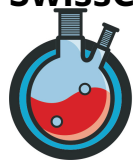


**CHEMISTRY.
OLYMPIAD.CH**

CHEMIE-OLYMPIADE
OLYMPIADES DE CHIMIE
OLIMPIADI DELLA CHIMICA

SwissChO 2023 - Theoretical Final Exam



General Information

Instructions

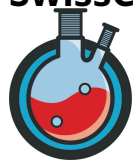
- Write your name on each page and number these.
- You have three hours to solve the problems. Wait for the **START** signal before you begin.
- Use a new page for each problem. Clearly indicate what problem you are working on.
- Write all necessary calculations legibly.
- Put your pages into the provided 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 **10** problems.

Viel Erfolg!

Bonne chance!

Buona fortuna!

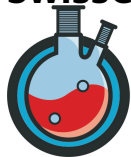
Good luck!



Physical Constants and Formulae

Constants

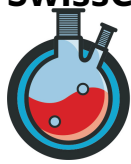
Planck constant	$h = 6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant	$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$
Speed of light	$c = 2.998 \times 10^8 \text{ m s}^{-1}$
Elementary charge	$e = 1.602 \times 10^{-19} \text{ C}$
Avogadro constant	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Universal gas constant	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
Faraday constant	$F = 9.648 \times 10^4 \text{ C mol}^{-1}$
Standard pressure	$p_0 = 1 \times 10^5 \text{ Pa}$
Electronvolt	$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
Absolute zero	$0 \text{ K} = -273.15 \text{ }^\circ\text{C}$
Ångstrom	$1 \text{ Å} = 1 \times 10^{-10} \text{ m}$
Pi (π)	$\pi \approx 3.141592$
Euler's number	$e \approx 2.718281$



Formulae and Equations

Ideal gas law	$pV = nRT = Nk_B T$
Gibbs free energy	$\Delta G = \Delta H - T\Delta S$
Relation between ΔG and K	$\Delta G = -RT \ln(K)$
Relationship between ΔG and ΔE_{cell}	$\Delta_r G^0 = -nF\Delta E_{cell}^0$
Nonstandard ΔG	$\Delta_r G = \Delta_r G^0 + RT \ln(Q)$
Reaction quotient Q for reaction $aA + bB \rightleftharpoons cC + dD$	$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
Nernst equation	$E = E^0 - \frac{RT}{nF} \ln(Q)$
Electric current	$I = \frac{Q}{t}$
Arrhenius law	$k = Ae^{-\frac{E_A}{RT}}$
Lambert-Beer law	$A = \epsilon Lc = \log\left(\frac{I_0}{I}\right)$
Buffer equation	$\text{pH} = \text{pK}_a + \log\left(\frac{[A^-]}{[HA]}\right)$
Energy of a photon	$E = h\nu = \frac{hc}{\lambda}$
Half life for a first-order reaction	$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$
Activity of a radioactive sample	$A = kN$
Surface area of a sphere	$A = 4\pi R^2$
Volume of a sphere	$V = \frac{4\pi}{3} R^3$

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



Periodic Table of the Elements

Periodic Table of Elements

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01															9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31															17 Cl 35.45	18 Ar
19 K 39.10	20 Ca 40.08	21 Sc	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 La	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 Ac	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]			

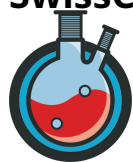
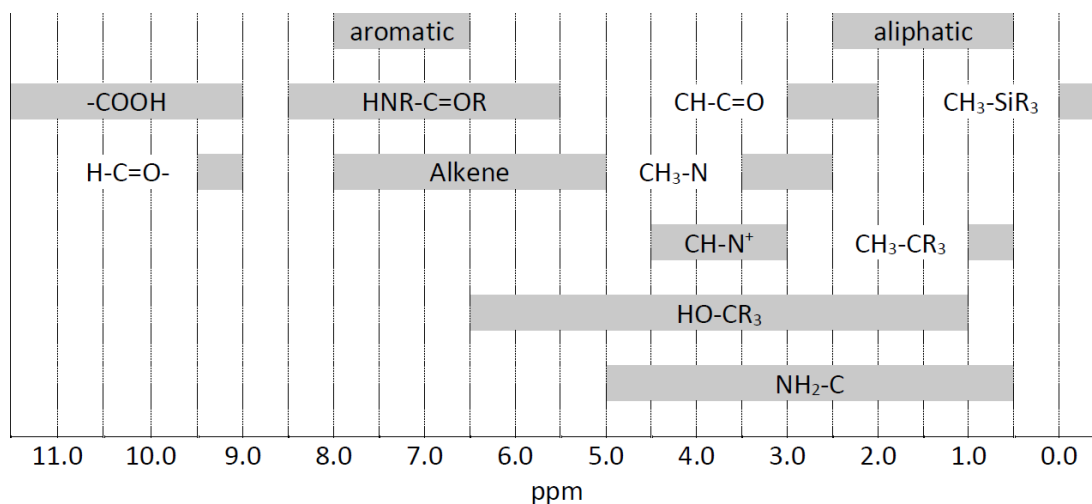
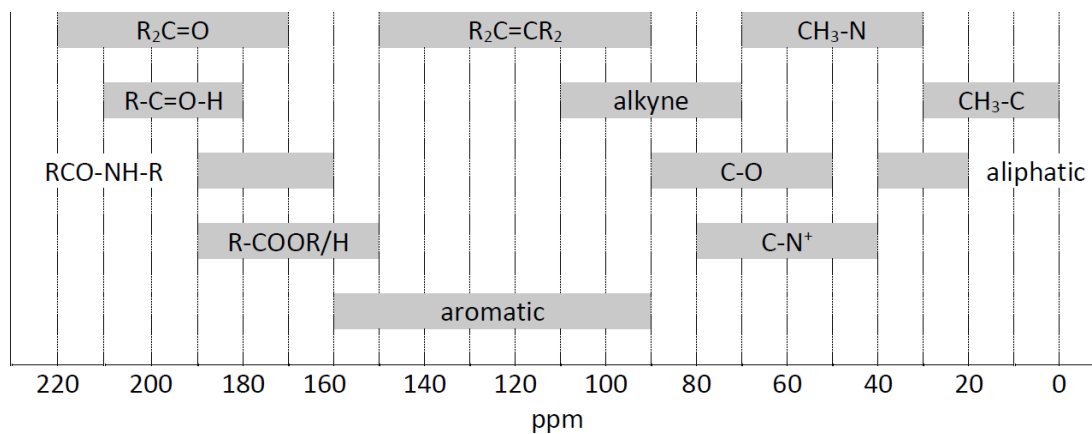


