SwissChO Final Exam 2024

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

G0-1

English (Official)

General Information

Instructions

- Write your name on each sheet.
- You have three hours to solve the problems. Wait for the **START** signal before you begin.
- Write all calculations legibly.
- Clearly state which assumptions you are making, if you do.
- 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 you have been given permission to do so.
- Only answers written **on the question sheets** can be considered. You may use the reverse side if you require more space.
- This exam has **10** problems.

Viel Erfolg!

Bonne chance!

Buona fortuna!

Good luck!

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Physical Constants and Formulae

Constants

Planck constant	$h = 6.626\,070\,15 \times 10^{-34}\ \mathrm{J\,s}$
Boltzmann constant	$k_B = 1.380\,649 \times 10^{-23}\ \mathrm{J\,K^{-1}}$
Speed of light	$c = 2.997\,924\,58 \times 10^{8}\ \mathrm{m\,s^{-1}}$
Elementary charge	$e = 1.602\,176\,634 \times 10^{-19}\ \mathrm{C}$
Avogadro constant	$N_A = 6.022\,140\,76 \times 10^{23}\ \mathrm{mol^{-1}}$
Universal gas constant	$R = 8.314\,462\,\mathrm{J\,mol^{-1}\,K^{-1}}$
Proton mass	$m_{p^+} = 1.672\,621\,923\,69 \times 10^{-27}\ \mathrm{kg}$
Neutron mass	$m_{n^0} = 1.674\,927\,498\,04 \times 10^{-27}\ \mathrm{kg}$
Atomic mass unit	$u = 1.660\,539\,066\,60 \times 10^{-27}\ \mathrm{kg}$
Faraday constant	$F = 9.6485 \times 10^{4}\ \mathrm{C\,mol^{-1}}$
Standard pressure	$p_0 = 1.00 \times 10^{5}\ \mathrm{Pa}$
Electronvolt	$1\ \mathrm{eV} = 1.602\,176\,634 \times 10^{-19}\ \mathrm{J}$
Absolute zero	$0\ \mathrm{K} = -273.15\ ^{\circ}\mathrm{C}$
Ångstrom	$1\ \text{Å} = 1 \times 10^{-10}\ \mathrm{m}$
Pi (π)	$\pi \approx 3.141592$
Euler's number	$e \approx 2.718281$

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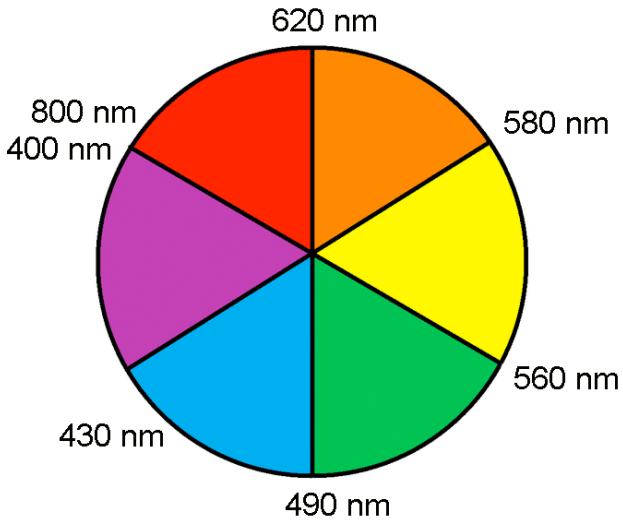
Formulae and Equations

Ideal gas law	$pV = nRT = Nk_BT$
Gibbs free energy	$\Delta G = \Delta H - T\Delta S$
Relation between ΔG and K	$\Delta G = -RT\ln(K)$
Reaction quotient Q for reaction aA+bB $\rightleftharpoons$ cC+dD	$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
Relationship betwen ΔG and ΔE_{cell}	$\Delta_r G^\circ = -nF\Delta E_{\text{cell}}{}^\circ$
Nonstandard ΔG	$\Delta_r G = \Delta_r G^\circ + RT\ln(Q)$
Nernst equation	$E = E^\circ - \frac{RT}{zF}\ln(Q)$
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	$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$
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 calculations of equilibrium constants and all concentrations, refer to the standard concentration $1\,\text{mol}\,\text{dm}^{-3} = 1\,\text{mol}\,\text{L}^{-1}$. If not stated otherwise in the task, consider all gases ideal throughout this exam.



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Periodic Table of Elements

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]

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Score Sheet

NOT TO BE FILLED OUT BY PARTICIPANT

Name of participant: _____

Problem	Title	Maximum Points	Achieved Points	Pages
Q1	The Burning of Stuff	25.0 pt		4
Q2	Crystal Clear Chemistry	14.0 pt		3
Q3	The Nature of Strong Acids	16.0 pt		3
Q4	Many-Facetted Oxides of Chlorine	21.0 pt		4
Q5	The Power of the Core	19.0 pt		4
Q6	Down the Rabbit Hole: Frémy's Salt	21.0 pt		4
Q7	Concerning Amines	20.5 pt		4
Q8	Trouble with Hydrogen	19.0 pt		4
Q9	One Ring	24.0 pt		5
Q10	Total Synthesis of (+)-Roseophilin	25.0 pt		4
Total		204.5 pt		37

The Burning of Stuff (25.0 pt)

The Burning of Stuff with Oxygen

In order to obtain the best yield of thermal power, hydrocarbon fuels in engines, power plants and explosives are burned to CO_2 and H_2O. In rockets, however, the best performance is obtained if the combustion reaction balances to CO, N_2, H_2O, HF and HCl.

RP-1, a kerosene-like rocket fuel, was burned with liquid oxygen in the first stage of the Saturn V rocket.

A combination of fuel and oxidiser commonly used, eg. by the Proton-M rocket, is that of unsymmetrical dimethylhydrazine (UDMH, $(CH_3)_2NNH_2$) and dinitrogen tetroxide N_2O_4.

1.2 **Write down** a balanced equation for the burning of UDMH with N_2O_4 in a rocket motor. 2.0 pt

SOLUTION:

$2\,(CH_3)_2NNH_2 + 3\,N_2O_4 \longrightarrow 4\,CO + 8\,H_2O + 5\,N_2$

2 pt for correct reaction, 1 pt for balanced to CO_2, -1pt for other errors

Both rocket propellants and explosives often cannot rely on external oxidisers like atmospheric oxygen, but have to bring them along. These compounds contain both fuel and oxidiser in one compound. Among those, alkyl nitrates are prominent compounds, consisting entirely of a hydrocarbon moiety *with one or more* nitrate groups ($R{-}ONO_2$) attached. They have an equal or positive oxygen balance, meaning that they can be burned without extra oxygen or actually liberate oxygen in the process. The best performance with minimal corrosion issues is obtained if the reaction properly balances to combustion products according to their intended use.

1.3 For both use as explosive and rocket propellant each, **find** and **draw** the smallest possible alkyl nitrate with a neutral oxygen balance. In addition, **write down** the balanced equation for the separate combustion of both. 6.0 pt

Explosive:

Propellant:

SOLUTION:
Explosive: Ethylene dinitrate $NO_3{-}CH_2CH_2{-}NO_3 \longrightarrow 2\,CO_2 + 2\,H_2O + N_2$
Propellant: any isomer of propyl dinitrate $NO_3{-}(CH_2)_3{-}NO_3 \longrightarrow 3\,CO + 3\,H_2O + N_2$

3 pt each: 2 for each correct structure, 1 pt for combustion equation. -1 pt for errors, -1 pt for structures with both nitrates bound to the same carbon. 2 pt for overall coherent, answer with wrong structure

Isopropyl nitrate (propan-2-yl nitrate) is produced by the reaction of isopropanol (propan-2-ol) with nitric acid in the presence of sulfuric acid. If this reaction is not conducted carefully, large amounts of N_2O_4 and an organic byproduct derived from the alcohol are obtained instead of the desired nitrate.

1.4 **Draw** the structure of the byproduct and **write down** a balanced equation, leading entirely to the undesired byproduct, N_2O_4 and other byproducts if necessary. 2.0 pt

SOLUTION:
Acetone CH_3COCH_3
$C_3H_8O + 2\,HNO_3 \longrightarrow 2\,H_2O + N_2O_4 + C_3H_6O$
SOLUTION:
The byproduct is acetone.
1 pt for acetone by structure, 0.5 pt by name
1 pt for balanced equation,
1 pt overall for other sensible product. N_2O_4 has to be liberated and some oxidation has to happen.

The Burning of Stuff with Fluorine

In principle, the oxidiser in a combustion reaction does not have to be oxygen, but can also be a halogen like fluorine. From 1950 - 1980, a lot of experiments have been performed to use fluorine and fluorinated compounds as rocket propellants.

1.5 **Draw** the structure, including lone pairs, and **name** the correct VSEPR geometry of NF_3, ClF_3 and ClF_5. 6.0 pt

Compound	Structure	Name of geometry
NF_3		
ClF_3		
ClF_5		

SOLUTION:

- NF_3: (Trigonal) pyramidal
- ClF_3: T-shaped
- ClF_5: Square pyramidal

2 pt each, 1 pt if either drawn structure or name is correct, or if drawn structure and name are both false, but match each other. -1 pt for errors in structure like wrong electron count

Burning carbon-containing fuels with fluorine oxidisers presents a number of challenges. Consider the burning of UDMH with ClF_5.

1.6 **Determine** all stoichiometric coefficients $a - f$. 3.0 pt

$a\,(CH_3)_2NNH_2 + b\,ClF_5 \longrightarrow c\,HCl + d\,HF + e\,CF_4 + f\,N_2$

$a =$ _____, $b =$ _____, $c =$ _____, $d =$ _____, $e =$ _____, $f =$ _____

SOLUTION:

$3\,C_2H_8N_2 + 8\,ClF_5 \longrightarrow 8\,HCl + 16\,HF + 6\,CF_4 + 3\,N_2$

a = 3, b = 8, c = 8, d = 16, e = 6, f = 3

3 pt, 0.5 for each correct

-1 pt per error

You see that a lot of the oxidiser is needed, which is not very efficient. In addition, CF_4 is a very poor propellant exhaust. Good exhaust products are very light, mono- or diatomic gasses which liberate a lot of energy in their formation. It is thus imperative to find an oxygen-containing additive that will not react with ClF_3 or ClF_5 and fulfills the other conditions.

