SwissChO Central Exam 2025

CHEMISTRY.
OLYMPIAD.CH
CHEMIE-OLYMPIADE
OLYMPIADES DE CHIMIE
OLIMPIADI DELLA CHIMICA

G0-1

English (Official)

General Information

Instructions

- You have three hours to solve the problems. Wait for the **START** signal before you begin.
- 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 in the given spaces** can be considered.
- This exam has **14** problems.

Viel Erfolg!

Bonne chance!

Buona fortuna!

Good luck!

Physical Constants and Formulae

Constants

Planck constant	$h = 6.626 \times 10^{-34}\,\mathrm{J\,s}$
Boltzmann constant	$k_B = 1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
Speed of light	$c = 2.998 \times 10^{8}\,\mathrm{m\,s^{-1}}$
Elementary charge	$e = 1.602 \times 10^{-19}\,\mathrm{C}$
Avogadro constant	$N_A = 6.022 \times 10^{23}\,\mathrm{mol^{-1}}$
Universal gas constant	$R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$
Faraday constant	$F = 9.648 \times 10^{4}\,\mathrm{C\,mol^{-1}}$
Standard pressure	$p_0 = 1 \times 10^{5}\,\mathrm{Pa}$
Electronvolt	$1\,\mathrm{eV} = 1.602 \times 10^{-19}\,\mathrm{J}$
Absolute zero	$0\,\mathrm{K} = -273.15\,^{\circ}\mathrm{C}$
Ångstrom	$1\,\mathrm{Å} = 1 \times 10^{-10}\,\mathrm{m}$
Pi (π)	$\pi \approx 3.141592$
Euler's number	$e \approx 2.718281$
Earths gravitational constant	$g \approx 9.81\,\mathrm{m\,s^{-1}}$

Formulae and Equations

Ideal gas law	$pV = nRT = Nk_BT$
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}	$\Delta_r G^0 = -nF\Delta E^0_{cell}$
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	$\mathrm{pH} = \mathrm{pK}_a + \log\left(\frac{[A^-]}{[HA]}\right)$
Definition of $\mathrm{pK_a}$	$\mathrm{pK_a} = -\log\left(\frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}\right)$
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	$V = \frac{4\pi}{3}R^3$
Displacement under acceleration	$s = v_0 t + \frac{1}{2}at^2$

For the calculation of equilibrium constants and 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 exam.

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Periodic Table of the Elements

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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]

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Score Sheet

NOT TO BE FILLED IN BY PARTICIPANT

Name of participant:

Problem	Title	Maximum points	Achieved points	Pages
Q1	Multiple Choice	10.5		2
Q2	Carbonic, Amino and Lewis acids	10.0		3
Q3	Cooked under Pressure or Explosion	8.5		2
Q4	Candles Burn Down Slowly	7.0		2
Q5	Electroreduction of CO_2	11.0		4
Q6	The Shape of Things	6.0		2
Q7	Saturated Solutions	9.0		2
Q8	Total Synthesis of NH_3	14.0		3
Q9	Reactions in Organic Chemistry	6.0		3
Q10	"Hidden Achirality"	7.5		3
Q11	Once Upon a Time, There Was a Chemist	9.0		3
Q12	pKa and Buffers	7.0		2
Q13	Thermodynamics of Organic Chemistry	10.0		4
Q14	Disentangling the Cotton Candy	6.5		3
Total	SwissChO Central Exam 2025	122.0		38

Multiple Choice

There is only **one correct answer for each task**. If only the correct box is checked (☒), the points are awarded. If multiple answers are checked or none, 0 points are awarded.

1.1 **Select** which form of matter is **incorrectly** assigned. 1.0 pt

- ☐ Mercury in a barometer: an element
- ☐ Paint: a mixture
- ☐ Tap water: a compound
- ☐ Helium in a balloon: an element

1.2 **Select** the answer that includes all processes involving **chemical** changes. 1.0 pt

I. Rusting of iron
II. Pouring hydrochloric acid over a piece of iron
III. Freezing of water
IV. Burning a piece of wood
V. Pressurizing a cooking pot by heating water inside

- ☐ II and V
- ☐ I, II, III, IV, and V
- ☐ III and IV
- ☐ I, II, and IV
- ☐ II, III, and V

1.3 **Select** the correct number of atoms in $5.0\,\text{g}$ of $CuSO_4 \cdot 5\,H_2O$. 2.0 pt

- ☐ $1.8 \cdot 10^{-3}$
- ☐ $2.1 \cdot 10^{-2}$
- ☐ $2.5 \cdot 10^{23}$
- ☐ $1.2 \cdot 10^{22}$

1.4 **Select** the correct weight percent of carbon ($\%w_C$) in C_4H_7OH. 1.0 pt

- ☐ 17%
- ☐ 4%
- ☐ 31%
- ☐ 67%

1.5 **Select** the total number of p-electrons in a Cd atom (uncharged). 1.0 pt

- ☐ 6
- ☐ 18
- ☐ 12
- ☐ 48

1.6 **Select** the element/ion with an electron configuration of $1s^2\,2s^2\,2p^6$. 1.0 pt

- ☐ Ne
- ☐ F^-
- ☐ Na
- ☐ Not enough information to uniquely determine the element/ion

1.7 **Select** which of the following ions/atoms has the largest radius. 1.0 pt

- ☐ Kr
- ☐ Br^-
- ☐ Rb^+
- ☐ F^-

1.8 Consider the hypothetical equilibrium: 1.5 pt

$$A + 2\,B \rightleftharpoons C + \frac{3}{2}\,D$$

with an equilibrium constant $K_c = 5.0$ (which is defined and used without units).
Select the correct value of K_c for the equilibrium:

$$2\,C + 3\,D \rightleftharpoons 2\,A + 4\,B$$

- ☐ 5.0
- ☐ 0.04
- ☐ 10.0
- ☐ 0.2
- ☐ It cannot be uniquely determined with the information provided

1.9 Consider the gas-phase equilibrium: 1.0 pt

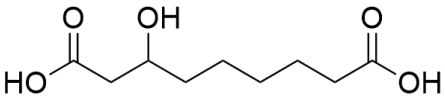
$$2\,H_2O\,(g) \rightleftharpoons 2\,H_2\,(g) + O_2\,(g)$$

Given that the reaction is endothermic, **select** the effect of decreasing the temperature while keeping the pressure constant on the equilibrium constant K_c.