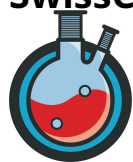
Table of NMR Chemical Shifts

^1H NMR Chemical Shift



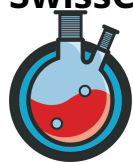
^{13}C NMR Chemical Shifts





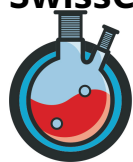
¹H Coupling Constants

Connectivity	Specification	$ J_{ab} /\text{Hz}$
$\text{R}_2\text{CH}_a\text{H}_b$	-	4 - 20
$\text{R}_2\text{CH}_a-\text{CR}_2\text{H}_b$	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
$\text{R}_2\text{CH}_a-\text{CR}_2-\text{CR}_2\text{H}_b$	freely rotating rigid	<0.1 1 - 8
$\text{RCH}_a=\text{CRH}_b$	<i>cis</i> <i>trans</i>	7 - 12 12 - 18
$\text{R}_2\text{C}=\text{CH}_a\text{H}_b$	-	0.5 - 3
$\text{H}_a(\text{CO})-\text{CR}_2\text{H}_b$	-	1 - 3
$\text{RH}_a\text{C}=\text{CR}-\text{CR}_2\text{H}_b$	-	0.5 - 2.5



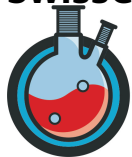
IR Spectroscopy Table

Vibrational Mode	$\tilde{\nu}/\text{cm}^{-1}$	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 $\text{R}\equiv\text{C}-\text{H}$ (stretching)	3300	strong
alkene $\text{R}=\text{C}-\text{H}$ (stretching)	3100 - 3000	weak
alkane $\text{R}-\text{C}-\text{H}$ (stretching)	2950 - 2840	weak
aldehyde $\text{R}-\text{(CO)}-\text{H}$ (stretching)	2900 - 2800	weak
nitrile $\text{C}\equiv\text{N}$ (stretching)	2250	strong
alkyne $\text{C}\equiv\text{C}$ (stretching)	2260 - 2100	variable
aldehyde $\text{C}=\text{O}$ (stretching)	1740 - 1720	strong
anhydride $\text{C}=\text{O}$ (stretching 1)	1840 - 1800	weak
anhydride $\text{C}=\text{O}$ (stretching 2)	1780 - 1740	strong
ester $\text{C}=\text{O}$ (stretching)	1750 - 1720	strong
ketone $\text{C}=\text{O}$ (stretching)	1750 - 1710	strong
amide $\text{C}=\text{O}$ (stretching)	1700 - 1500	strong
alkene $\text{C}=\text{C}$ (stretching)	1680 - 1600	weak
aromatic $\text{C}=\text{C}$ (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 $\text{C}-\text{O}-\text{C}$ (stretching)	1250 - 1050	strong
alcohol $\text{C}-\text{OH}$ (stretching)	1200 - 1020	strong
nitro NO_2 (stretching 1)	1600 - 1500	strong
nitro NO_2 (stretching 2)	1400 - 1300	strong
sulfonate $\text{S}=\text{O}$ (stretching 1)	1400 - 1200	strong
sulfonate $\text{S}=\text{O}$ (stretching 2)	1100 - 1000	strong
halide $\text{C}-\text{F}$ (stretching)	1400 - 1000	strong
halide $\text{C}-\text{Cl}$ (stretching)	800 - 600	strong
halide $\text{C}-\text{Br}$ (stretching)	600 - 500	strong
halide $\text{C}-\text{I}$ (stretching)	500	strong

**Score Sheet****NOT TO BE FILLED IN BY PARTICIPANT**

Name of participant:

Problem	Title	Maximum points	Achieved points	Pages
Q1	Cool High-Temperature Superconductors	15.0		2
Q2	Equilibria of Lime Scale Formation in Hard Water	15.0		2
Q3	Thermodynamics in a Car Engine	15.0		2
Q4	Electrochemistry of Chromium	14.0		2
Q5	Enzyme Kinetics	14.5		2
Q6	The Diversity of Nickel	14.0		2
Q7	Biomolecules - Carbohydrates and Peptides	14.0		2
Q8	Analysis of an Unknown Compound	15.5		3
Q9	Playing with Cyclohexenone	14.0		2
Q10	Total Synthesis of Cidofovir	16.0		2
Total		147.0		21



Cool High-Temperature Superconductors (15.0 points)

Yttrium barium copper oxide (YBCO) is a ceramic high-temperature superconductor. It is the first material to achieve superconductivity above the temperature of liquid nitrogen and it is based on research done at the IBM laboratory in Zürich. One variant of YBCO has the chemical composition of $\text{Y}_\alpha\text{Ba}_\beta\text{Cu}_\gamma\text{O}_{\delta-\epsilon}$ (with $0 \leq \epsilon \leq 0.5$). The following image depicts an idealized rectangular unit cell (lattice parameters: $a = 3.82 \text{ \AA}$, $b = 3.89 \text{ \AA}$ and $c = 11.68 \text{ \AA}$) of the YBCO crystal with an $\epsilon = 0.0$.

Note: If you cannot determine the coefficients $\alpha - \delta$ in the following exercises, the majority of the points will still be awarded if you use the variables instead of their numerical values in the calculations.

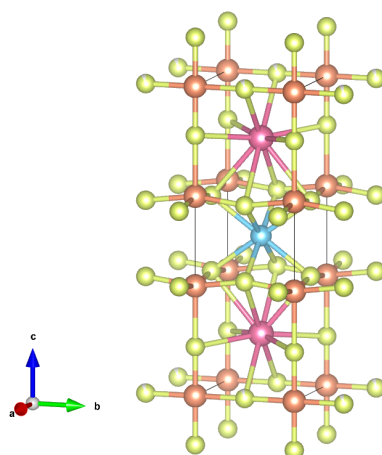
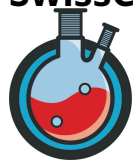


Figure 1.1: Idealised unit cell of a YBCO crystal with $\epsilon = 0.0$. Note that not all depicted atoms are part of the unit cell.