1.7 **Select** the suitable additive from the list below and **write down** a balanced combustion reaction with UDMH and ClF_3. 4.0 pt

Possible candidates are:

☐ $NH_3 \cdot H_2O$ ☐ ClO_3F ☐ HIO_4

SOLUTION:

Additive: ClO_3F

$3\,C_2H_8N_2 + 5\,ClF_3 + 2\,ClO_3F \longrightarrow 7\,HCl + 17\,HF + 3\,N_2 + 6\,CO$

4 pt, -1 pt for single mistake, max 2 pt for wrong, consistent answer, max 3 pt for balanced reaction with wrong additive

Crystal Clear Chemistry (14.0 pt)

Corundum (Al_2O_3) is an abundant, hard and colourless mineral. Its crystal structure is given by hexagonal packing, meaning every Al ion is octahedrally surrounded by six oxide ions. Corundum has a density $\rho = 3.87\,\mathrm{g\,cm^{-3}}$. Crystallographically, the volume of its unit cell was determined to be $V_{\mathrm{cell}} = 262.26\,\text{Å}^3$.

2.1 **Give** the oxidation state and electron configuration of every ion in corundum. 2.0 pt

Al ion in Al_2O_3:
Oxidation state: _____, Electron configuration: _____

O ion in Al_2O_3:
Oxidation state: _____, Electron configuration: _____

SOLUTION:
O: -II, Al +III; both have the electron configuration of $[\mathrm{Ne}] = 1s^2 2s^2 2p^6$
0.5 pts for each correct oxidation state and electron configuration. 2.0 pts total.

2.2 Assume corundum to be a fully ionic solid. **Compare** the radii of the two ions. **Explain** your reasoning. 2.0 pt

SOLUTION:
The O^{2-} ion will be larger than the Al^{3+} ion. The effective core charge of Al^{3+} will be larger, having 13 protons, whereas oxygen only has 8 protons. Therefore, the electrostatic interactions between the electrons and core will be stronger in Al.
1.0 pt for the correct size comparison. 1.0 pt for the correct reasoning. 2.0 pts total.

2.3 **Determine** the number of Al_2O_3 units N_{cell} contained per unit cell. 3.0 pt

$N_{cell} =$ _____

SOLUTION:

The mass of corundum per unit cell is $m_{cell} = V_{cell} \times \rho$

The number of moles per unit cell are therefore $n_{cell} = \frac{m_{cell}}{M}$.

The number of Al_2O_3 units are therefore $N_{cell} = n_{cell} \times N_A = \frac{m_{cell}}{M} \times N_A = \frac{V_{cell} \times \rho}{M} \times N_A \approx \frac{2.6226 \times 10^{-28}\,m^3 \times 3.87 \times 10^3\,kg\,m^{-3}}{2 \times 26.98\,g\,mol^{-1} + 3 \times 16.00\,g\,mol^{-1}} \times \frac{1000\,g}{kg} \times 6.022 \times 10^{23}\,mol^{-1} = 5.99 \approx 6$

Each unit cell contains 6 units of Al_2O_3.

2.0 pts for correct mathematical reasoning/calculations. 1.0 pt for the correct numerical result. 3.0 pts total

Ruby is a red precious gemstone, almost entirely consisting of corundum. The colouration of rubies comes from the substitution of some of the Al ions in the crystal lattice with Cr ions in the same oxidation state. Therefore, the composition of ruby can be written as $Al_{2-\alpha}Cr_\alpha O_3$. In a certain ruby, one in 62 Al ions has been replaced by Cr.

2.4 **Determine** α and the mass percentage of Cr (%w/w) for this sample. 2.0 pt

$\alpha =$ _____, mass percentage: _____ $\%w/w$

SOLUTION:

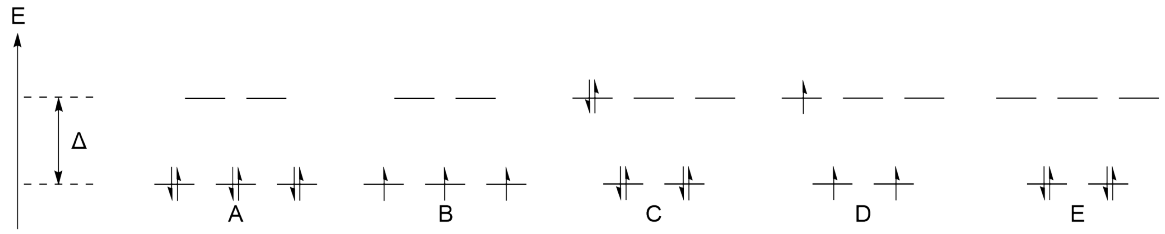
Per 1 mol of the ruby, there are 2 mol of cations, consisting of Al^{3+} + Cr^{3+}. The ratio of the two is $\frac{1}{62}$.

Therefore, $\alpha = \frac{2}{62} = 0.032$, to give $Al_{1.968}Cr_{0.032}O_3$

The mass percentage is %w/w = $\frac{0.032 \times 52\,\text{g mol}^{-1}}{3 \times 16\,\text{g mol}^{-1} + 1.968 \times 27\,\text{g mol}^{-1} + 0.032 \times 52\,\text{g mol}^{-1}} = 1.62\%w/w$

1.0 pt for the correct value of α. 1.0 pt for the correct numerical value for the mass percentage. 2.0 pts total.

The Cr ions in ruby are surrounded by the same geometrical arrangement of oxide ions as the Al ions. Depicted below, you find different crystal field splittings, all with the same splitting energy Δ.



2.5 **Assign** the correct field splitting of the Cr ions in ruby to one of the splittings A - E. 2.0 pt

☐ A ☐ B ☐ C ☐ D ☐ E

SOLUTION:

☐ A
☒ B
☐ C
☐ D
☐ E

Cr(III) is a d^3 metal center, meaning only B and D remain.
Now, the ion is octahedrally surrounded, meaning that the crystal splitting with 2 top orbitals (e_g) and three lower orbitals (t_{2g}).
Therefore, it must be B.
2.0 pts for the correct choice of B. No points if any other/or multiple have been ticked.
2.0 pts total.

In ruby, the energy splitting $\Delta = 2.32\,\text{eV}$.

2.6 **Calculate** the wavelength λ of light in nm that is responsible for this transition. **Explain**, if this transition is a plausible cause for the colouration of the ruby. 3.0 pt

$\lambda =$ _____ nm

SOLUTION:

Rearranging $E = h \times \frac{c}{\lambda}$ gives $\lambda = h \times \frac{c}{E}$

$E = 2.32\,\text{eV} \times 1.602 \times 10^{-19}\,\text{J eV}^{-1} = 3.71 \times 10^{-19}\,\text{J}.$

$\lambda = h \times \frac{c}{E} = 6.62 \times 10^{-34}\,\text{J s}^{-1} \times \frac{2.997 \times 10^{8}\,\text{m s}^{-1}}{3.71 \times 10^{-19}\,\text{J}} = 534.41\,\text{nm}.$

This is a transition in the green-blue part of the visible spectrum. The ruby absorbs this light, meaning it will appear as the complimentary colour of the absorption: red-orange. This is indeed the origin of the colour of ruby.

1.0 pt for the correct formula. 1.0 pt for the correct numerical result. 1.0 pt for the correct explanation. 3.0 pts total.

The Nature of Strong Acids (16.0 pt)

Nitric Acid

Nitric Acid, HNO_3, is not only a strong acid, but also a powerful oxidiser at high concentrations. At concentrations above ca. 65% (weight percent %w/w), two main forms are common. White fuming nitric acid, WFNA, and red fuming nitric acid, RFNA. While WFNA almost exclusively consists of HNO_3 and some water, RFNA contains notable amounts of N_2O_4 in addition to water and HNO_3.

A sample of 1.57 g RFNA is generously diluted with water. Then, an excess of formaldehyde (H_2CO) is added and left to react with all N_2O_4 present in the sample. This reaction yields formic acid (HCOOH, $pK_a = 3.76$) and NO. The NO is no longer relevant in this experiment. The sample is then titrated with two indicators and 1.400 M NaOH solution. The first indicator transition is observed after 14.78 ml. The second transition with phenolphthalein occurs after an additional 2.68 ml NaOH is added.

3.1 **Select** an indicator suitable to serve as the first indicator. 1.0 pt

☐ Methylene blue (pH 7)
☐ Phenolphthalein (pH 9.1)
☐ Bromophenol blue (pH 3.8)
☐ Thymol blue (pH 2.0)

SOLUTION:
Thymol blue
first indicator shows HNO_3, second formic acid. pK_a of the first indicator has to be 1 unit or more below the pK_a of formic acid
1 pt

3.2 **Calculate** the composition of the sample as weight percentages (%w/w). 3.0 pt

SOLUTION:
14.78 ml * 1.4M = 20.69 mmol * 63 g / mol = 1.303 g / 1.570 = 83 % HNO_3
2.68 ml * 1.4 M = 3.75 mmol / 2 (stoichiometric ratio 1 N_2O_4 = 2 HCOOH) = 1.87 mmol * 92 g / mol = 0.172 g / 1.57 = 11% N_2O_4
by difference 6% H_2O
1 pt for HNO_3, 1.5 pt for N_2O_4, 0.5 pt for water.
-1 pt per error

On titration of a 1.97 g sample of WFNA, the endpoint is reached with 1.400 M NaOH at 23.0 ml. At first, this result seems unusual.

3.3 **Calculate** the mass fraction of HNO_3 as weight percentage (%w/w) in the sample. 2.0 pt

SOLUTION:
103%.
23.0 mL * 1.40 mmol mL−1 = 32.2 mmol * 63 mg mmol−1 = 2.03 g/1.97 g = 1.03
2 pt, unit other than mass percent or weight fraction but correct numbers 1 pt, correct calculation but wrong numbers 1pt, -1 pt per error

3.4 **Pick** the species that is responsible for the unusual result and **calculate** its ratio to HNO_3 in the sample. No other species are contained. 3.0 pt

☐ $H_2N_2O_6$ ☐ N_2O_4 ☐ N_2O_5 ☐ $N_3O_3H_3$

Ratio HNO_3 : species _____

SOLUTION:
0.0322 mol = x HNO_3 + 2y N_2O_5
x mol *63 g/mol + y mol * 108 g/mol = 1.970 g
x= 0.0257, y= 0.00325
HNO_3 7.91 : 1 N_2O_5

3 pt, 1 pt for correct species, 2 for calc. max 1 pt total for correct math with wrong species
-1 pt per error

Mixed Acids

Nitration chemistry is a relatively old field of organic chemistry. Classically, an aromatic ring is nitrated using a mixture of H_2SO_4 and HNO_3.

The activation step of the reaction produces the active species, which then undertakes the nitration step.