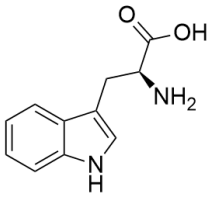
- ☐ K_c will increase
- ☐ K_c will decrease
- ☐ K_c is not affected
- ☐ Not enough information provided to predict what happens

Carboxylic, Amino and Lewis acids

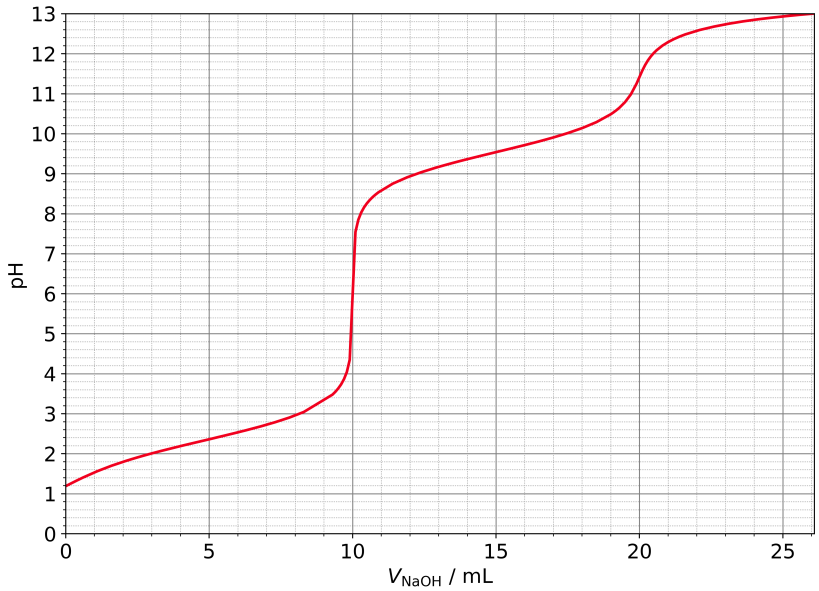
2.1 **Mark** the most acidic proton of the acid below. **Give** a short explanation. 2.0 pt



You found the amino acid tryptophan in the chemical cabinet and decided to improve your titration skills. Unfortunately, your scale broke and you have no idea how much tryptophan you dissolved. After setting the pH to 1.3 with HCl, you titrated the solution with a premixed 1.000 M NaOH titrant and used a pH-meter to plot the graph below. Furthermore you added some Alizarin Yellow R, a pH indicator, which changes colour from yellow to red at pH 11.5.

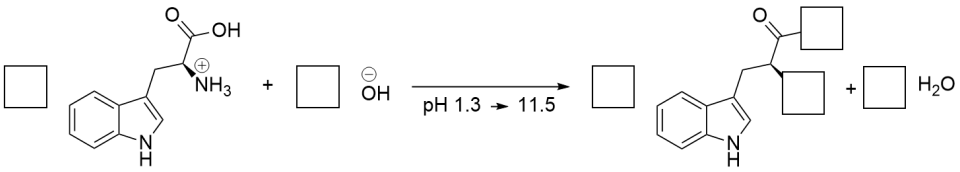


Tryptophan



2.2 **Read** the pK_a values of tryptophan from the titration curve. 1.0 pt

2.3 **Complete** the stoichiometric equation of the entire titration by adding the coefficients of all species as well as the missing atoms in the Lewis formula of the deprotonated tryptophan species. 2.0 pt
Hint: Have a look at the titration curve before you start.



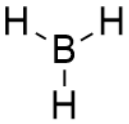
2.4 **Calculate** the amount of tryptophan *n* (mmol) in your sample. **Show** your calculations. 2.0 pt

n = _____ mmol

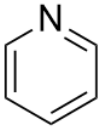
There exists another acid-base concept by Lewis. A Lewis acid possesses an empty orbital, through which it can accept an electron pair from a Lewis base. A Lewis base possesses a filled orbital (often a lone pair, sometimes a π bond), whose electron pair can be donated to a Lewis acid.

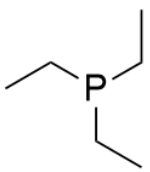
2.5 **Indicate** for the following ions and molecules whether they are Lewis acids or Lewis bases. 3.0 pt

Ni^{2+}



○ Lewis acid	○ Lewis acid	○ Lewis acid
○ Lewis base	○ Lewis base	○ Lewis base
○ Neither	○ Neither	○ Neither





○ Lewis acid	○ Lewis acid	○ Lewis acid
○ Lewis base	○ Lewis base	○ Lewis base
○ Neither	○ Neither	○ Neither

Cooked under Pressure or Explosion

Pressurized cooking pots are used to cook food more quickly and efficiently by raising the boiling point of water, allowing food to reach higher temperatures without losing moisture. However, opening the lid of a pressurized pot poses danger, which we aim to quantify in this problem.