1.00 g of a YBCO ceramic with a known $\epsilon = 0.25$ is dissolved in excess sulfuric acid. Only a white precipitate **A** (0.70 g) remains, which is removed. To the remaining solution, NH_3 is added in excess. At first, a gelatinous precipitate forms, part of which redissolves upon further addition of NH_3 . The remaining precipitate however is removed and heated strongly, and a new Y^{3+} -containing compound **B** (0.17 g) is formed under the loss of 19% of its weight in H_2O . The remaining intensely blue solution is then heated until only dark blue crystals remain. Upon further heating, the blue colour first becomes lighter and vanishes completely at last, yielding white crystals. These are left out in the air for a few days, gaining 56% in weight and once again turning into blue crystals **C** (1.13 g).

1.1	Determine the chemical formulae of compounds A – C .	1.5pt
1.2	Calculate $\alpha - \delta$, assuming them to be integers.	5.0pt
1.3	Note the number of atoms of each element per unit cell. Assign the colours to each of the elements (Y, Ba, Cu, O).	2.5pt



1.4 Calculate the density of the YBCO crystal in g cm^{-3} , assuming $\epsilon = 0.25$.

4.0pt

The first synthesis of YBCO was performed by heating the corresponding metal carbonates in an oxygen atmosphere to around 1300°C .

1.5 Write a balanced chemical equation for this reaction ($\epsilon = 0.25$).

1.0pt

Newer methods for the synthesis of YBCO often make use of nitrate salts, which are dissolved in water to better mix the metals. This solution is then boiled off, and the remaining powder is baked. This solution is a light blue in colour.

1.6 Assign each metallic ion in solution a colour and **propose** a reason as to why some of them lack colour.

1.0pt



Equilibria of Lime Scale Formation in Hard Water (15.0 points)

The seemingly trivial phenomenon of hard water, which residents of cantons sitting on top of chalk or limestone deposits experience, actually has to do with several equilibria. Firstly, it is about the solubility of carbon dioxide and lime (calcium carbonate) in water and about multiple different, but related, equilibria of carbonic acid formation and deprotonation.

Under laboratory conditions, lime ($K_{sp} = 3.36 \times 10^{-9} \text{ mol}^2 \text{ L}^{-2}$) is to be precipitated freshly and in small particles from a freshly prepared and filtered calcium hydroxide ($K_{sp} = 5.02 \times 10^{-6} \text{ mol}^3 \text{ L}^{-3}$) solution by bubbling a dosed amount of carbon dioxide through it.

The initial conditions are given as a $0.01 \text{ mol L}^{-1} \text{ Ca(OH)}_2$ solution.

Note: You will need to make some assumptions throughout this problem. Clearly **state** which assumptions you make and why they are sensible in this context.

2.1 Determine if such a concentration of Ca(OH)_2 is theoretically possible under standard conditions. Also **calculate** the initial pH and pOH of this solution. 2.5pt

2.2 Formulate a balanced chemical equation for the reaction of lime with carbonic acid - as it can occur during the decomposition of lime-containing rock. **Give** an explanation why the product is easily dissolved away. 1.0pt

The Erlenmeyer rule (according to Emil Erlenmeyer - yes, the one with the flask!), which was postulated around 1885 states that molecules with two OH groups attached to the same C are generally unstable and will decompose quickly. Therefore, only about 1% of all dissolved CO_2 actually forms carbonic acid.

2.3 Calculate the molar amount of CO_2 that would theoretically have to be introduced into 0.5 L of our solution for maximum precipitation of lime. **Argue** why the $\text{CO}_2 - \text{H}_2\text{CO}_3$ equilibrium is irrelevant in this reaction. 1.5pt

CO_2 is fairly soluble in water, with 1.7 g L^{-1} and 3.3 g L^{-1} at 20°C and 0°C , respectively.

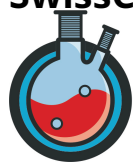
Equilibrium	pK_a
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	6.46
$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$	10.40

2.4 Calculate both the maximum concentration of CO_2 at 20°C and the pH of such a solution (applying the Erlenmeyer rule). 1.5pt

0.5 L of our Ca(OH)_2 solution is added to 0.2 L of a saturated CO_2 solution at 20°C and the precipitation of finely divided lime is observed. For now, you can assume that H_2CO_3 and OH^- react directly to *only* form CO_3^{2-} and that no HCO_3^- is formed.

2.5 Calculate the pH of the remaining solution. 2.5pt

However, in reality, while mixing the two solutions, some of the freshly precipitated lime will already react with excess carbonic acid, dissolving once again (see **2.2**).

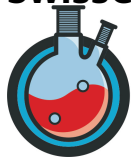


2.6 Determine the mass of lime precipitated in the reaction.

3.0pt

If the precipitation of lime scale is fresh and without proper crystallisation, the lime can be redissolved by adding more CO_2 to the solution.

2.7 Draw the $[\text{Ca}^{2+}]$ concentration of our initial solution as a function added CO_2 , labelling all major Ca^{2+} salts (dissolved or precipitated) at their respective intervals of occurrence. 3.0pt



Thermodynamics in a Car Engine (15.0 points)

In a car engine, in addition to the familiar oxidation of the hydrocarbon mixture, atmospheric oxygen also reacts with nitrogen that is inevitably present to form nitrogen oxides.

These oxides are often called "NO_x", with *x* being either 1 or 2.

3.1 Write the reaction equation for the formation of the simplest nitrogen oxide, **1.0pt**
drawing the complete Lewis formula of the product.

3.2 Elaborate on why NO₂ is more likely to dimerise than NO. **0.5pt**

The following table depicts standard enthalpies of formation $\Delta_f H^0$, standard entropies S^0 and heat capacity C_p for various nitrogen- and oxygen-containing species.

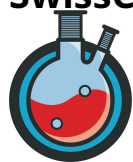
Compound	$\Delta_f H^0 / \text{kJ mol}^{-1}$	$S^0 / \text{J mol}^{-1} \text{K}^{-1}$	$C_p / \text{J mol}^{-1} \text{K}^{-1}$
N ₂ (g)	0	192	29.12
N (g)	473	153	
NH ₃ (g)	-46	192	35.06
NH ₃ (l)	264		
NH ₃ (aq)	-80	111	
NO (g)	90	211	29.84
NO ₂ (g)	33	240	37.20
N ₂ O (g)	82	220	38.45
N ₂ O ₄ (g)	9	304	77.28
N ₂ O ₅ (s)	-43	178	
O ₂ (g)	0	205	29.36
O (g)	249	161	
O ₃ (g)	143	239	39.29

3.3 Calculate the enthalpy change $\Delta_r H^0$ of the reaction described in **3.1** at 25 °C **1.0pt**
and **suggest** how you need to change the temperature to decrease the yield of the product.