3.5 **Write down** a balanced equation which shows this activation step and **draw** the structure of the active species. 2.0 pt

SOLUTION:
$H_2SO_4 + HNO_3 \longrightarrow H_2O + HSO_4^- + NO_2^+$
NO_2^+ is active species, $O{=}N^+{=}O$ for 1pt, $O{=}N^{2+}{-}O^-$ for 0.5 pt, $O^- {-} N^{3+} {-} O^-$ for 0 pt.
1 pt for correct equation,
if balanced equation to sensible, wrong product 0.5 pt, + 0.5 pt for a sensible, wrong structure

If a series of nitration experiments is conducted using pure HNO_3 and H_2SO_4 of increasing water content, a sudden drop in reaction rate is observed if 15% water (%w/w) or more is contained in the sulfuric acid.

3.6 **Explain** this drop in reactivity. 2.0 pt

SOLUTION:
At 85% H_2SO_4, the composition is $H_2SO_4 \cdot H_2O$, which sharply reduces the ability of the sulfuric acid to draw water and thus the driving force for the formation of NO_2^+ is significantly lowered.

This effect can be counteracted by removing water from the reaction mixture by some means.

3.7 **Select** for all methods proposed below, whether or not they are effective at removing water from a nitration reaction without severely impacting reaction progress. 3.0 pt

Method	Effective	Not effective
$MgSO_4$	☐	☐
Ac_2O (acetic anhydride)	☐	☐
P_2O_5	☐	☐
saturated NaCl solution	☐	☐
azeotropic distillation with toluene	☐	☐
H_2SO_4	☐	☐

SOLUTION:
correct: Ac_2O, P_2O_5, H_2SO_4
incorrect:
$MgSO_4$ (base), NaCl sat. (contains water), azeotropic distillation (toluene is nitrated)
1 pt per correct mark, -1 pt per wrong mark

Many-Facetted Oxides of Chlorine (21.0 pt)

In nature, element 17 — chlorine — is most commonly encountered in its simple anionic form as chloride minerals. However, chlorine is capable of forming compounds in various oxidation states, such as NaClO. Bleach, also known as Eau de Javel (named after the district of Paris where it was first industrially produced), is a common household chemical consisting of a very basic solution of 15 %w/w NaClO and 0.5 %w/w NaCl. In this composition, bleach has a density $\rho = 1.21\ \text{g mL}^{-1}$.

4.1 **Determine** the molar concentration of NaClO and NaCl in bleach. 2.0 pt

$c_{\text{NaClO}} =$ _____ mol L^{-1}, $c_{\text{NaCl}} =$ _____ mol L^{-1}

SOLUTION:

Per $V = 1$ L, there is $\rho \times V = 1.21$ kg of solution.
15% of that is $m_{\text{NaClO}} = 181.5$ g and 0.5% is $m_{\text{NaCl}} = 6.05$ g.
Now, we apply $c = \frac{m}{M \times V}$, yielding
$c_{\text{NaClO}} = 2.438\ \text{mol L}^{-1}$
$c_{\text{NaCl}} = 0.104\ \text{mol L}^{-1}$
1.0 pt for the correct mathematical reasoning. 0.5 pts for each correct numerical result. 2.0 pts total.

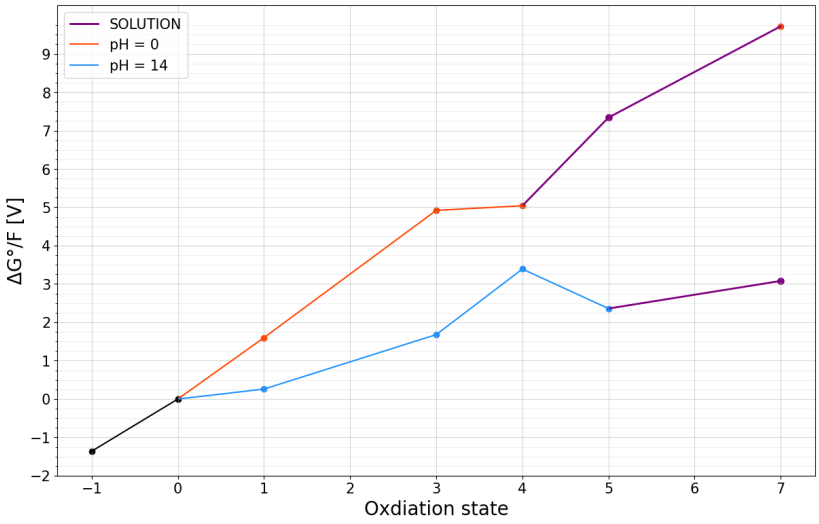
Given below is a table containing different standard reduction potentials of chlorine-containing species at pH = 0 and pH = 14 at 25 °C.

Reduction (ions shown in protonated form)	E°_{red} at pH = 0 / V	E°_{red} at pH = 14 / V
$Cl_2 \longrightarrow HCl$	1.36	1.36
$HClO \longrightarrow HCl$	1.48	0.81
$HClO_2 \longrightarrow HCl$	1.57	0.76
$ClO_2 \longrightarrow HCl$	1.28	0.95
$HClO_4 \longrightarrow HClO_3$	1.19	0.36
$HClO_3 \longrightarrow HCl$	1.45	0.62

4.2 **Fill** in the missing data points of Cl(V) at pH = 0 and Cl(VII) at pH = 14 on the Frost diagram below. **Provide** the values of $\frac{\Delta G^\circ}{F}$ in volts for these two species. 4.0 pt

$\frac{\Delta G^\circ}{F}$(Cl(V), pH=0) = _____ V, $\frac{\Delta G^\circ}{F}$(Cl(VII), pH=14) = _____ V

SOLUTION:



$\frac{\Delta G^\circ}{F} = -zE^\circ_{red}$

For Cl(V) at pH $= 0$, this comes out to be $1.45\,\text{V} \times 6 - 1.36\,\text{V} = 7.34\,\text{V}$

For Cl(VII) at pH $= 0$, this comes out to be $0.36\,\text{V} \times 2 + 0.62\,\text{V} \times 6 - 1.36\,\text{V} = 3.08\,\text{V}$

0.5 pts for each correctly placed datapoint. 1.0 pt for the correct mathematical reasoning (via ΔG). 1.0 pt for each correct numerical result. 4.0 pts total.

4.3 **State** whether hypochlorous acid (HClO) can be obtained by addition of strong acid to bleach. **Write down** the relevant chemical equation(s). 2.0 pt

SOLUTION:

As seen in the Frost diagram, the reduction potential of $Cl(I)$ species is strongly dependent on pH. At pH = 0, these species are less stable, up to a point, where it will comproportionate with Cl^-. (Imaginary line between the two points passes above Cl_2).

Therefore, it is not possible to obtain HClO by acidifying the bleach.

$ClO^- + Cl^- + 2\,H^+ \longrightarrow Cl_2 + H_2O$ (or equivalent eq.)

1.0 pt for the correct statement. 1.0 pt for the correct chemical equation. 2.0 pt total.

You work in a lab that deals with various minerals and metal powders. One day, you spill some red realgar powder (As_4S_4) on your favourite lab coat, from where it won't come out. After some deliberation and research, you reach for bleach to remove the stain. Your research indicates that among the products of the reaction between realgar and bleach are sulfuric and arsenic acid (H_3AsO_4), which can be easily washed out.

4.4 **Write down** a fully balanced chemical equation of the reaction taking place. 3.0 pt

SOLUTION:
$As_4S_4 + 22\,NaClO + 10\,H_2O \longrightarrow 22\,NaCl + 4\,H_3AsO_4 + 4\,H_2SO_4$
0.5 pts for the presence of H_2O. *0.5 pts for the precense of* NaCl. *2.0 pts for the correct stoichiometry. 3.0 pts total.*

On a different day, you are working with a blend of (semi-)precious metal powders (Au, Rh, Pd, Ir, Cu, Rh). Unfortunately, you once again spill some of the powder on the same lab coat. Remembering what happened before, you apply bleach to oxidise the metals to their oxides/hydroxides. These can then be washed out in a solution of dilute acid. A table of the reduction potentials of the metals at pH = 14 and 25 °C is given below.

Reduction	E°_{red} / V
$Cu(II) \longrightarrow Cu$	0.34
$Ru(II) \longrightarrow Ru$	0.46
$Rh(III) \longrightarrow Rh$	0.83
$Pd(II) \longrightarrow Pd$	0.95
$Ir(III) \longrightarrow Ir$	1.15
$Au(I) \longrightarrow Au$	1.69

4.5 **Select** which metals are oxidised (or not oxidised) by NaClO under standard conditions at pH = 14. 3.0 pt

Metal	Oxidised	Not oxidised
Cu	☐	☐
Ru	☐	☐
Rh	☐	☐
Pd	☐	☐
Ir	☐	☐
Au	☐	☐

SOLUTION:

Metal	oxidised	not oxidised
Cu	☒	☐
Ru	☒	☐
Rh	☐	☒
Pd	☐	☒
Ir	☐	☒
Au	☐	☒

Under standard conditions at pH = 14, the reduction potential of the ClO^- is 0.81 V. Any metal with an oxidation potential that is lower than that, will be oxidised. This is only the case for Cu and Ru.
0.5 pts for each correct tick. 0.0 pts for a row if more than one ticked. 3.0 pts total.

Curiously, under real conditions, more metals are oxidised by bleach than expected.

4.6 **State** which other metal(s) is/are also oxidised by bleach with the concentrations from **4.1**. **Note**: if you could not determine the concentrations of the species in **4.1**, use the ratio $\frac{c_{\text{NaCl}}}{c_{\text{NaClO}}} = 0.04$. 3.0 pt

SOLUTION:

Because we are not under standard conditions, we have to determine the new EMF ΔE.

Using the Nernst equation, we can see that

$\Delta E = \Delta E^\circ - \frac{RT}{zF} \ln\left(\frac{c_{\text{NaCl}}}{c_{\text{NaClO}}}\right)$.

For $T = 298.15\,\text{K}$ and $z = 2$, this yields $\Delta E = \Delta E^\circ - \frac{59\,\text{mV}}{2} \log\left(\frac{0.104\,\text{mol L}^{-1}}{2.438\,\text{mol L}^{-1}}\right) = \Delta E^\circ - \frac{59\,\text{mV}}{2} \log\left(0.0427\right) = 0.81\,\text{V} - 29.5\,\text{mV} \times (-1.370) = 0.85\,\text{V}$.

This potential is higher than that of Rh^{3+} at 0.83 V (0.85 V if the hint was used), meaning Rh metal will be oxidised.

1.0 pt for the use of the Nernst equation. 1.5 pts for the correct numerical result. 0.5 pts for the correct choice of Rh. *-0.5 pts for each incorrect choice. 3.0 pts total.*

Not satisfied with the results, you reach for an acidic solution of $HClO_2$: HCl in a molar ratio 100 : 1. You also experiment with heat.

4.7 **Calculate** the minimum temperature in K, at which the reduction potential of the mixture given in the text is greater than that of all the metals in the powder. 4.0 pt

$T =$ _____ K

SOLUTION:

Once again, the Nernst equation needs to be applied. As given, the ratios of the concentrations will be 0.01.