For simplifications we make the following assumptions:

- Both pressure and volume of anything other than water vapor can be neglected.
- The cooking pot is of cylindrical shape with a radius of $R = 10\,\text{cm}$ and height of $h = 20\,\text{cm}$ which results in a volume $V = 6300\,\text{cm}^3$.
- When the pot is heated above $100\,^\circ\text{C}$, all water inside has evaporated.
- All gasses involved behave like ideal gasses.
- Air resistance (friction with air) can be neglected.
- Ambient pressure is $p_0 = 1\,\text{bar}$.

3.1 **Calculate** the number of moles of H_2O molecules (n_{H_2O}) in $36\,\text{g}$ of water. 1.0 pt

$n_{H_2O} =$ _____ mol

3.2 **Calculate** the pressure p in Pascal (Pa) in the pot with $n_{H_2O} = 2\,\text{mol}$ water inside that was heated to $T = 120\,^\circ\text{C}$. 1.5 pt

$p =$ _____ Pa

3.3 Our cooking pot can withstand an over-pressure $\Delta p_{\text{max}} = 2\,\text{bar}$. **Calculate** the maximum amount of water n_{max} in mol to be added such that a temperature of $T = 125\,^{\circ}\text{C}$ can be reached. 2.0 pt

$n_{\text{max}} =$ _____ mol

In the following part we want to find out what happens if the lid of the pressurized pot was opened. Assume the mass of the lid to be $m_{\text{lid}} = 3\,\text{kg}$.

3.4 The pot was heated to reach above maximum pressure to $p_{\text{explode}} = 3\,\text{bar}$ and exploded within $t_{\text{open}} = 0.001\,\text{s}$ (assume the force was acting on only on the lid for only this time), such that the lid came flying straight up. **Calculate** the height h in meters, the lid can reach if there is no roof it will crash into. 4.0 pt

$h =$ _____ m

Candles Burn Down Slowly

Candles burn steadily, providing a simple model for studying reaction kinetics in combustion. Through this task, you will analyze the factors influencing the rate of reaction and the nature of the combustion process.

4.1 Assume the candle paraffin wax consists of only $C_{31}H_{64}$. **Write** down the balanced reaction equation when the candle burns completely. 1.0 pt

4.2 Assuming an elementary reaction, **write** down the general rate law for the reaction. **Determine** the reaction order with respect to the reagents and the overall order. 1.0 pt

In order to find out more about the reaction kinetics, five identical candles were placed in closed reactors with different partial pressures p_{O_2} in the atmosphere. The following measurements were obtained:

p_{O_2} (bar)	Burning time (h)
10.0	0.10
8.0	0.16
6.0	0.26
3.0	1.1
1.0	9.8

4.3 Judging from the data in the table above, **estimate** the experimental reaction order for O_2 (it's a whole number). 2.0 pt

4.4 **Explain** the discrepancy between the experimental and the theoretical reaction order. 1.0 pt

4.5 Briefly **describe** with a way to experimentally determine the reaction order with respect to the paraffin wax $C_{31}H_{64}$. 2.0 pt

Electroreduction of CO_2

Electroreduction enables the conversion of CO_2 into feedstock chemicals and fuels, helping to close the carbon cycle and keep atmospheric CO_2 levels at bay. This process holds potential for sustainable fuel production and carbon-neutral industrial applications. In this problem, you will discover which products can be obtained and what are the limitations.

Use the following data to solve the tasks:

Half-Reaction	Standard Potential (E°/V)
$Li^+ + e^- \longrightarrow Li$	-3.04
$2\,CO_2 + 2\,H^+ + 2\,e^- \longrightarrow HOOCCOOH$	-0.43
$Cd^{2+} + 2\,e^- \longrightarrow Cd$	-0.40
$CO_2 + 2\,H^+ + 2\,e^- \longrightarrow CO + H_2O$	-0.11
$CO_2 + 2\,H^+ + 2\,e^- \longrightarrow HCOOH$	-0.11
$HCOOH + 2\,H^+ + 2\,e^- \longrightarrow HCHO + H_2O$	-0.03
$2\,H^+ + 2\,e^- \longrightarrow H_2$	0.00
$HCHO + 2\,H^+ + 2\,e^- \longrightarrow CH_3OH$	0.13
$C + 4\,H^+ + 4\,e^- \longrightarrow CH_4$	0.13
$Cu^{2+} + 2\,e^- \longrightarrow Cu$	0.34
$CH_3OH + 2\,H^+ + 2\,e^- \longrightarrow CH_4 + H_2O$	0.5
$CO + 2\,H^+ + 2\,e^- \longrightarrow C + H_2O$	0.52
$Ag^+ + e^- \longrightarrow Ag$	0.80
$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$	1.23

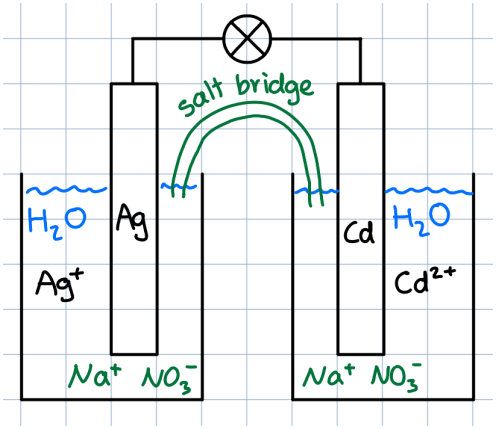
Selection of standard reduction potentials.