3.4 Calculate the entropy change ΔS^0 for the reaction taking place under **3.1**. **0.5pt**

3.5 Determine the equilibrium constant K_p of the formation of NO at 25 °C. **2.0pt**

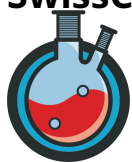
To simulate combustion in a cylinder, a sturdy vessel (500 mL) is filled with 10% fuel and 90% atmospheric air (80% nitrogen, 20% oxygen) at 25 °C. It is then sealed tightly and heated to 1900 °C. During combustion, all fuel and half of the oxygen are consumed. You can assume that the combustion products occupy the same volume as the consumed reactants. Further on, assume that nitrogen oxide formation only starts after the combustion is completed.



3.6 Calculate both the new enthalpy change $\Delta_r H$ and the new K_p under these conditions. 3.0pt

3.7 Calculate the partial pressures $p_c()$ of nitrogen and oxygen in the cylinder after combustion, but before any nitrogen oxide is formed. 2.0pt

3.8 Calculate the mass of nitrogen oxide that can be expected to be produced per combustion. **Note:** If you could not determine K_p in **3.6**, you may use the approximation $K'_p = 1.0 \times 10^{-3}$. 5.0pt



Electrochemistry of Chromium (14.0 points)

Latimer diagrams are especially useful when it comes to summarizing the electrochemistry of elements. Below, you are given the Latimer diagram of chromium in acidic solution.

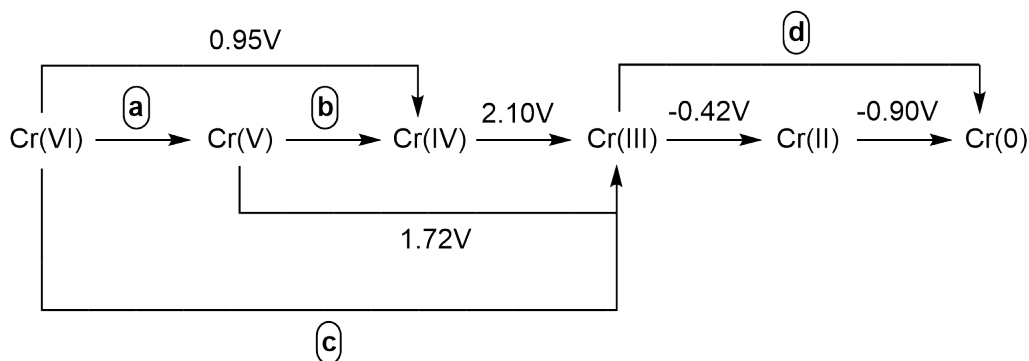


Figure 4.1: Latimer diagram for Cr in acidic solution.

4.1 Calculate the missing potentials a-d.

2.0pt

4.2 Determine, for the calculated potentials, whether the corresponding reductions are exergonic or endergonic.

1.0pt

The same information as in a Latimer diagram may also be represented by a Frost diagram, where $\frac{\Delta G}{F}$ is plotted versus oxidation states. Frost diagrams show the peaks and valleys in an "energy landscape".

A Frost diagram for Cr in both acidic and basic solutions is given below.

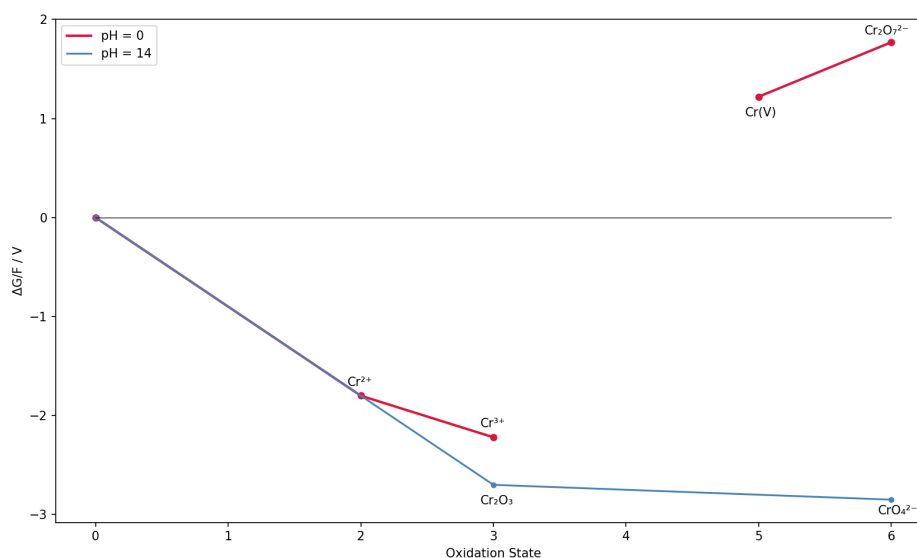
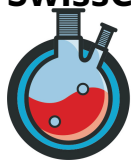


Figure 4.2: Incomplete dual Frost diagram of Cr in basic and acidic aqueous solutions.



- 4.3** **Draw** a complete Frost diagram of Cr in acidic solution, **adding** the missing point Cr(IV). 1.5pt

Frost diagrams are handy to ascertain the thermodynamic stability of an oxidation state.

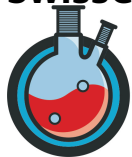
- 4.4** **Elaborate** on the thermodynamic stability of Cr(II) and Cr(VI) and **provide** whether these oxidation states can be produced as a result of a disproportionation. 3.0pt

- 4.5** **Calculate** the standard cell potential of the comproportionation of Cr^{3+} and another Cr-species to form Cr(II). 1.5pt

Cr(VI) is a strong oxidizer in acidic solutions. However, it is remarkably stable in basic solutions. This means, that the reduction potential E_{red} is dependent on pH.

- 4.6** **Give** a balanced half-reaction equation for the reduction of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} in aqueous acidic solution. 1.0pt

- 4.7** **Give** an equation for the non-standard reduction potential of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} , which is linearly dependent on pH at 25 °C. 4.0pt



Enzyme Kinetics (14.5 points)

Enzymes are an important class of biomolecules. They catalyze biological reactions that could otherwise not run fast enough to sustain life. After completion of the reaction, an enzyme is again present in the same form as it has been before the reaction. One enzyme can therefore catalyze many turnovers of a reaction.