$\Delta E = \Delta E^\circ - \frac{RT}{zF} \ln(0.01)$

Solving for T gives

$T = zF \times \frac{\Delta E^\circ - \Delta E}{\ln(Q) R}$

The most "noble" among the metals in the powder is Au with $\Delta E^\circ = 1.69\,\text{V}$. ($\Delta E^\circ = 1.57\,\text{V}$, $\Delta E = 1.69\,\text{V}$ for the bleach)

Plugging this in gives

$T = 4 \times 96\,485\,\text{C mol}^{-1} \times \frac{-0.12\,\text{V}}{\ln(0.01) \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1}} = 1209.6\,\text{K}.$

0.5 pts for the use of the Nernst equation. 0.5 pts for using gold. 1.0 pt for the correct ratio inside the log. 1.0 for the correct rearrangement to yield T. 1.0 pt for the correct numerical result. 4.0 pts total.

Perhaps it is time to buy a new lab coat...

The Power of the Core (19.0 pt)

Hint: this problem deals with radiochemistry and isotopes. For full marks, give every element as a definded isotope, with the number of protons and rounded mass like $^{4}_{2}$He.

As one of the so-called transuranic elements, californium cannot be found in nature. Instead, Cf isotopes have to be made. A direct way to a light californium isotope is the bombardment of ^{238}U with ^{12}C, leading to the formation of a californium isotope along with the release of six neutrons.

5.1 **Write down** the equation to produce californium from uranium by bombardment with carbon, as described above. 2.0 pt

SOLUTION:
$^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{244}_{98}\mathrm{Cf} + 6\,{}^{1}_{0}\mathrm{n}$
2 pt, 1 pt for reaction to $^{250}_{98}$Cf, -1 pt per error

5.2 The californium isotope ^{242}Cf exhibts both α and β^- decay modes. **Write down** the balanced equations for both decay modes. 4.0 pt

α:

β^-:

SOLUTION:
α decay: $^{242}_{98}\mathrm{Cf} \longrightarrow {}^{238}_{96}\mathrm{Cm} + {}^{4}_{2}\alpha$
β^- decay: $^{242}_{98}\mathrm{Cf} \longrightarrow {}^{242}_{99}\mathrm{Es} + {}^{0}_{-1}\mathrm{e}$
1 pt for α decay, 3 pt for β^- decay
-1 pt for errors, 1 pt for correct β^+ decay to $^{242}_{97}$Bk (berkelium)
Neutrinos can be left out without penalty

Suppose a mass of 50.4 µg of pure ^{252}Cf with a half-life of 2.645 years.

5.3 **Calculate** the number of decays per second of the sample, assuming it is 100% pure. 3.0 pt

$A =$ _____ Bq

SOLUTION:

From formulae in the preamble: $t_{1/2} = \frac{ln(2)}{k}$ rearranges to $k = \frac{ln(2)}{t_{1/2}}$ has to be multiplied by number of atoms

$A = \frac{ln(2) * \frac{50.4\ \mu g}{252\ g\ mol^{-1}}}{2.645\ years} = 1.662 * 10^{-15}\ mol\ sec^{-1} * N_A = 1GHz = 1GBq = 1 * 10^9\ sec^{-1}$

3 pt, 1 pt for proper manipulation of formula, 2 pt for numbers, -1 pt for errors, 1 pt total max for result in mol per sec or different units

5.4 From the value obtained above, **calculate** the remaining activity after 264 days. 2.0 pt
Note: if you have not obtained a solution in task **5.4**, you may use $A = 1$ TBq as the initial activity.

$A =$ _____ Bq

SOLUTION:

$A = 1\ GBq * e^{\frac{ln(2)}{t_{1/2}} * t} = 0.827\ GBq$

replacement answer $A = 1\ TBq * e^{\frac{ln(2)}{t_{1/2}} * t} = 0.827\ TBq$

2 pt, 1 pt for formula, -0.5 per error, full marks for replacement answer

Upon fission, ^{252}Cf does not break into two equal parts, but into a light and heavy fragment. In this process, some excess neutrons and a decent amount of energy are liberated.

Consider the reaction: $^{252}\text{Cf} \longrightarrow {}^{99}\text{Mo} + {}^{151}\text{Ba} + 2\ {}^{1}\text{n}$

5.5 **Calculate** the energy liberated per fission event following this decay path. 3.0 pt
Furthermore, **calculate** the temperature a 3 kg sample of water at 25 °C reaches, if all the energy of 10 µg of ^{252}Cf decaying as shown above is turned into heat and contained in the water.
Some useful numbers:
Exact masses: ^{252}Cf: 252.0816 u, ^{99}Mo: 98.9077 u, ^{151}Ba: 150.9508 u, n: 1.0087 u
Physical data on water: $C_p = 4184\,\text{J K}^{-1}\,\text{kg}^{-1}$, $\Delta H_{\text{vap}} = 2257\,\text{J kg}^{-1}$, $\Delta H_{\text{fus}} = 333\,\text{J kg}^{-1}$

$E =$ _____ J

$T =$ _____ °C

SOLUTION:
$252.0816 - 98.9077 - 150.9508 - 2 * 1.0087 = 0.2057\ u = 3.4169 * 10^{-28} * c^2 = 3.0709 * 10^{-11}\ J$ per decay
$10\ \mu g/252.0816\ g/mol * 6.023 * 10^{23}\ per\ mol = 2.3881 * 10^{16}$ decays
$2.3881 * 10^{16} * 3.0709 * 10^{-11} = 733362\ J/4184\ J/kg/K/3\ kg = 58.43\ K = 83.43$°C

^{151}Ba then rapidly decays through a series of identical decay modes to a stable isotope of mass 151 and a proton : neutron ratio of 0.72.

5.6 **Provide** the decay mode as well as the stable isotope reached. 2.0 pt

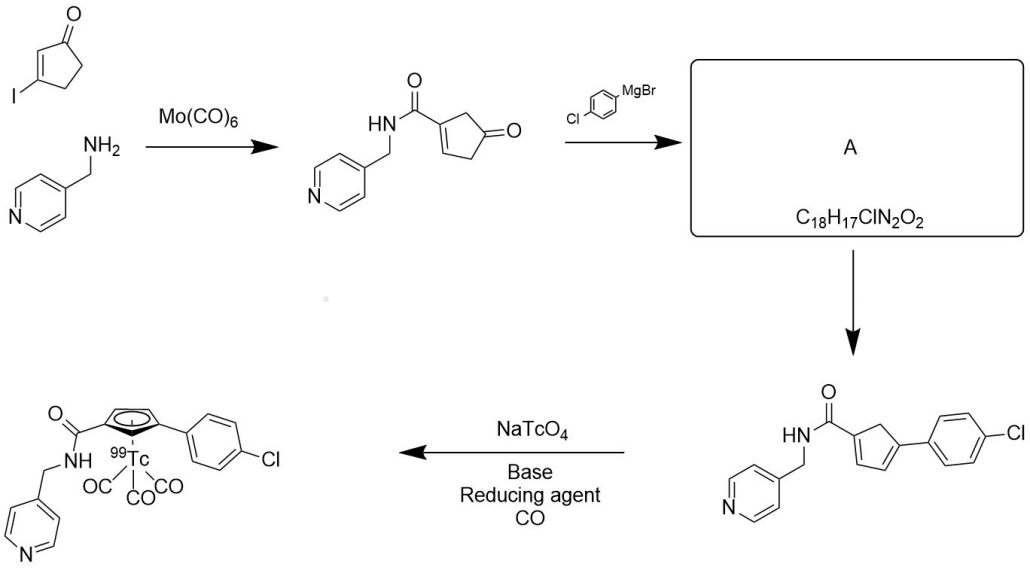
Decay mode: _____

Isotope: _____

SOLUTION:
β^- and ^{151}Eu
1 pt each

Meanwhile, ^{99}Mo can be extracted chemically from among the fission products as MoO_4^- salt. It then decays to the metastable ^{99m}Tc (half-life 6 h) which ejects a photon to reach the long-lived ^{99}Tc. This decay is very useful in diagnostics. To this end, the research group of Roger Alberto at the Univeristy of

Zürich synthesised a compound to which Tc could be attached. The last steps of the synthesis are shown below.



5.7 **Draw** the structure of A. 2.0 pt

SOLUTION:
Tertiary alcohol given by the grignard reaction between the ketone and the Ar-MgBr.

5.8 **Explain** why the base required to deprotonate the cyclopentadiene ring can be much weaker than what is normally needed to deprotonate an allylic position. 1.0 pt

SOLUTION:
Cyclopentadienyl (Cp) anion is aromatic

Down the Rabbit Hole: Frémy's Salt (21.0 pt)

While digging through your local library's old and dusty chemistry books, you read on a strongly yellowed and faded page about a peculiar compound called "Frémy's salt". Supposedly, it is an inorganic potassium salt with interesting properties. Unfortunately, a lot of the page has become illegible over the years of the book collecting dust. Having piqued your interest, you head to your lab to prepare a sample to deduce its structure and properties. The synthetic scheme found in the book is depicted below.

$$KNO_2 + 2\,KHSO_3 \longrightarrow K_3\mathbf{X} + H_2O \quad (1)$$

$$3\,K_3\mathbf{X} + KMnO_4 + 2\,H_2O \longrightarrow 3\,K_2\mathbf{Y} + MnO_2 + 4\,KOH \quad (2)$$

$K_3\mathbf{X}$ is an intermediate product in the formation of Frémy's salt ($K_2\mathbf{Y}$). It is stated that **X** is a symmetrical, trianionic species containing only terminal oxygen atoms.

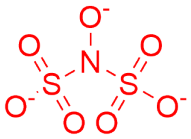
6.1 **Write down** the sum formula of **X** and **draw** its Lewis structure. 3.0 pt

Sum formula: _____

SOLUTION:

Sum formula: $NS_2O_7^{3-}$

Structure:

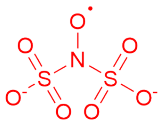


1.0 pts for the correct sum formula. 2.0 pts for the correct structure. 3.0 pts total.

The second reaction gives a solution of Frémy's salt ($K_2\mathbf{Y}$) by the oxidation of $K_3\mathbf{X}$. The book explains that in this reaction, the connectivity of the molecule is unchanged.

6.2 Using reaction **(2)**, **draw** the structure of **Y**. **State** what is special about the electronic properties of **Y.** 2.0 pt

SOLUTION:



Y

or the radical on any other sensible atom

The oddity in the electronic structure is that Y is a radical. This is due to the fact that all X are only being oxidised by 1 electron. As the connectivity remains unchanged, this odd-electron species must be a radical.