5.1 **Write** down the spontaneous overall reaction in a Ag/Ag^+ vs. Cd/Cd^{2+} cell. 1.0 pt

5.2 **Calculate** the electromotive force (potential) U in V of the $[Cd/Cd^{2+}] - [Ag/Ag^+]$ cell from the previous task under standard conditions. 1.0 pt

$U =$ _____ V

5.3 **Label** the electrodes in the scheme with anode/cathode and **indicate** the flow of electrons during discharge. 1.0 pt



5.4 **Provide** the oxidation state of C in the following compounds: 1.75 pt

- CH_4 : _____
- CO : _____
- CO_2 : _____
- HCHO : _____
- HCOOH : _____
- HOOCCOOH : _____
- CH_3OH : _____

5.5 Using the provided standard reduction potentials, **determine** which oxidation state of C (out of the ones determined in the task above) is the most stable. **Reason** your answer with a calculation. 4.0 pt

5.6 **Write** down the overall reaction for the reduction of CO_2 to $CH_4 + O_2$ by H_2 and **reason** whether the $[Cd/Cd^{2+}] - [Ag/Ag^{+}]$ cell from the first task can provide the driving force. 2.25 pt

Hint: If you did not find the value for the $[Cd/Cd^{2+}] - [Ag/Ag^{+}]$ cell voltage, use $1.5\,V$.

The Shape of Things

Hint: for full points, draw structures including lone electron pairs where needed to illustrate why a certain geometry is obtained.

6.1 For each of the given molecules, **choose** the correct VSEPR structure around the central atoms (S, N and Si). 1.5 pt

SF_6	NO_3^-	Me_3SiCl
☐ Pentagonal pyramidal	☐ Trigonal distorted	☐ Tetrahedral
☐ Hexagonal planar	☐ Trigonal planar	☐ Seesaw (Bisphenoidal)
☐ Octahedral	☐ Trigonal bipyramidal	☐ Square planar

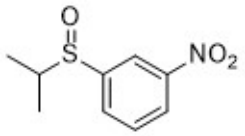
6.2 Beyond IF, there exist *three* higher valent, uncharged interhalogen compounds of iodine and fluorine (IF_n). For each, **draw** the corresponding compound so that the 3D arrangement is clearly displayed and **state** the corresponding sum formula. 3 pt

Sum formula = _____

Sum formula = _____

Sum formula = _____

6.3 The compound shown below is isopropyl 3-nitrophenyl sulfoxide. 1.5 pt
Draw the proper geometry at the sulfur atom. In addition, **choose** if the compound is chiral or not. You may use *iPr* (for isopropyl) and *Ar* (for 3-nitrophenyl) as abbreviations for the respective groups when drawing.



☐ chiral ☐ symmetrical

Saturated Solutions

Imagine you are in the lab and would like to prepare an aqueous solution of specific ionic concentrations. However your scale broke and all you have are the values for the solubility products provided in the table below, the respective salts and as much water as you need. This means you can only confidently prepare saturated solutions; Let's see how far you can get with that.

Salt	K_s (in water)
AgCl	$1.9 \cdot 10^{-4}$
AgBr	$1.3 \cdot 10^{-5}$
Ag_2CO_3	$3.5 \cdot 10^{-3}$
$AgNO_3$	216
$CaCl_2$	74.5
$CaBr_2$	143
$CaCO_3$	$6.2 \cdot 10^{-4}$
$Ca(NO_3)_2$	121.2

Solubility products of the salts available. The values can be treated as the product of the concentrations of the contained ions in mol/L. Example: $K_s^{CaCl_2} = [Ca^{2+}] \cdot [Cl^-]^2 \,/\, mol^3/L^3$.

7.1 **Calculate** the concentrations $c_{Ca^{2+}}, c_{CO_3^{2-}}$ in a saturated solution of $CaCO_3$ in mol/L. 1.0 pt

$c_{Ca^{2+}} =$ _____ mol/L $c_{CO_3^{2-}} =$ _____ mol/L

7.2 **Calculate** the concentrations $c_{Ag^+}, c_{CO_3^{2-}}$ of in a saturated solution of Ag_2CO_3 in mol/L. 1.0 pt

$c_{Ag^+} =$ _____ mol/L $c_{CO_3^{2-}} =$ _____ mol/L

7.3 **Determine** what happens if you mix a saturated solution of AgBr with a saturated solution of AgCl in a $1:1$ ratio. **Reason** your answer. 2.0 pt

7.4 **Calculate** the concentration $c_{Ca^{2+}}$ in mol/L for a solution saturated with both $CaBr_2$ and $CaCl_2$. 5.0 pt

$c_{Ca^{2+}} =$ _____ mol/L

Total Synthesis of NH_3

Industrially, NH_3 is produced from H_2 and N_2 by the Haber-Bosch process. In this task we will investigate the thermodynamics of the process.

8.1 **Write down** the balanced reaction equation (equilibrium) for the Haber-Bosch process with coefficient 1 for ammonia. 1.0 pt

The Haber-Bosch process is typically conducted at a temperature of about $T = 400\,^\circ\text{C}$ and a pressure of about 200 bar. The reaction enthalpy and entropy, which we both assume to be temperature independent, are about $\Delta H = -46\,\text{kJ/mol}$ and $\Delta S = -124\,\frac{\text{J}}{\text{mol K}}$.