- 5.1 State** which parameter of a reaction is changed by the enzyme. In keywords, **note** what the change is. 1.0pt

In the following, you can see the reaction equation for an enzyme-catalyzed reaction



in which E denotes the enzyme, S the substrate, ES the enzyme-substrate complex and P the product. k_i are the rate constants.

- 5.2 Write** the differential rate laws for the following three concentrations: [S], [ES] and [P]. 3.0pt

The steady state assumption assumes that the concentration of a certain intermediate in a reaction is constant over time, which allows to simplify the rate laws. The condition of a (more or less) constant concentration of an intermediate is what we typically observe in an enzymatic reaction. For the following tasks, consider that the enzyme can be present in two different forms, E and ES, and that the total enzyme concentration $[E]_0$ must stay constant.

- 5.3 Explain** what change you expect for [ES], if the substrate concentration is increased. 1.0pt

- 5.4 Applying** the steady-state assumption for the enzyme-substrate complex, **write** the expression for [ES] based on the correct rate law that you found in **5.2**. E_0 and ES should be the only enzyme-containing species in your final equation. 3.0pt

For the next step, consider that the reaction rate is proportional to the concentration of the enzyme-substrate complex according to

$$\frac{v}{v_{\max}} = \frac{[ES]}{[E]_0} \quad (2)$$

- 5.5 Rearrange** the equation that you obtained in **5.4** so that you have an expression for v that does no longer depend on [ES]. 1.0pt

The parameter K_M (Michaelis constant) corresponds to the concentration of substrate that leads to a half-maximal reaction rate.

- 5.6 Develop** a simplified expression for K_M that only contains rate constants. Show your working. 2.0pt



5.7 Simplify the expression for v for the following three cases:

2.0pt

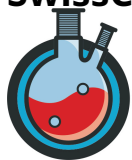
(i) $[S] \gg K_M$

(ii) $[S] = K_M$

(iii) $[S] \ll K_M$

5.8 For cases (i) and (ii) **5.7**: **Write** the expression for the concentration of the enzyme-substrate complex as a function of the total enzyme concentration.

1.5pt



The Diversity of Nickel (14.0 points)

Nickel forms a variety of coordination compounds with different characteristics. Metallic nickel was one of the first metals which could be purified very to a high degree (>99.99%) thanks to the Mond process invented by Ludwig Mond in 1890. In the process, metallic nickel reacts with four equivalents of carbon monoxide to only produce a volatile liquid coordination complex **C** (MW: 170.73 g mol⁻¹), which can then be distilled. Upon heating, metallic nickel is once again formed.

6.1 Write down the forward reaction described above. **Assign** oxidation numbers to all atoms in the product. 2.5pt

6.2 **Elaborate** on the thermodynamic driving force of the decomposition of complex **C** at higher temperatures. 1.0pt

Depending on the nature and geometry of the ligands around the metal centre, the 5 different d-orbitals are split into different energy levels, according to crystal field theory. The different splittings are depicted below.

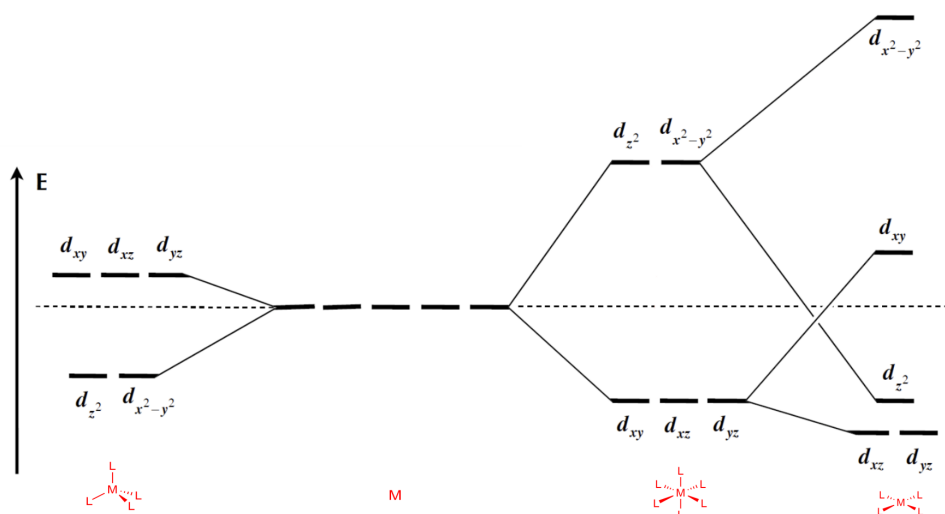
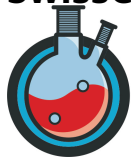


Figure 6.1: Different energy levels of the d-orbitals depending on coordination geometry.

Certain types of nickel-complexes such as [Ni(PPh₂Bn)₂Cl₂] exist in two forms **A** and **B**. **A** is diamagnetic and has a deep red colour, whereas **B** is paramagnetic.

6.3 **Determine** the number of d-electrons in these complexes. 1.0pt

6.4 **Draw** the orbital diagrams with all d-electrons of the metal centre of compounds **A** and **B** on your answer sheet, labelling all orbitals and **using** the same energy axis for both of the compounds. 3.0pt



- 6.5** Draw all possible structures of **A** as well as **B**. Establish all relations between the isomers (constitutional isomer, enantiomer, diastereomer...). 3.0pt

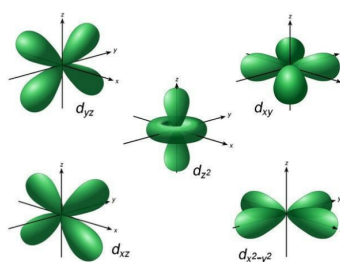
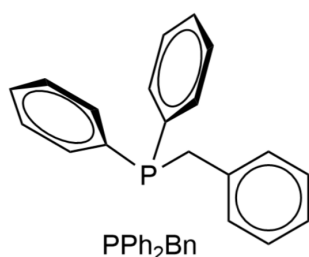
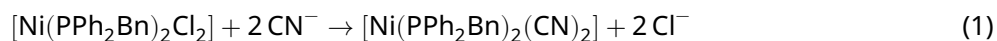


Figure 6.2: left: Structure of the PPh_2Bn ligand. right: Shapes of the d-orbitals.