1.0 pt for the correct structure. 1.0 pts for seeing, that it is a radical. 2.0 pts total.

You perform the reaction described in the book and find that although all permanganate has been used up, your solution remains a deep purple colour. This must be the colour of Frémy's salt. While cooling your solution down to obtain the crystalline product, you observe an orange solid **Z** slowly precipitating from the solution as the purple colour fades. Elemental analysis of **Z** reveals the following:

Element	K	N	S	O
%w/w of **Z**	29.1	5.2	24.0	41.7

6.3 **Determine** the molar ratio of all elements in compound **Z** and **state**, whether it matches that of Frémy's salt. 3.0 pt

K : N : S : O = _____ : _____ : _____ : _____

SOLUTION:

For simple calculations, everything is done for 1 g of **Z**.

The number of moles of an element $n_i = \frac{wt\%_i}{M_i}$.

For each element per gram:

K: 7.44 mmol

N: 3.71 mmol

S: 7.49 mmol

O: 26.1 mmol

Dividing each value by 3.71 mmol gives a ratio of K : N : S : O = 2.00 : 1.00 : 2.01 : 7.03 $\approx$ 2 : 1 : 2 : 7 (or any multiple).

This ratio matches that of Frémy's salt.

0.5 pts for the correct mathematical approach. 0.5 pts for every correct stoichiometric coefficient. 0.5 pts for the correct statement (it matches). 3.0 pts total.

The book has a section on the magnetic properties of the compounds, but only the title is still barely legible, however, you would like to know more. Naturally, you get an incredibly strong neodymium magnet and perform tests on K_2**Y** and **Z**. During your experiments, you see that the purple compound K_2**Y** is magnetically attracted but **Z** is slightly repelled by a magnetic field.

6.4 **Explain** the magnetic properties of K_2**Y** and **Z** and what can be concluded about their electronic structures. 2.0 pt

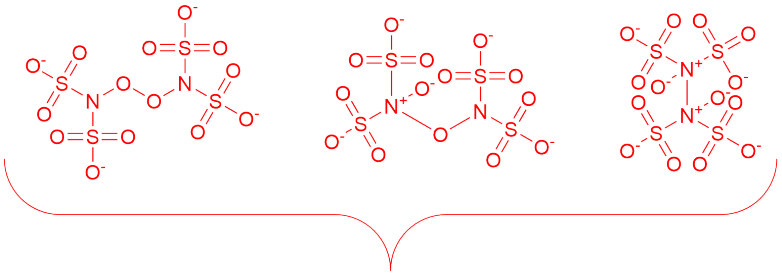
SOLUTION:

K_2**Y** is paramagnetic and **Z** is diamagnetic. Therefore, K_2**Y** must have unpaired electrons (as suspected in **6.2**) and **Z** must only contain paired electrons and is not a radical.

0.5 pts for each correct assignment of dia-/paramagnetic. 0.5 pts for each correct line of reasoning about their electronic structures. 2.0 pts total.

6.5 **Suggest** two possible structures for **Z**. 2.0 pt

SOLUTION:



Z

any two of these three

1.0 pt for each correct structure. 2.0 pts total.

You are baffled by the vivid purple colouration of a solution of Frémy's salt. Even upon the addition of a small crystal of the orange **Z** to copious amounts of water, the solution is dyed to an almost black colour. Because of your fascination, you investigate the solution's spectroscopic properties. You measure the ratio of the intensities of the radiation leaving the sample I to that of the incoming radiation I_0 of the following solutions of the compounds in a cuvette of length $l = 1$ cm at $\lambda = 475$ nm.

$[K_2\mathbf{Y}]$ / mol L^{-1}	5.30×10^{-5}	9.50×10^{-5}	2.15×10^{-4}	3.75×10^{-4}	4.55×10^{-4}	4.85×10^{-4}
$\frac{I_0}{I}$	1.26	1.53	2.58	5.28	7.51	8.61

6.6 **Determine** the molar extinction coefficient ϵ in $\mathrm{L\,mol^{-1}\,cm^{-1}}$ for K_2**Y** at this wavelength. 3.0 pt

$\epsilon =$ _____ $\mathrm{L\,mol^{-1}\,cm^{-1}}$

SOLUTION:

There are multiple ways of solving this exercise. Because the data was chosen neatly, all the following methods yield about the same result:

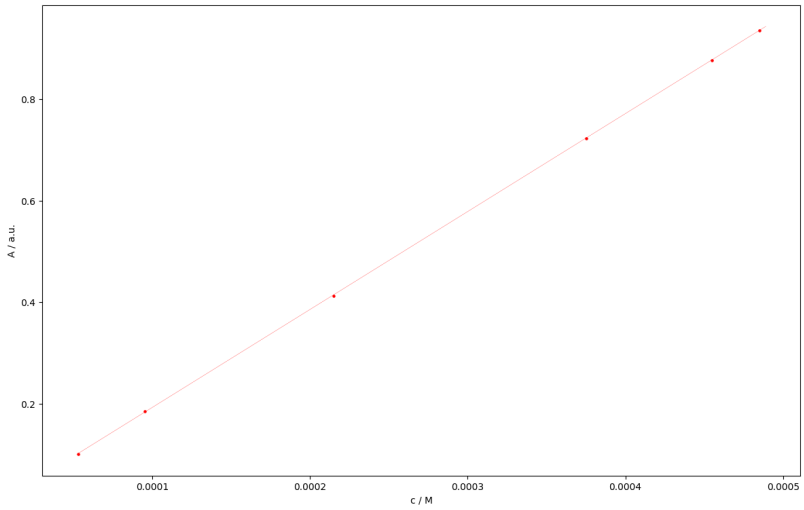
1. Linear regression (probably not possible with their calculators)
2. Drawing a trendline by hand
3. Connecting the first and the last points

Before any of this can be applied, the graph needs to be linearised first.

Beer-Lambert tells us that $\log\left(\frac{I_0}{I}\right) = A = \epsilon \times l \times c$.

Therefore, $\epsilon = \frac{\log\left(\frac{I_0}{I}\right)}{l \times c}$.

Taking the log of the data gives a nice linear plot like the following:



The data fits very nicely and either just taking the slope or doing fancy math yields:

$\epsilon = 1926\,\mathrm{L\,mol^{-1}\,cm^{-1}}$.

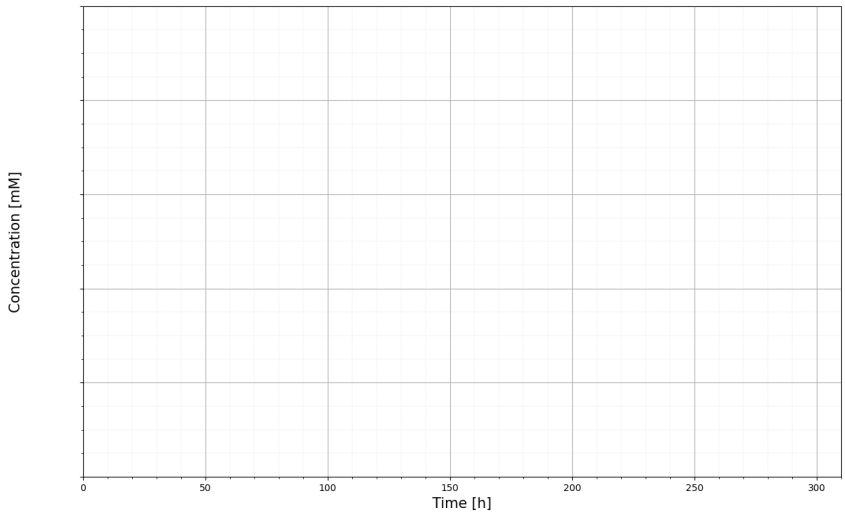
Any result between $1733\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ and $2119\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ should give full marks. ($\pm 10\%$)

0.5 pts for using Lambert-Beer. 0.5 pts for the correct rearrangement to yield ϵ. 2.0 pts for the correct numerical result. 3.0 pts total.

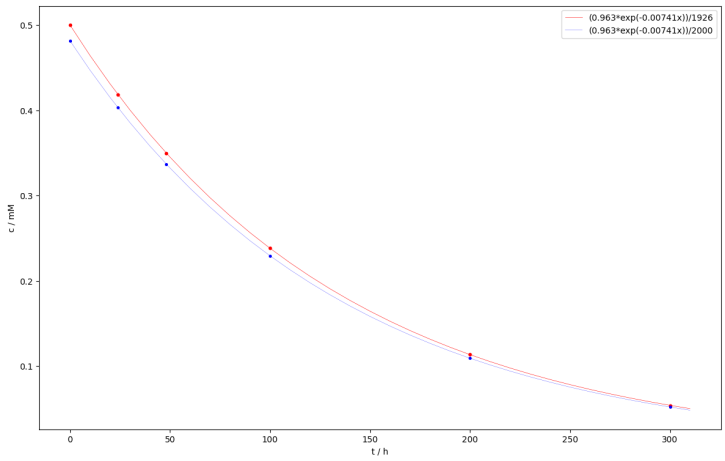
Satisfied with the experiments for the day, you leave the lab and return after a few days. To your shock, you notice that the dark purple colouration has significantly faded. Frémy's salt seems to be somewhat unstable. You record the same sample at different times throughout the next days and obtain the following data:

t / h	0	24	48	100	200	300
A	0.963	0.806	0.674	0.459	0.219	0.104

6.7 In the diagram below, **plot** the concentration of Frémy's salt as a function of time. **Note:** if you could not determine ϵ in **6.6**, use $\epsilon' = 2000\,\text{L mol}^{-1}\,\text{cm}^{-1}$. 3.0 pt



SOLUTION:
Beer-Lambert once again tells us that $c = \frac{A}{\epsilon \times l}$.
Plotting the concentration gives rise to the following graph (exponential decay):



3.0 pts for the correct plot. 3.0 pts total.

6.8 **Determine** the total empirical order of the decomposition reaction of Frémy's salt as well as the rate constant k. 3.0 pt

Order: _____, k = _____

SOLUTION:

As seen in **6.8**, the decomposition follows an exponential decay. Therefore, the reaction must be of first order overall.

Using the linearisation from above, a linear regression or "connecting the dots" can be used, as above.

This gives a slope $k = 0.007\,414\,\text{h}^{-1}$.