8.2 **Choose** which classification suits the forward reaction best. 1.0 pt

- ☐ Endothermic
- ☐ Exothermic
- ☐ Neither of the above

8.3 **Reason** why the reaction is conducted under such high pressure **and** temperature. 2.0 pt

8.4 **Calculate** the reaction free energy ΔG under reaction conditions in kJ/mol NH_3. 1.0 pt

$\Delta G =$ _____ kJ/mol NH_3

8.5 **Calculate** the equilibrium constant K_p. If you could not solve the previous task, use $\Delta G = 20\,\text{kJ/mol}$. 2.0 pt

$K_p =$ _____

8.6 Given initial pressures of $p^{\text{ini}}_{\text{H}_2} = 150\,\text{bar}$ and $p^{\text{ini}}_{\text{N}_2} = 50\,\text{bar}$ **set up** the fourth order polynominal in p_{NH_3} in the form 4.0 pt

$$a \cdot p^4_{\text{NH}_3} + b \cdot p^3_{\text{NH}_3} + c \cdot p^2_{\text{NH}_3} + d \cdot p_{\text{NH}_3} + e = 0$$

with a, b, c, d, e known constants (**determine** these constants). Solving the equation would yield the equilibrium partial pressure p_{NH_3}. You **do not need to solve** the equation.

$p_{\text{NH}_3} =$ _____ bar

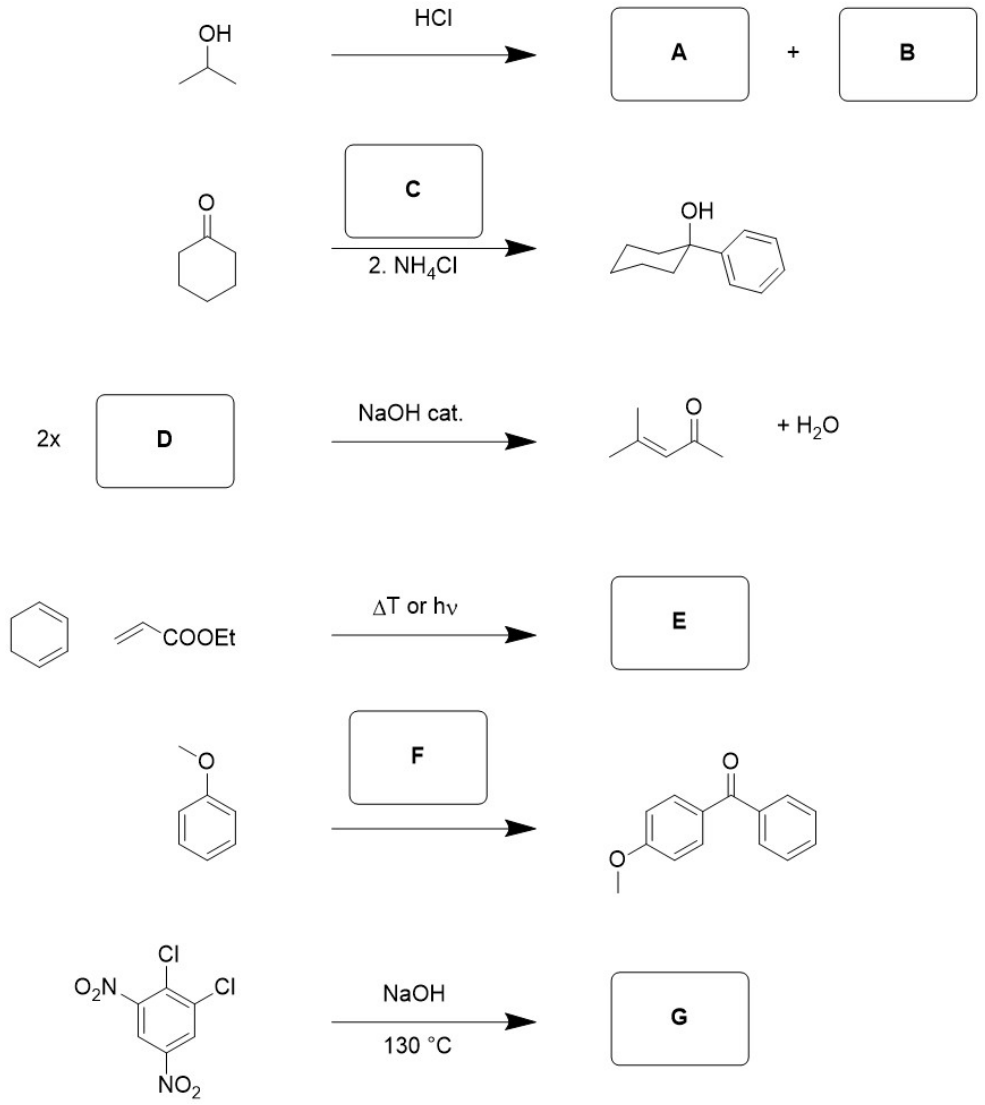
8.7 **Calculate** the yield of the reaction in %, using $p_{NH_3} = 0.01$ bar. 1.0 pt

yield = _____ %

8.8 The theoretically achievable yield seems to be quite small. **Suggest** up to two measures to convert more starting material. 2 pt

Reactions in Organic Chemistry

9.1 **Draw** the structures and or required reagents into the respective boxes **on the following pages**. An aqueous workup is always assumed to be included. 0.0 pt



9.1a 3 pt

A

B

C

9.1b 3 pt

D

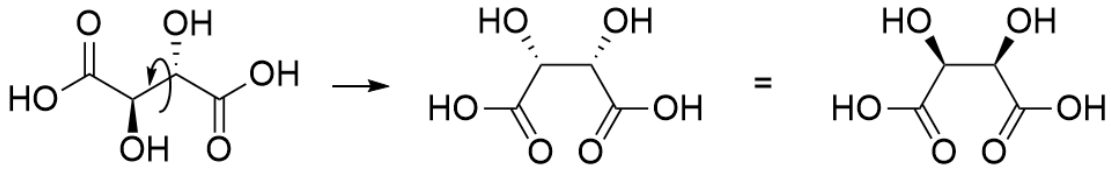
E

F

G

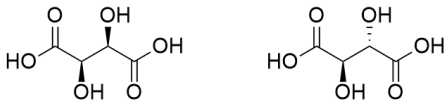
"Hidden Achirality"