- 6.6** Elaborate on whether you would assume the colour of **B** to be closer to blue or red, compared to **A**. 1.5pt

In a ligand exchange reaction, the chloro ligands are substituted for cyano ligands as follows:



This new complex only exists as a square-planar complex. The splitting in the crystal field increase according to the spectrochemical series of ligands as follows:



- 6.7** Give a reason for why $[\text{Ni}(\text{PPh}_2\text{Bn})_2(\text{CN})_2]$ only exists in a single isomer. 1.0pt

- 6.8** Judging on the colour of **A**, make an educated guess about the colour of $[\text{Ni}(\text{PPh}_2\text{Bn})_2(\text{CN})_2]$. 1.0pt



Biomolecules - Carbohydrates and Peptides (14.0 points)

Sugars contain carbon, hydrogen and oxygen in the atomic ratio of 1 : 2 : 1 (C : H : O). When Emil Fischer started his research on sugars in the year 1884, only three sugars with the molecular formula $C_6H_{12}O_6$ have been known. Two of them, glucose and galactose, have been known to be aldohexoses with the same constitution: $CHO-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CH_2OH$.

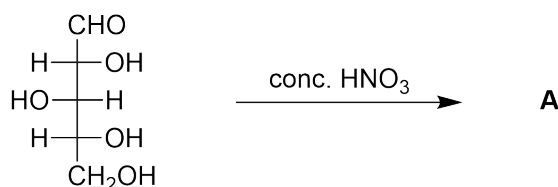
7.1 Calculate how many stereoisomers of aldohexoses exist.

1.0pt

Both the aldehyde group and the hydroxy group of an aldose can be oxidized by concentrated nitric acid to yield a carboxylic acid. Oxidation of xylose leads to xylaric acid.

7.2 Draw the product **A** of the reaction shown below.

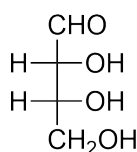
1.0pt



7.3 Explain the optical activity of xylaric acid. **State** how such a compound is called.

1.5pt

7.4 Below, you can see the structure of D-erythrose. **Copy** the structure on your answer sheet and **draw** all stereoisomers. **Note** the relationship (enantiomer, diastereomer) between each combination of two structures.

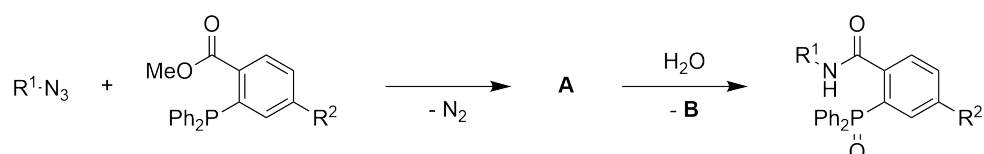


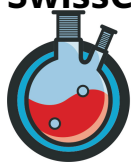
Peptides are polymers composed from amino acids. Formally, a peptide is formed by condensation of amino acids under loss of water. There are many different ligation methods to join two peptide fragments together. We will have a look at some of them in the following.

The Staudinger ligation joins an azide and a phosphine reagent together.

7.5 Draw the intermediate **A** and compound **B** for the Staudinger ligation.

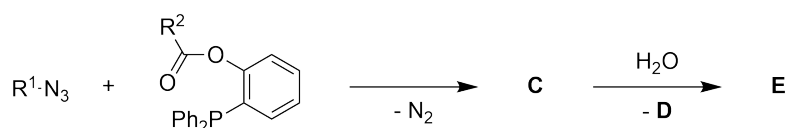
1.5pt





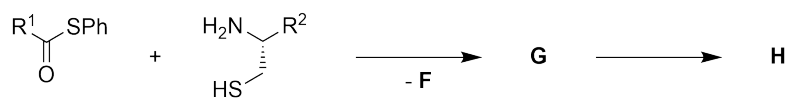
With a mechanism similar to the one above, the traceless Staudinger ligation joins two peptides with a native amide bond.

7.6 Draw intermediate **C**, compound **D** and product **E** of the traceless Staudinger ligation 3.0pt ligation.



Another ligation method that leads to a native amide bond is the native chemical ligation, which necessarily requires an N-terminal cysteine in one fragment. This method was reported in 1994 and marks the starting point of the development of numerous reactions such as the two above.

7.7 Draw compound **F**, intermediate **G** and product **H** of the native chemical ligation 2.5pt





Analysis of an Unknown Compound (15.5 points)

You find an unknown sample in your lab and decide that you want to identify the substance. For the whole task, keep in mind that you have **ONE compound** and that there are **NO charges** present on the molecule!

To start the analysis you determine the contents of individual elements in your sample. In the first step, you determine the carbon and hydrogen content using the setup depicted below. A sample of known mass is burned in a glass tube which is supplied with pure oxygen, yielding the following substances after combustion: carbon dioxide, water, various nitrous oxides and excess oxygen. The gases then pass through the two consecutive U-tubes.

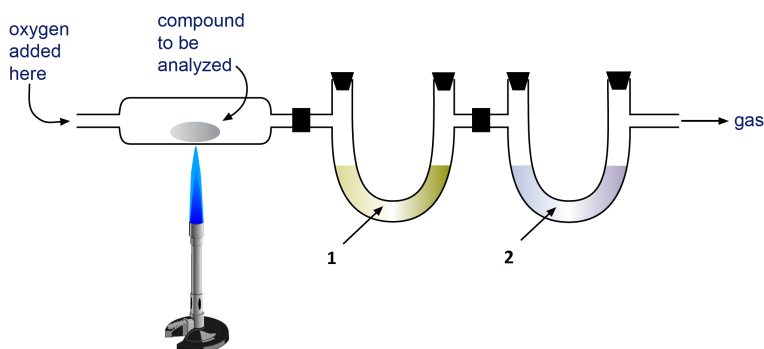


Figure 8.1: Setup for the combustion analysis.

- 8.1** Of the two U-tubes, one contains sodium hydroxide solution and the other contains dry calcium chloride. **Explain** the use of each of the two tubes and **state** (if necessary) the correct order of the tubes. 1.5pt

In your next step, you determine the nitrogen content. You start with a new weighed sample and add concentrated sulfuric acid, then you heat the sample. All organic nitrogen in the sample is converted to ammonium ions. You add sodium hydroxide to lower the pH, which converts the ammonium ions to ammonia.