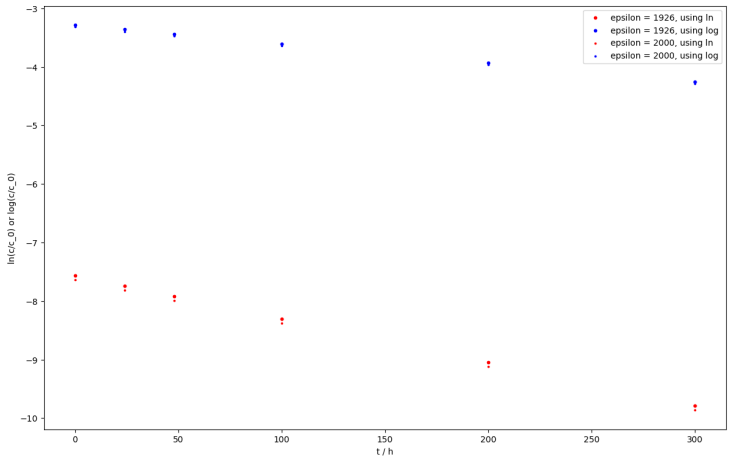
We will accept results between $k = 0.006\,66\,\text{h}^{-1}$ and $0.008\,14\,\text{h}^{-1}$.($\pm 10\%$)

If instead of ln, log is used, the result will be $k' = 0.003\,220\,\text{h}^{-1}$.

We will accept results between $k = 0.002\,898\,\text{h}^{-1}$ and $0.003\,542\,\text{h}^{-1}$. ($\pm 10\%$)

Note: depending on convention, the result might be negative.

2.0 pt for stating that it is 1st order. 1.0 pts for the correct numerical value of k. 3.0 pts total.



Concerning Amines (20.5 pt)

Amines are ubiquitous in medicinal chemistry. They are useful to get the drug molecule into solution as protonated and therefore soluble salt, offer key steric and electronic interactions with the drug target and are also very versatile handles for chemistry to link fragments together.

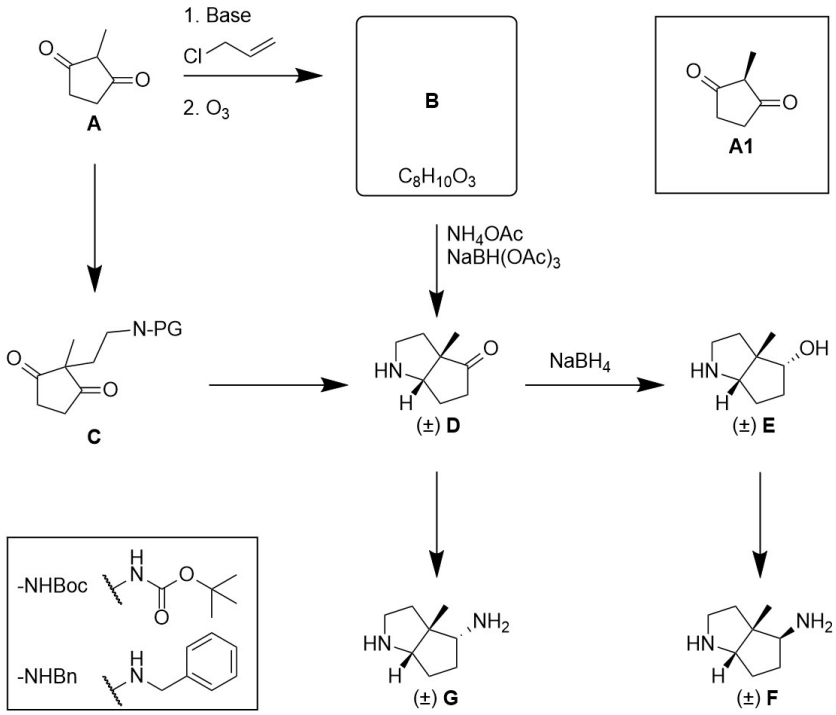
Amongst the most versatile tools for amine chemistry are two reactions: the reductive amination and the Staudinger reaction.

1. **The reductive amination** is a reaction sequence consisting of the condensation of a ketone or aldehyde with an amine to the respective imine, which is then reduced to the amine, usually with $NaBH(OAc)_3$ or $NaBH_3(CN)$. While it can be used in the reaction, $NaBH_4$ also reduces the carbonyl compounds, making the reaction much less economical and high-yielding.
2. **The Staudinger reaction** is a reduction of an azide moiety to an amine using PPh_3 and water. At first, a highly N-nucleophilic iminophosphorane intermediate $R{-}N{=}PR_3$ is formed, from which the amine is released by hydrolysis.

7.1 There are two aspects to the Staudinger reaction which drive it very strongly towards the side of the products. **Name** both. 2.0 pt

SOLUTION:
Extrusion of N_2 and the formation of $OPPh_3$

The compounds here discussed are building blocks for potentially very potent inhibitors of various kinases, a very large and important class of enzymes.



7.2 **Draw** the structure of **B**. 2.0 pt

SOLUTION:
Aldehyde

7.3 **Select** for all the reagents provided below, whether or not they are suitable to obtain **C** from **A**. The N-PG moiety in **C** can be $-NH_2$, $-N_3$, $-NHBn$, $-NHBoc$. 2.0 pt

Reagent	Suitable	Not suitable
$Cl-CH_2CH_2-NH_2$, NaOH	☐	☐
$HO-CH_2CH_2-NHBoc$, HCl	☐	☐
$Br-CH_2CH_2-N_3$, NaH	☐	☐
$Cl-CH_2CH_2-NHBn$, NaH	☐	☐

SOLUTION:
$Br-CH_2CH_2-N_3$, NaH
all others either don't react or produce copious side products
2 pt, 0 for others

7.4 **Select** for all conditions provided below, whether or not they are suitable to turn **C** to **D**, with regards to your choice for the N-PG moiety. 2.0 pt

Condition	Suitable	Not suitable
$NaBH(OAc)_3$	☐	☐
$NaBH(OAc)_3$, then H_2, Pd/C	☐	☐
HCl then $NaBH(OAc)_3$	☐	☐
PPh_3 then $NaBH(OAc)_3$	☐	☐

SOLUTION:
Conditions have to match the previous selection.
PPh_3 option is correct,
technically, HCl for Boc, H_2, Pd/C for Bn, only $NaBH(OAc)_3$ for amine
1 pt for those

7.5 Compound **D** is obtained as a racemic mixture. **Determine** the absolute configuration at the quaternary position according to the CIP rules of the enantiomer drawn in the scheme above. 2.0 pt

Configuration: _____

SOLUTION:

(S)

Priority: 1 - carbonyl, 2 - amine, 3 - CH_2, 4 - CH_3

7.6 **Explain** why **A1** cannot be used to selectively synthesise one enantiomer of **D**. Where possible, **illustrate** your answer. 2.0 pt

SOLUTION:

A is not chiral, and if it were, it would tautomerise.

1 pt for each argument. 0.5 pt each for a sensible structure or drawing

7.7 Both the reduction of the ketone to **E** as well as the reductive amination to **G** produce the same configuration. This is fairly obviously dictated by sterics. **Draw** a structure illustrating this. 3.0 pt

SOLUTION:
The ketone/imine has a distinct endo face, which is much harder to attack

7.8 **Name** the stereochemical relation between **F** and **G**. 1.5 pt

SOLUTION:
Diastereomers or more precisely epimers 1.5 pt for epimers, 1 pt for diastereomers

The diamine cores **F** and **G** can then be functionalised at the nitrogen atoms to obtain active compounds.

7.9 **Draw** the structure of the compound obtained if acetic acid CH_3COOH is added to a solution of **G** and left to react. 1.0 pt

SOLUTION:
The acetate salt. No points for the amide or any other reaction.

7.10 If ethyl sulfonyl chloride ($EtSO_2Cl$) is added to a solution of **F**, a major and a minor isomers are obtained, crystalising out of the solution. **Draw** the structures of both in the appropriate boxes. 3.0 pt

Major product

Minor product

SOLUTION:
Major: sulfonamide of the primary amine, HCl salt
Minor: sulfonamide of the secondary amine, HCl salt.
each 1 pt for the structure, 0.5 pt for making HCl salts, 0.5 pt for assigning them correctly

Trouble with Hydrogen (19.0 pt)

Liquefied hydrogen is a promising potential energy carrier for applications such as hydrogen fuel cells. On an industrial scale, cooling hydrogen can be troublesome, as will be examined in the following. The underlying phenomenon taking place is the interconversion between two energetically different forms of dihydrogen (H−H): para- and orthohydrogen. A table with thermodynamic data on hydrogen is provided below.

Boiling point	20.3 K
Heat of vapourisation ($\Delta H^\circ_{\text{vap}}$)	0.90 kJ mol^{-1}
Enthalpy of formation of parahydrogen (g) ($\Delta_f H^\circ_{\text{para}}$)	0.00 kJ mol^{-1}
Enthalpy of formation of orthohydrogen (g) ($\Delta_f H^\circ_{\text{ortho}}$)	1.46 kJ mol^{-1}
Density of liquid H_2 at boiling point ($\rho_{H_{2(l)}}$)	0.071 g cm^{-3}
Average heat capacity ($C_p(H_{2(g)})$)	24.9 J mol^{-1} K^{-1}

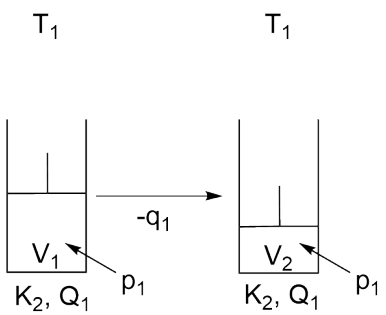
The equilibrium of the two forms of hydrogen (spin-isomers) is dependent on temperature. However, the conversion between the two spin-isomers is kinetically very slow. To differentiate between the equilibrium state and the current (out-of-equilibrium) state, a reaction quotient is introduced. The reaction quotient Q is the same mathematical expression as the equilibrium constant K.

$$Q = K = \frac{[H_2]_{\text{ortho}}}{[H_2]_{\text{para}}}$$

The difference between K and Q is that for K the equilibrium concentrations are used, whereas Q uses the current concentrations (which might be different from the equilibrium concentrations).

We have taken $V_0 = 10.0\,\text{L}$ of pure hydrogen gas at 298.15 K (at K_1) in a perfectly isolated piston and have cooled it to its boiling point (T_1) under constant atmospheric pressure (p_1). This gives a volume of $V_1 = 0.68\,\text{L}$ of hydrogen gas with a new equilibrium constant K_2, however the contents are still at Q_1.

The hydrogen is now condensed, however, the temperature is kept constant at T_1.



8.1 **Determine** the volume V_2 in mL of liquefied hydrogen inside the piston. 2.0 pt

$V_2 =$ _____ mL

SOLUTION:

$V = \frac{m}{\rho_{H_2 l}}$

$m = nM = 0.401\ \text{mol} \times 2.016\ \text{g mol}^{-1} = 0.808\ \text{g}.$

$V = \frac{0.808\ \text{g}}{0.071\ \text{g cm}^{-3}} = 11.38\ \text{cm}^3 = 11.38\ \text{mL}.$

0.5 pts for the correct formula for m. 0.5 pts for the correct formula for V_2. 1.0 pts for the correct numerical result. 2.0 pts total.