While we often think of every molecule with stereocenters as chiral, not all of them are. The exception are so called *meso*-molecules, which possess an even number of stereocenters, while being achiral. This happens when the molecule has a confomer with a mirror plane, which annilates the chirality. An example of such a molecule is tartaric acid, which has two chiral forms as well as a achiral *meso* form. This symmetry causes the "*R*,*S*"- and the "*S*,*R*"- stereoisomer of tartaric acid to be one and the same.



meso-tartaric acid and its conformers with mirror planes

10.1 **Draw** the missing stereoisomer of tartaric acid. **Mark** the stereocenters of the three molecules and **determine** the absolute configuration (*R*/*S*) of all stereogenic centers. 2.5 pt



Besides "reducing" the amount of stereoisomers *meso*-compounds also have different properties compared to the chiral isomers. An example for this is the optical activity of a compound. Chiral, enantiopure molecules possess a specific rotation, which is an angle by which they rotate polarized light. In a sample with a mixture of the enantiomers the rotation is proportional to the concentration of the enantiomers. In *meso*-compounds the optical rotation is always 0°. (You can think of it as the stereocenters canceling eachother out.)

While the optic activity depends on many factors such as concentration and measuring conditions, the entire exercise assumes it is an intrinsic property of the compounds and neglects any not expicitly mentioned variables.

When browsing through a chemical cabinet you find two vials with tartaric acid. Vial **1** is labelled "L-(+)-tartaric acid + D-(−)-tartaric acid". You measured a specific rotation of −3.8 ° for vial **1**. Additionally you found the values below in a textbook.

	$\Delta\theta$ / °
L-(+)	+12.7°
D-(−)	−12.7°
meso	0°

10.2 **Determine** the composition of vial **1** from its specific rotation. 2.0 pt

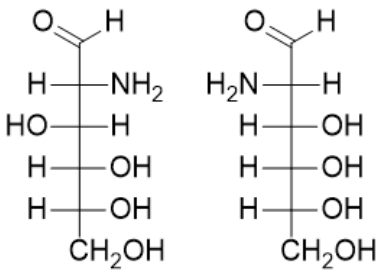
D-(−)-tartaric acid _____% L-(+)-tartaric acid _____%

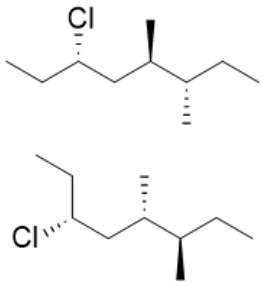
The label on vial **2** says that it contains D-(−)-tartaric acid and *meso*-tartaric acid in equal proportions. Three of your friends are debating about the optical rotation of this sample **2.** Friend A claims it will be around 0°, Friend B is convinced it will be around −6°, while Friend C is sure it shoud be about −12°.

10.3 **State** which of your friends is right and **give** a reason for your decision. 1.0 pt

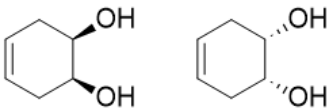
○ Friend A / 0° ○ Friend B / −6° ○ Friend C / −12°

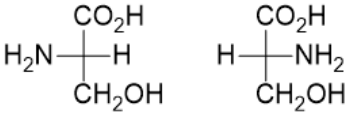
10.4 **Determine** if the following molecules are diastereoisomers, enantiomers or identical. 2.0 pt





○ Diastereomers	○ Diastereomers
○ Enantiomers	○ Enantiomers
○ Identical	○ Identical

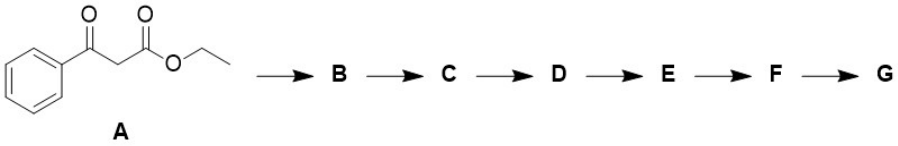




○ Diastereomers	○ Diastereomers
○ Enantiomers	○ Enantiomers
○ Identical	○ Identical

Once Upon a Time, There Was a Chemist

11.1	For compounds **A** to **G** in text, **draw** the appropriate structures in the boxes below. *Hint:* the reactions happen as described. On occasion, protecting group steps have been omitted or a minor isomer is selected as suits the needs of this problem.	0.0 pt



This is molecule **A**. It was reacted with NaH, leading to an aliphatic, carboanion intermediate, which in turn was reacted with acetaldehyde (ethanal) to yield the corresponding alcohol **B**, after mild acidic workup. A nitro group is then introduced in 2 position on the aromatic ring to give compound **C**. The aliphatic alcohol in the molecule is then converted to a bromide and the nitro group reduced to the amine using H_2 and a suitable catalyst, giving rise to compound **D** with the sum formula ($C_{13}H_{16}BrNO_3$). Compound **D** is then dissolved and heated with no reagent added, whereupon the amine displaces the bromide and the resulting product crystalises as the hydrobromide salt **E**. Oxidation of this compound with oxygen, accompanied by the ketone rearrangeing to the enol, yields compound **F**, 4-hydroxy-2-methylquinoline-3-carboxylic acid ethyl ester. To it, a large excess of MeMgBr is added, and the so obtained alcohol subjected to elimination to the corresponding double bond, finally yielding compound **G**.