- 8.2** You now have ammonia in an alkaline aqueous solution, however you do not know the exact amounts of sulfuric acid or sodium hydroxide solution that you have used in your experiment. **Describe** a procedure to quantify the ammonia. 1.5pt

Using your method of choice and some additional information, you could deduce that the sum formula of your compound is $C_9H_{11}NO_2$.

- 8.3** **Calculate** the number of double bond equivalents. 1.5pt

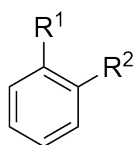
Your compound shows a strong band in the IR spectrum (not depicted) at around 1700 cm^{-1} .

- 8.4** **Note** what causes this vibration. 0.5pt

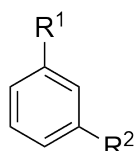
At the end of this task (page **Q8-3**), you find a ^1H -NMR spectrum of your compound.



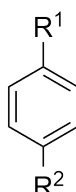
- 8.5 What is the substitution pattern on the aromatic ring? **Choose** one of the five patterns below. **Explain** your choice. 1.5pt



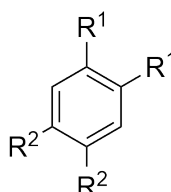
A



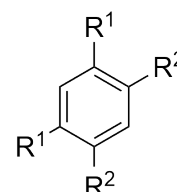
B



C



D



E

- 8.6 Considering peak D: This signal comes from one or more protons bound to a single atom. **Give** the element of this atom. **Comment** on the peak width. 1.0pt

- 8.7 Considering peak E: **Give** the letter of the other peak to which this/ these proton(s) couple to? **Explain** your answer. 1.0pt

- 8.8 In which of the following forms is the nitrogen atom present? **Choose** one of the following: amide, amine or nitro group. **Explain** your choice. 1.5pt

- 8.9 From the chemical shift of peak C, you see that the carbon atom carrying this/ these proton(s) is connected to a heteroatom. **Explain** what influence you expect on the proton chemical shift due to a heteroatom in this position. **Decide** what element the heteroatom is. 1.5pt

- 8.10 **Draw** all fragments that you could identify so far. If there are remaining atoms, list them too. 2.0pt

- 8.11 **Draw** the final compound based on the fragments that you listed in 8.10 and using all the information you got from solving tasks 8.3 to 8.9. 1.0pt

- 8.12 **Note** what causes the peak at 7.26 ppm. 0.5pt

- 8.13 **Note** what causes the peak at 0.00 ppm. 0.5pt

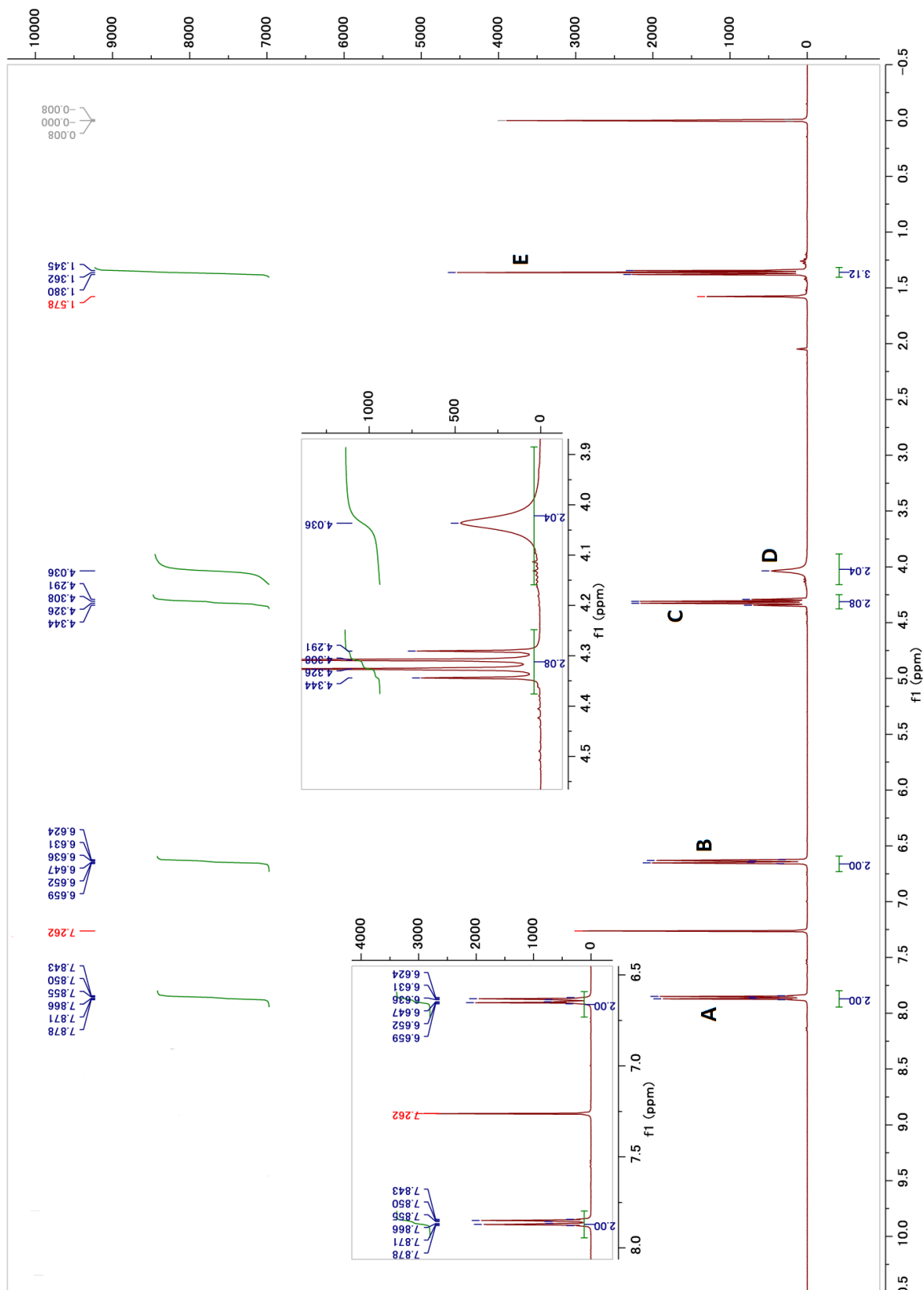
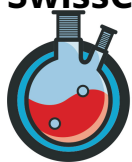


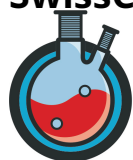
Figure 8.2: 400 MHz ^1H -NMR spectrum in CDCl_3 , the x-axis shows the chemical shift δ .