8.2 **Calculate** the amount of heat q_1 in J removed from the hydrogen in this phase transition. 2.0 pt

$q_1 =$ _____ J

SOLUTION:

$q_1 = -\Delta H^\circ_{\text{vap}} \times n = -0.90\ \text{kJ mol}^{-1} \times 0.401\ \text{mol} = -360.9\ \text{J}$

1.0 pt for the correct mathematical formula. 1.0 pt for the correct numerical result. -0.5 pt for incorrect sign. 2.0 pts total.

The trouble begins now: in the beginning of the 1900s, physicists observed that hydrogen exists in two energetically different states, depending on the spin alignment of the proton nuclei. There is parahydrogen with antiparallel alignment (↑↓) of the nuclear spins and orthohydrogen with parallel alignment (↑↑) of the nuclear spins.

At 25 °C, the equilibrium constant of the two forms $K_1 = \frac{p(\text{H}_{2\text{ortho}})}{p(\text{H}_{2\text{para}})} = 3.00.$

8.3 **Determine** ΔS° in J mol^{-1} K^{-1} for the conversion between the two forms at $T_0 =$ 298.15 K. 3.0 pt

$\Delta S^\circ =$ _____ J mol^{-1} K^{-1}

SOLUTION:

$K = 3$ means that $\Delta G^\circ = -2723.3$ J mol^{-1}. ($\Delta G^\circ = -RT \ln K$)

With $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, we get $\frac{-\Delta G^\circ + \Delta H^\circ}{T} = \Delta S^\circ$.

$\Delta S^\circ = \frac{-\Delta G^\circ + \Delta H^\circ}{T} = \pm 14.03$ J mol^{-1} K^{-1}.

$\pm$ due to the fact that the entropy is dependent on the direction of conversion.

1.0 pt for using $\Delta G = \Delta H - T\Delta S$. 1.0 pt for the correct formula for ΔS. 1.0 pt for the correct numerical result. 3.0 pts total.

At the boiling point of hydrogen, the equilibrium shifts to $K_2 = 0.002$. This value can be considered constant for small values of $T < 50$ K. The conversion between the two forms is kinetically very slow, taking a few days.

8.4 **Calculate** the enthalpy change ΔH of the liquid hydrogen by going from K_1 to K_2 in J. 4.0 pt

$\Delta H =$ _____ J

SOLUTION:

Solving the system of equations $\frac{o_i}{p_i} = K_i$ and $o_i + p_i = n$, $(i = 1, 2)$ gives $o_2 = 0.0008$

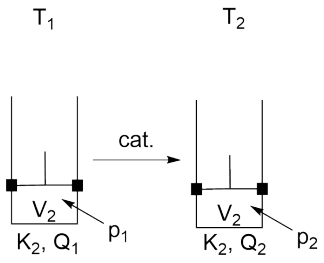
$\Delta n = \frac{3}{4} \times 0.401\,\text{mol} - 0.0008\,\text{mol} = 0.3008\,\text{mol} - 0.008\,\text{mol} \approx 0.300\,\text{mol}$.

Therefore, the change in internal energy is simply the enthalpy change times the amount of times this change is undergone.

$-\Delta H_{isomers} \times \Delta n = -438.00\,\text{J}$.

2.0 pts for the correct system of equations/formula for o/p. 1.0 pt for the correct Δn (starting from 3/4). 1.0 pt for the correct numerical result. -0.5 pt for the incorrect sign. 4.0 pts total.

Because of the rapid cooling and the slow interconversion, the contents of the piston are still the same as at $T_0 = 298.15\,\text{K}$ (Q_1). You plan on adding an extremely potent catalyst that can immediately return the mixture to its equilibrium ($Q_2 = K_2$). Before adding the catalyst, the piston was locked securely in place (as indicated by the black squares in the scheme), such that the volume will stay constant at V_2 at all times.



We now have to check, what the maximum pressure inside the piston will be and whether the piston could burst ($p > 10\,\text{MPa}$). Due to the build-up of the pressure inside the piston, the boiling point and

ΔH_{vap} will increase. However, as we are only interested in the maximum pressure possible, the same values for boiling point and ΔH_{vap} can be used. For the same reason, C_p can still be utilised, rather than C_V. The piston is fully insulated, meaning all energy will be kept inside the piston.

8.5 **Rationalise** why the assumptions that the boiling point and ΔH_{vap} stay constant are valid to calculate the maximum possible pressure produced inside the piston. 3.0 pt

SOLUTION:
The maximum possible pressure means the maximum possible energy going into boiling (expansion) and heating up (expansion) of the hydrogen.

A higher ΔH_{vap} means more energy is "sunk" into boiling the hydrogen.
A higher boiling point means that the remaining (liquid) hydrogen will need to be heated up (energy wasted), before it can boil.

Therefore, if we stick to the given values, we will see the maximum pressure produced.
2.0 pts for the notion that the lower values will leave behind "more" energy/"consume" less of it. 1.0 pt for the notion that the remaining energy is responsible for the build-up of the pressure. 3.0 pts total.

8.6 **Calculate** the temperature T_2 in K and maximum pressure p_2 in MPa inside the piston after addition of the catalyst. You may make the assumptions stated above and that the catalyst has no volume. **Note**: if you could not determine V_2 in **8.3**, you may use $V_2' = 10\,\text{mL}$ and if you could not determine ΔH in **8.7**, you may use $\Delta H' = -450\,\text{J}$. **State**, whether the piston is at risk of bursting at this pressure. 5.0 pt

$T_2 =$ _____ K, $p_2 =$ _____ MPa

☐ Piston will burst ☐ Piston will not burst

SOLUTION:

First, we need to calculate how much energy is needed to boil the hydrogen off. There are $n = 0.401\,\text{mol}$ of H_2 inside the container, which is initally at $T_1 = 20.3\,\text{K}$.

Now, $q_3 = \Delta H = 438\,\text{J}$ is released into the gas, which goes directly into boiling the hydrogen. The energy required is $-q_1 = 360.9\,\text{J}$, leaving behind $q_{\text{remain}} = 77.1\,\text{J}$ to heat up the gas.

Using C_p from above gives us $\Delta T = \frac{q_{\text{remain}}}{C_p \times n} = 7.70\,\text{K}$.

Therefore, $T_2 = 28.0\,\text{K}$.

$p_2 = \frac{nRT_2}{V_2} = \frac{0.401\,\text{mol} \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} 28.0\,\text{K}}{1.138 \times 10^{-5}\,\text{m}^3} = 8.21\,\text{MPa}$.

If $\Delta H' = -450\,\text{J}$ was used, $T_2' = 29.22\,\text{K}$ and $p_2' = 8.56\,\text{MPa}$ are obtained.

If $V_2' = 10\,\text{mL}$ was used, T_2 remains unchanged and $p_2'' = 9.34\,\text{MPa}$ is obtained.

If both $V_2' = 10\,\text{mL}$ and $\Delta H' = -450\,\text{J}$ were used, $T_2' = 29.22\,\text{K}$ and $p_2'' = 9.74\,\text{MPa}$ are obtained.

As all of these results are smaller than $p = 10\,\text{MPa}$, we can assume that the piston will not break.

0.5 pts for using ΔH as the "energy source". 1.0 pt for the process of boiling. 1.0 pt for the heating process. 1.0 pt for the process of pressure-buildup ($pV = nRT$). 1.0 pt for the correct numerical result. 0.5 pts for the correct statement, whether it will burst or not, depending on their value of p. 5.0 pts total.

One Ring (24.0 pt)

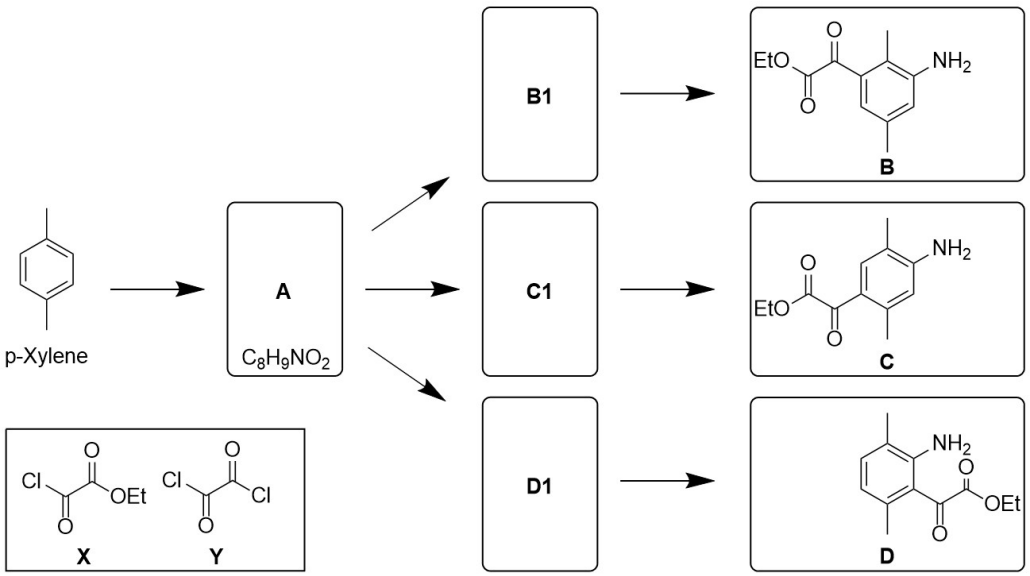
Hint: Reagents are displayed above a reaction arrow and, unless explicitly stated otherwise, only 1 eq. is added. Solvents are displayed under the reaction arrow and are present in a large excess (>10 eq.). Where written as text, the general expression is 'reagents in solvent'.

Benzene, toluene and xylenes – often abbreviated BTX – are a group of aromatic compounds of great importance. On the spectrum from crude oil to fine chemicals, these compounds are among the first to be isolated as pure compounds from crude oil distillates, with an annual volume of 40 million tonnes in 2010.

A BTX mixture can be obtained from the catalytic methylation of benzene. The crude reaction mixture contains one C_6 compound (benzene), one C_7 compound (toluene) and four C_8 compounds. These are *ortho*-, *meta*- and *para*-xylene (1,2- 1,3- and 1,4-dimethylbenzene respectively) along with a fourth compound which has been called 'the fourth xylene' on occasion, since it has the same sum formula C_8H_{10} and has an aromatic core.

9.1 **Draw** the sturcture of the 'fourth xylene'. 2.0 pt

Xylenes, despite their relatively simple structure, offer a rich chemistry and are ubiquitous in industry and daily life above and beyond use as a solvent.



