppm)
predictedSpectrum


6
4
7.3
7.2
7.1
δ (ppm)

PROBLEM 9 - FUNCTIONAL GROUP INTERCONVERSION 18.0 POINTS

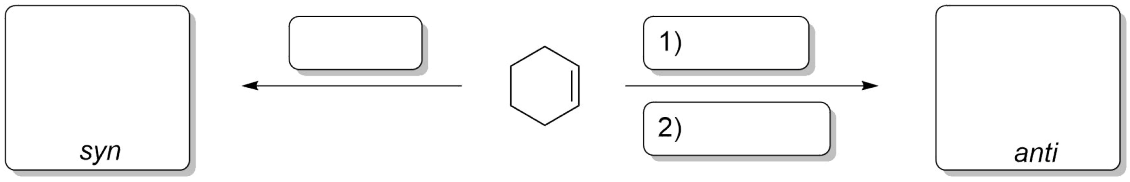
Functional Group Interconversions are reactions which interchange different functional groups into each other. This is important in the total synthesis of many natural products, as changing functional groups gives rise to new ways of thinking about the synthesis of a natural product. Below you will find two seemingly similar circles, with ways to interchange functional groups into one another.



9.1 Firstly, let's have a look at the two alkenes in the circle. The goal is to install a hydroxy group at the double bond of **1a** and **1b**. Please provide conditions **i** and **ii** with which to achieve the conversion to **2a** and **2b**.

i ii

9.2 Instead of one hydroxy group, we want to install two in a vicinal relationship. Give the conditions and the product for two ways which produce different diastereoselectivities.



9.3 **2a** and **2b** are oxidised to yield **3a** and **3b**. Please provide conditions **iii** for the reverse reaction.

iii

9.4 What would be the product when reacting **2b** with $KMnO_4$?

Product with $KMnO_4$

9.5 Compound **3a** is converted to **4** via a series of reactions. **4** then reacts to **1a** under conditions **iv**. Please give reaction conditions **iv**.

iv

9.6 Compound **1a** can be converted to **3b** by ozonolysis (conditions **vi**). The reverse reaction is achieved using conditions **v**. Please state the reaction conditions **v** and **vi**, as well as the name corresponding to conditions **v**.

Conditions v

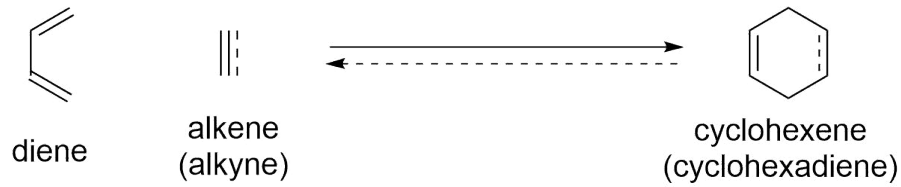
Name:

Conditions vi

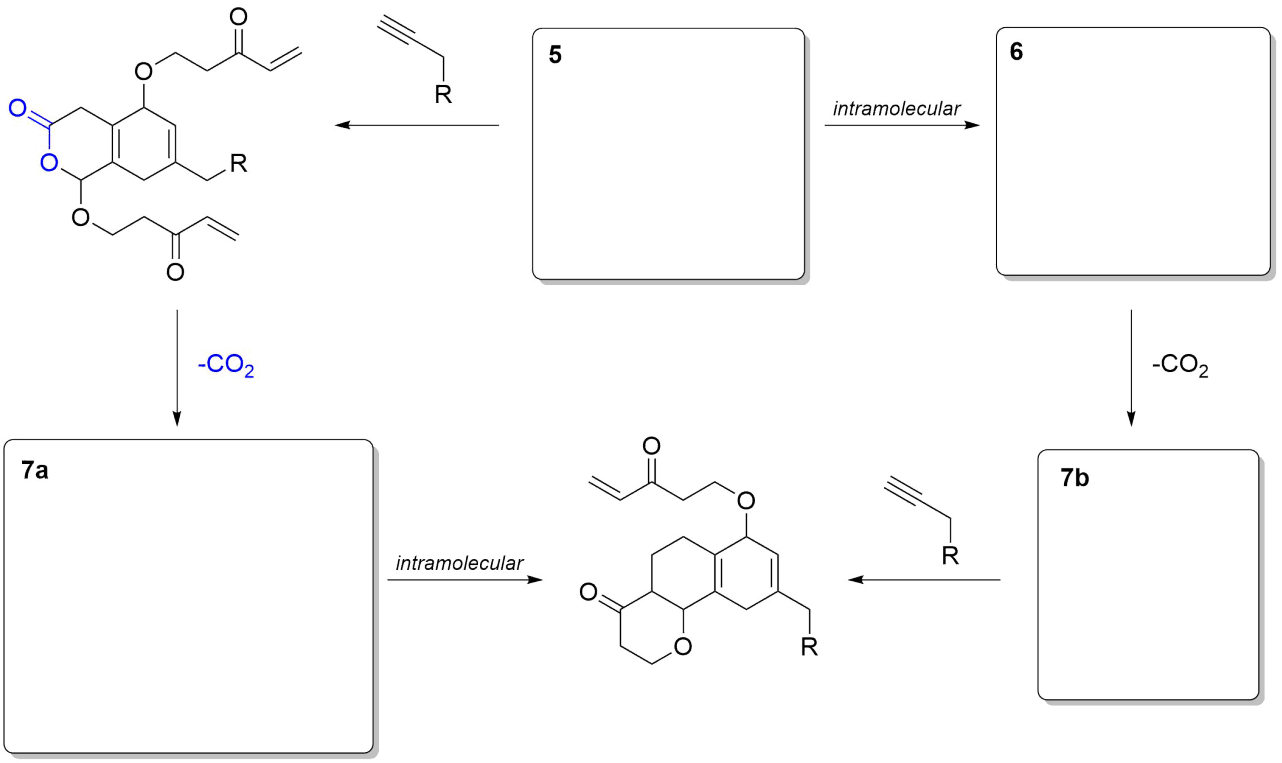
Name: Ozonolysis

9.7 As discussed before, the ketone **3a** can be converted to the alkyne **4** via a series of reactions. Please state a feasible way of doing so. (*Hint*: This can be achieved using only the reactions stated in the scheme above.)