[illegible]

9.1 Draw the structure of all products **A-I** and **G**. Draw the major product if there are multiple. You may neglect all stereochemistry. 8.0pt

9.3 Suggest suitable reagents for transformations **1**–**4**, that give the desired products. 2.0pt

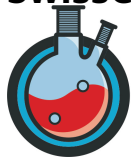
X $\xrightarrow{-\text{H}_2\text{O}}$ **Y**



9.4 Draw the structure of **X** and correctly **name** the reaction taking place. 1.5pt

Molecule **X** can be synthesized from some of the compounds occurring on the chart very easily.

9.5 Give the IUPAC name of one of these compounds and **suggest** a path to convert it to **X**. 1.5pt



Total Synthesis of Cidofovir (16.0 points)

Cidofovir, or Vistide, is a synthetic drug with a plethora of possible uses, which was first synthesised by Antonín Holý. Not only is it applied topically to treat warts, it has also shown effectiveness in treating viral infections in people who suffer from HIV.

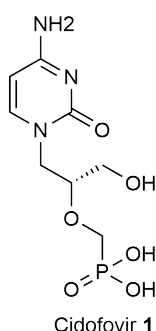


Figure 10.1: Structure of Cidofovir.

The key precursor for the synthesis is the enantiopure protected diol **4**. This product is obtained starting from commercially available L-Mannitol. The synthetic route is shown below.

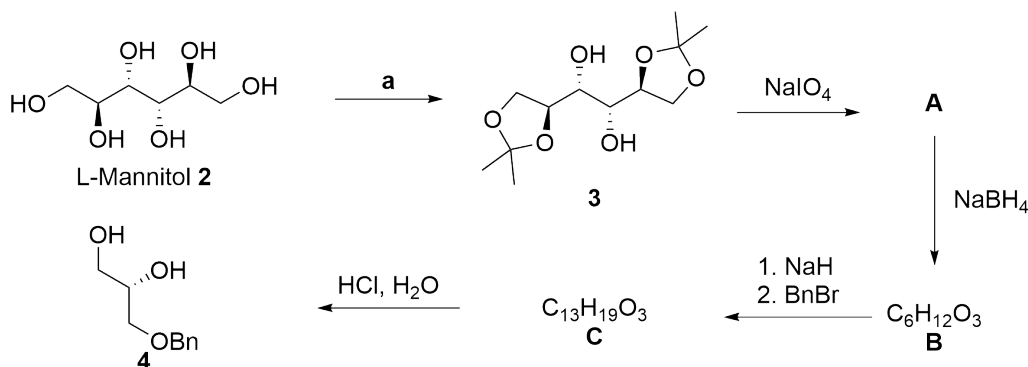


Figure 10.2: First steps in the synthesis of Cidofovir.

10.1 Draw all structures **A-C** with all necessary stereochemical information given. 3.0pt
Note: One equivalent of **3** will yield two equivalents of **A**.

10.2 Propose conditions for the transformation under **a**. 1.5pt

10.3 Draw all stereoisomers of **2** that could also be used to reach product **4**. 2.0pt

10.4 Name two reasons for why the steps from **B** to **C** and **C** to **4** must be performed in that order. 2.0pt

Product **4** is subsequently used in further steps to synthesise Cidofovir.

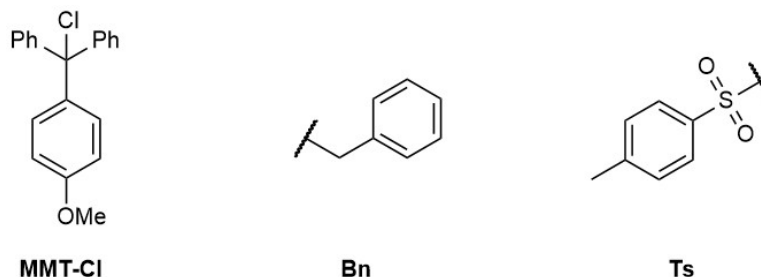


Figure 10.3: Full structures of certain abbreviations.

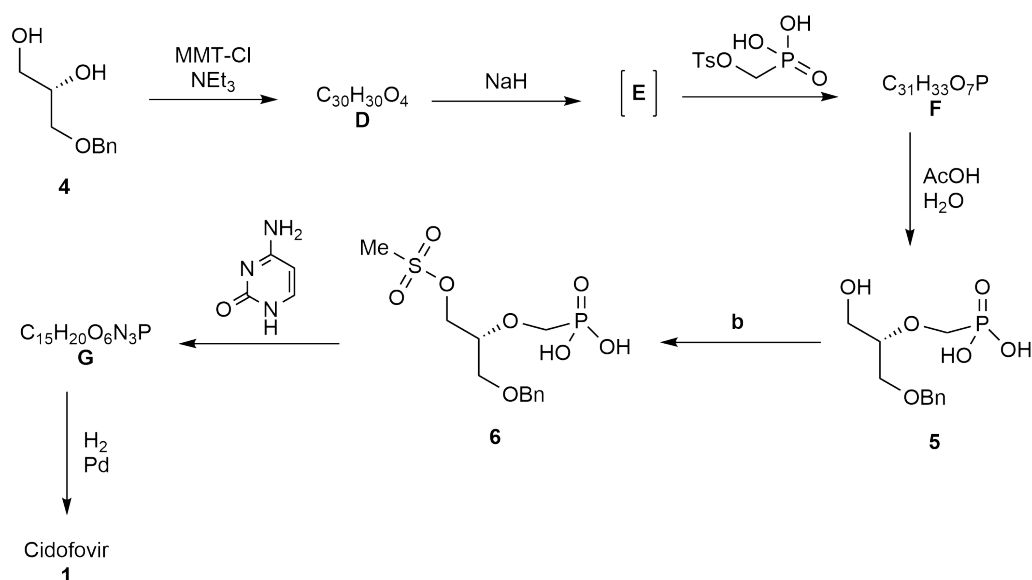


Figure 10.4: Final steps in the synthesis of Cidofovir.

10.5 Draw the structures of compounds **D**, **F**, **G** as well as intermediate **E** with correct stereochemistry. 4.0pt

10.6 Propose conditions for reaction **b**. 1.5pt

10.7 Give the name of the reaction occurring between **G** and **1**. What purpose did the fragment lost in this reaction serve? 2.0pt