11.1a 3 pt

B

C

11.1b 6 pt

D

E

F

G

pKa and Buffers

You want to conduct some acid base experiments in H_2O with some added H_2S to compare your results to the experiments in pure H_2O. Your first step is to calculate the pK_a of H_2S to assess its influence on your reactions.

You found that $c_{H^+} = 4 \cdot 10^{-4}$ mol dm^{-3} and $c_{HS^-} = 3 \cdot 10^{-5}$ mol dm^{-3}, while $c_{H_2S} = 1.2 \cdot 10^{-1}$ mol dm^{-3}.

12.1 **Calculate** the pK_a of H_2S. Use calculating K_a as an intermediate step. 2.0 pt

$K_a(H_2S)$ = _____ $pK_a(H_2S)$ = _____

During your research for your experiments you found the following pK_a data. (The pK_a of H_2S is from a very old textbook and probably quite off.)

	H_2O	H_2S	H_2Se	H_2Te
pK_a	14.0	5.5*	3.9	2.6

12.2 **Describe** the trend you observe within the pK_a data and **name** a reason for it. 1.0 pt

For your next experiment you need one liter buffer solution at pH 7.8. You have determined that you can make your own with a mixture of NaH_2PO_4 (pK_a 7.2) and Na_2HPO_4 (pK_a12.3). You already weighed in 2.4 g (0.020 mol) of NaH_2PO_4.

12.3 **Calculate** the amount (*n*) and mass (*m*) of Na_2HPO_4 you need to add to your solution. 3.0 pt

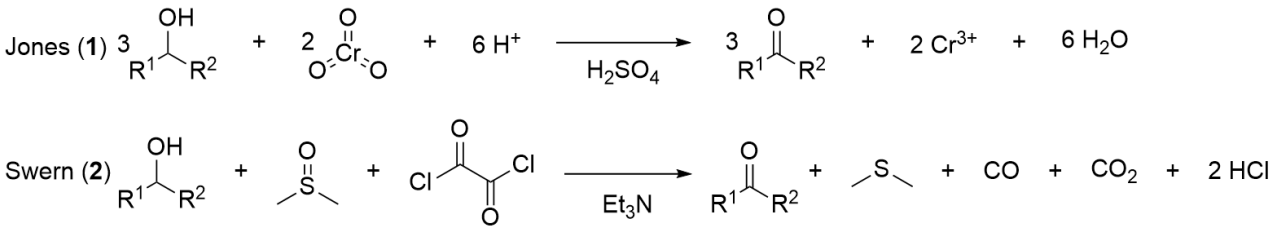
n of Na_2HPO_4 = _____ mol

m of Na_2HPO_4 = _____ g

12.4 **Explain** if this buffer is more stable towards acids or bases. 1.0 pt

Thermodynamics of Organic Chemistry

The functional group conversion of a secondary alcohol to a ketone can be achieved through several different reactions including the Jones (**1**) and Swern oxidation (**2**). You decide to study these two reactions from a thermodynamical point of view.



	$\Delta_f H^0$ / kJ mol^{-1}	S^0 / J mol^{-1} K^{-1}
Alcohol	−318	181
Ketone	−248	200
CrO_3	−587	73
Cr^{3+}	−167	−113
H^+	73	−25
H_2O	−286	70

13.1 **Calculate** the standard reaction enthalpy $\Delta_r H^0$ of the Jones oxidation (**1**) per mole of the alcohol. 2.0 pt

$\Delta_r H^0 =$ _____ kJ mol^{-1}

13.2 **Calculate** the standard reaction entropy $\Delta_r S^0$ of the Jones oxidation (**1**) per mole of the alcohol. 2.0 pt

$\Delta_r S^0 =$ _____ J mol^{-1} K^{-1}

During your research you found for the Swern oxidation (**2**) that $\Delta_r H = -112$ kJ mol^{-1} and $\Delta_r S = 523$ J mol^{-1} K^{-1} for one mole of the alkohol when you conducted the reaction at -60°C.

13.3 **Calculate** the Gibbs free energy $\Delta_r G$ of the Swern oxidation (**2**) for one mole of the alkohol at -60°C. 2.0 pt

$\Delta_r G =$ _____ kJ mol^{-1}

	$\Delta_r H^0$ / kJ mol^{-1}	$\Delta_r S^0$ / J mol^{-1} K^{-1}	$\Delta_r G$ / kJ mol^{-1}
Jones (**1**)	−400*	70*	−391
Swern (**2**)	−112	523	−240*

13.4 **Compare** the reaction entropy of the two reactions and **name** two reasons for their difference. You may use the values in the table above for your reasoning. (Values marked * are hints if you are unsure about your calculations.) 1.0 pt

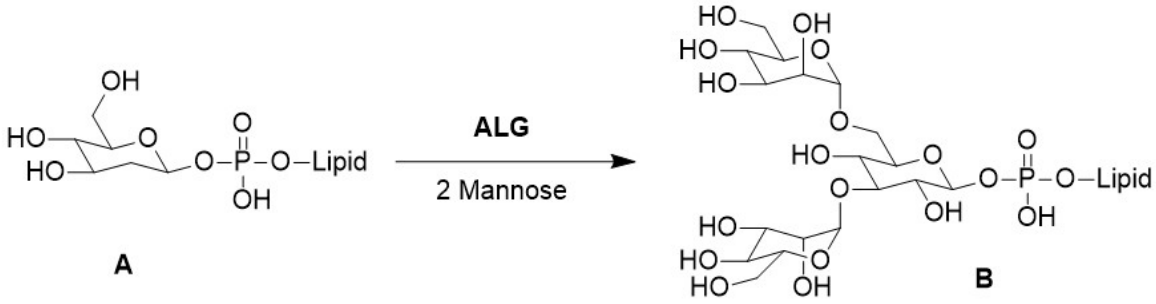
13.5 **Elaborate** on the effect of the reaction enthalpy of the Jones reaction on the course of the reaction as well as its practical application. You can use the values in the table above for your reasoning. (Values marked * are hints if you are unsure about your calculations.) 2.0 pt

During your latest synthesis in the lab, you need to oxidise a secodary alkohol to its ketone.