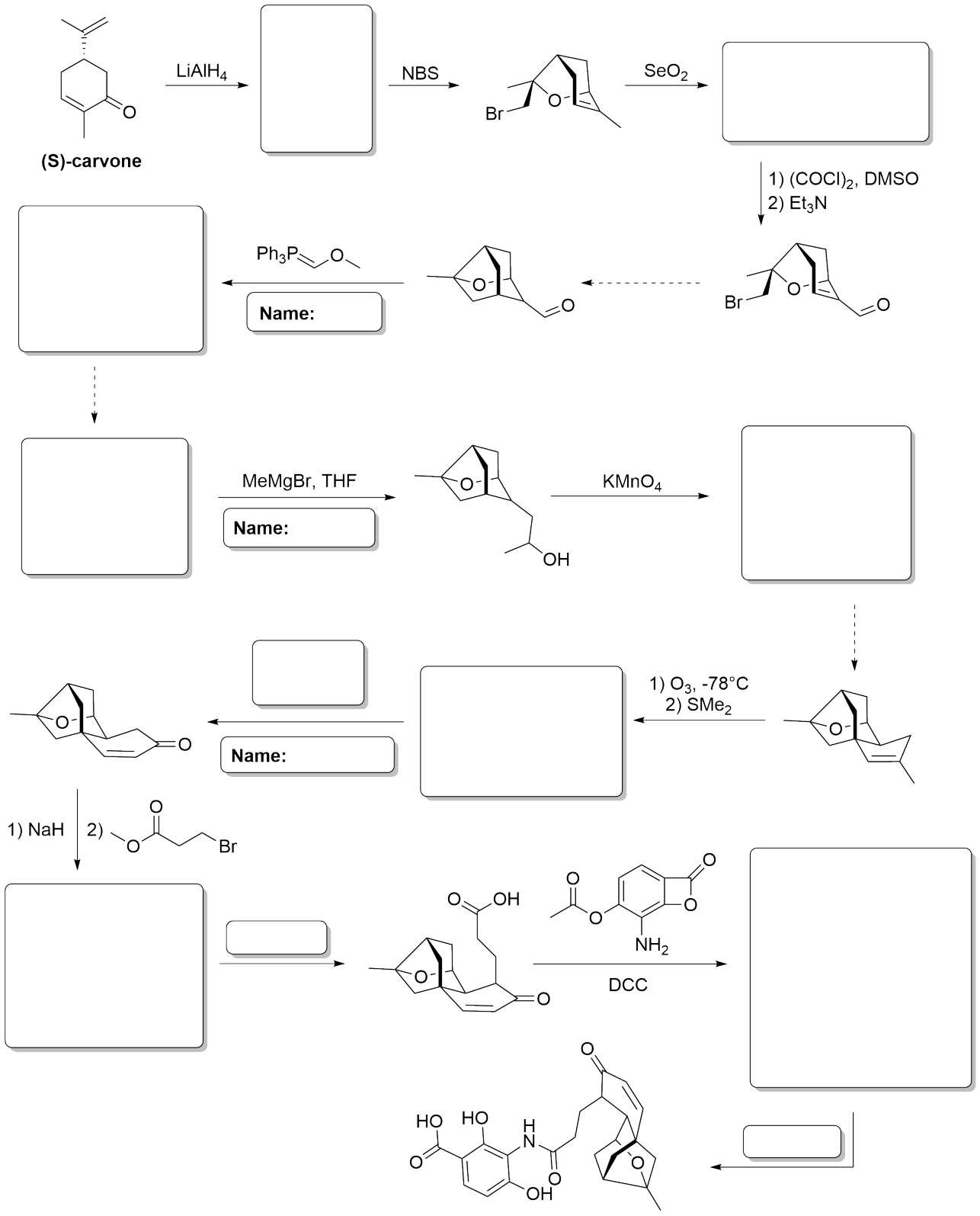
Now that we have discussed some functional group interconversions, we want to do some chemical transformations with one of these products. The reaction we are going to look at is called Diels-Alder Cycloaddition and is depicted below. The reaction converts a diene and an alkene or an alkyne to a cyclohexene or cyclohexadiene. This reaction can also run in reverse under the given conditions.



9.8 The alkyne **4** could also react with substrate **5** in the following reactions to yield the product shown below. However, **5** could also react with itself to yield product **6**. Both products can then react to give products **7a** and **7b**. These can then react further to give the final product of the reaction. Please provide the structures of compounds **5**, **6**, **7a**, and **7b**.


5
6
intramolecular
-CO2
-CO2
7a
7b
intramolecular
R

PROBLEM 10 - TOTAL SYNTHESIS OF PLATENSIMYCIN FROM (*S*)-CARVONE 14.0 POINTS



10.1 Fill in the missing reagents, reaction intermediates/products, and names of the reactions where indicated.