13.6 **Rationalise** which of the two reaction you would use and **give** a reason for your choice. 1.0 pt

Disentangling the Cotton Candy

Sugars are ubiquitous in biological systems. We shall now examine an example of how carbohydrates are used on the molecular level. First, we will investigate an enzyme called **ALG**. **ALG** takes molecules like **A**, and adds two mannose units to it. This gives rise to compound **B**. In two experiments, we shall try to find out more about this process.



14.1 An experiment was made, where 10 µmol/L **A**, 1nmol/l **ALG** and varying concentrations of mannose were mixed. Then, the time it took to convert 50% of the mannose was measured ($t_{1/2}$). This gave the following numbers: 1.0 pt

Mannose conc. [µmol/L]	$t_{1/2}$ [min]
2	17.5
5	7
7	5

Select the reaction order with respect to mannose of the overall reaction.
Then, **select** the proper conclusion that can be drawn from the data.

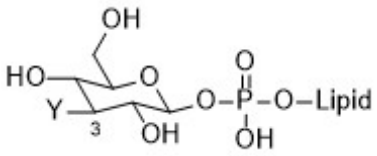
Reaction order

☐ 0
☐ 1
☐ 2
☐ Higher, or not an even number

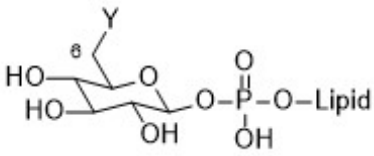
Conclusion

☐ no conclusion can be drawn from this data
☐ one mannose is added after the other
☐ both mannose units are added at the same time

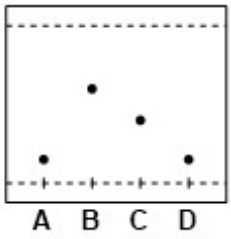
In a second experiment, compounds **C** or **D** were subjected *separately* to conditions that usually work to turn **A** to **B**, using **ALG**. **C** and **D** both were chemically modified so that **ALG** still accepts it as substrate, but cannot attach a mannose in 3 or 6 position respectively. The TLC shows compounds **A** and **B** as reference, as well as the reaction products of **C** or **D** with **ALG.**



C



D



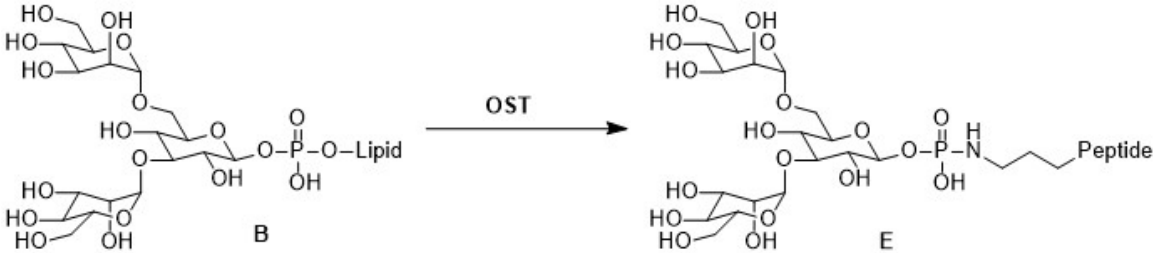
14.2 **Choose** a group suitable for *Y* in the above structures. The aim of this replacement is to prevent the attachment of a mannose group without modifying the steric and electronic properties of the molecule so much that the molecule is no longer accepted by the enzyme. It also has to be relatively stable in the aqueous medium of cells. 1.0 pt

☐ $-N_3$ ☐ -F ☐ -SMe ☐ -I

14.3 **Choose** the correct conclusions that can be drawn from the experiment above. 1.0 pt

☐ The experiment failed - no conclusion
☐ Both mannose units can be added independent of eachother
☐ A mannose has to be added first at the 3-OH
☐ A mannose has to be added first at the 6-OH

In the next step, the **OST** enzyme uses **B** to label a peptide with the carbohydate moiety. We chose to use radioisotope labeling to investigate the activity of **OST**. To that end, **B** containing ^{32}P was synthesized.



B E

14.4 **Complete** the reaction through which ^{32}P is obtained. 1.0 pt

$$\_\_\_\_\_ + {}^{1}_{0}n \longrightarrow {}^{32}P + {}^{1}H^{+} + e^{--}$$

14.5 ^{32}P decays through β^- decay mode with a half-life of 14.3 days. **Write** the correct decay reaction. 1.0 pt

A solution of radioactive **B** was prepared, with an activity of 3.39 GBq/mL. From this solution, a sample was reacted with **OST** for 24 h and the obtained **E** was removed. The remaining solution was measured at 2.53 GBq/mL.

14.6 **Calculate** the yield (in %) of radioactive **E** that was created by **OST**. You may assume that no time was lost in handling the sample. 1.5 pt

_____ %