9.2 **Select** for all conditions provided below, whether or not they are suitable to turn *p*-xylene into **A**. 2.0 pt

Conditions	Suitable	Not suitable
N_2O_5 in CH_2Cl_2	☐	☐
HNO_3 in H_2SO_4	☐	☐
NO_2BF_4 in MeCN	☐	☐
HNO_3 in Ac_2O	☐	☐

SOLUTION:
All are good, 0.5 pt each

9.3 **Draw** all possible isomers of **A**. 1.0 pt

SOLUTION:
There is only one.

9.4 Select a structure drawn in the previous task **9.3**, **draw** it and **write down** the number of NMR signals observed in ^{1}H NMR. 1.0 pt

Number of signals: _____

SOLUTION:
5 signals for nitro-*p*-xylene, 1 pt 0.5 pt if it matches the structure with the correct number of signals.

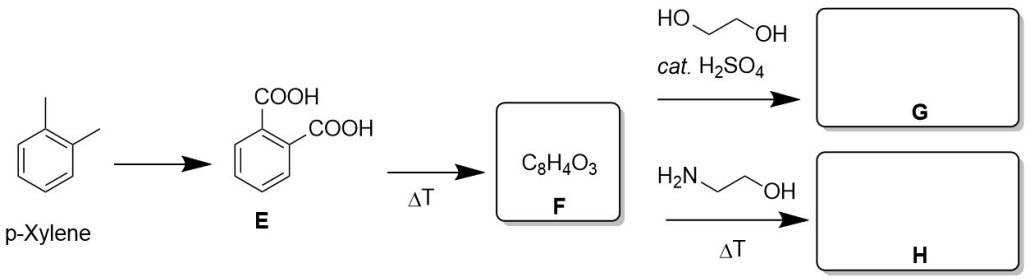
9.5 Using **A** as the starting material, **B**, **C** and **D** can be obtained in a few steps. From the conditions given below, **match** the conditions to the correct products. 3.0 pt
Note: Under 1. are reagents for the step leading to the intermediates **B1**, **C1** and **D1**, under 2. those leading on to the finished product.
Note: Pd,V/C denotes a palladium-vanadium catalyst which selectively reduces aromatic nitro groups to amines, leaving ketones, esters and other functionalities untouched.

Conditions	**Products (B/C/D)**
1. H_2, Pd, V/C then NaH, **Y**; 2. $AlCl_3$, then NaOEt in EtOH	
1. **X**, $AlCl_3$; 2. H_2, Pd, V/C	
1. H_2, Pd, V/C, then NaH, **X**; 2. **X**, $AlCl_3$ then NaOEt in EtOH	

SOLUTION:
Conditions: 1 for D, 2 for B, 3 for C
1 pt each correct, 0 for false

9.6 **Draw** the structures of the intermediates **B1**, **C1** and **D1**. 9.0 pt

SOLUTION:
B1: the nitro analogue of C
C1: the respective amide of 2,4-xylidine
D1: the amido acyl chloride R-NH-CO-COCl
3 pt for each structure. -1 pt for errors, 1 pt total if wrong but sensible with the previous answer. For each structure, 1 pt is awarded min. if the following elements are contained:
B1: is still nitro C1: amide or amine D1: cyclisable amide or bicyclic. amine functions as a covalent directing group



9.7 When looking at the pK_a values of **E**, the second deprotonation step is about one unit higher than the 1,3- and 1,4-diacids. **Draw** a structure illustrating the reason behind this difference. 1.0 pt

SOLUTION:
The two *ortho*-carboxylic groups 'balance' the second proton between them through intramolecular hydrogen bonding, making it much less acidic.

9.8 **Draw** the structure of **F**. 1.0 pt

SOLUTION:
Phtalic anhydride
1 pt

9.9 Product **G** is a polymeric compound. **Draw** the structure of one repeating unit. 2.0 pt

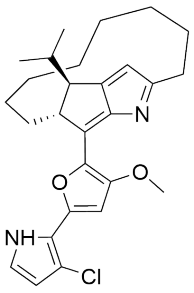
SOLUTION:
Polyester. 2 pt
1 pt for proper use of polymer brackets, 1 pt for structure inside

9.10 If the reaction is run with ethanolamine rather than ethylene glycol, the product obtained is **H**, which is not a polymer, but a molecule with a molecular mass below 200 u. **Draw** the structure of **H**. 2.0 pt

SOLUTION:
The hydoxyethylphtalimide. 2 pt
0.5 pt for an amide

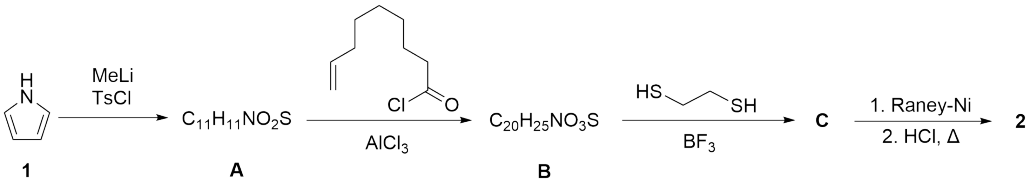
Total Synthesis of (+)-Roseophilin (25.0 pt)

(+)-Roseophilin is an antibiotic produced by the bacterium *Streptomyces griseoviridis*, which has been under investigation for its antitumor activity. The investigation of roseophilin and related compounds has led to the development of Obatoclax, an experimental drug with potential effectiveness against leukaemia and lung cancer.



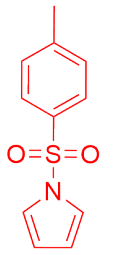
(+)-Roseophilin

The synthesis of (+)-roseophilin explored in this exercise is based on P. G. Harran's route starting from pyrrole (**1**), which is converted into **2**, employing, among other things, Raney-Nickel, a versatile reagent which can reduce sulfides into alkanes.

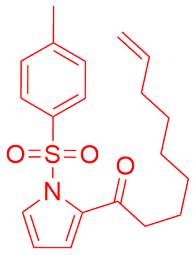


10.1 **Draw** the structures of **A**, **B** and **C**. **Note**: **C** contains two five-membered rings. 6.0 pt

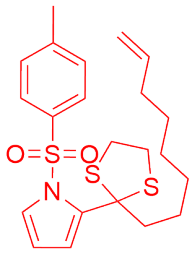
SOLUTION:
NOTE: For all structures IN THIS EXERCISE, SENSIBLE abbreviations, such as the ones used in the exercise, are permitted. Any ambiguous abbreviations/shortcuts for otherwise correct structures give deductions of -0.5 pts.



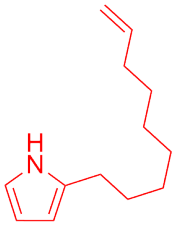
$C_{11}H_{11}NO_2S$
A



$C_{20}H_{25}NO_3S$
B



$C_{22}H_{29}NO_2S_3$
C



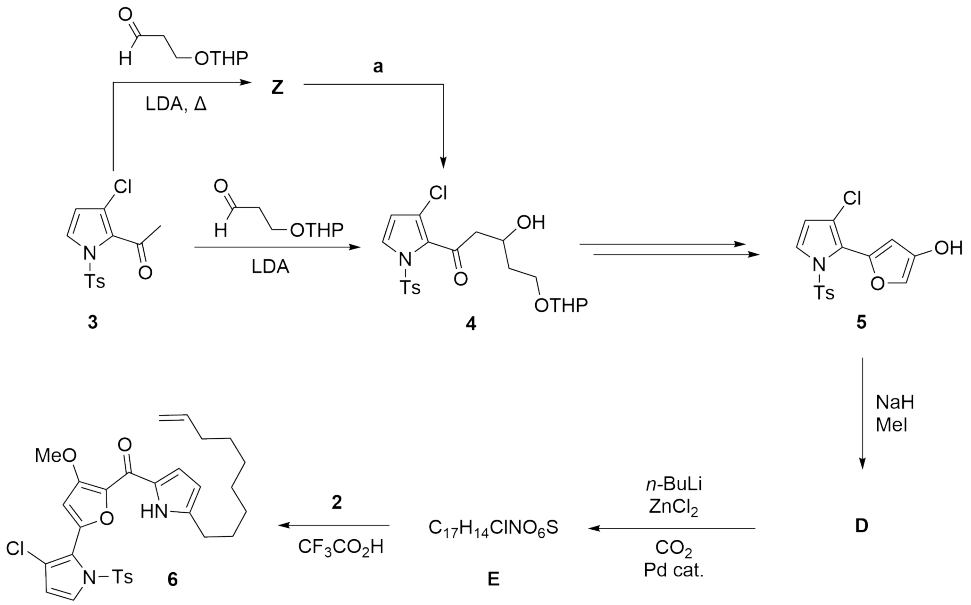
$C_{20}H_{27}NO_2S$
2

1.5 pts for each correct structure. 6.0 pts total.

10.2 **Give** the name of the reaction that is taking place between **A** and **B**. 1.0 pt

SOLUTION:
Friedel-Crafts acylation
1.0 pt total.

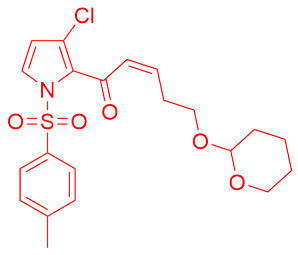
The synthesis then takes the substituted pyrrole **3**, modifies it and finally combines it with fragment **2** to give **6** — the almost complete backbone of roseophilin.



The steps from **3** to **6** explore well-established reagents and employ the use of organozinc reagents, which turn carbon into a powerful nucleophile, akin to Grignard reagents.

10.3 If the reaction from **3** to **4** is heated, a different product (**Z**) is formed. **Draw** the structure of said product. 2.0 pt

SOLUTION:



$C_{21}H_{24}ClNO_5S$

Z

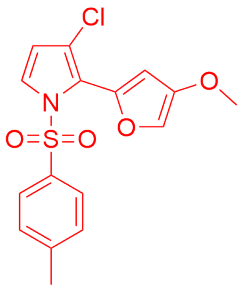
cis- and *trans*-products both permitted
2.0 pts total.

10.4 **Suggest** conditions **a** to convert **Z** into **4**. You may consider the THP group to be stable under reasonable conditions for **a**. 1.0 pt

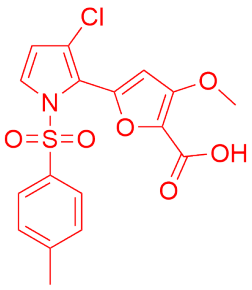
SOLUTION:
Any strong aqueous acid should do.
$H_2SO_4 + H_2O$ for example.
1.0 pt total.

10.5 **Draw** the structures of **D** and **E**. 4.0 pt

SOLUTION:



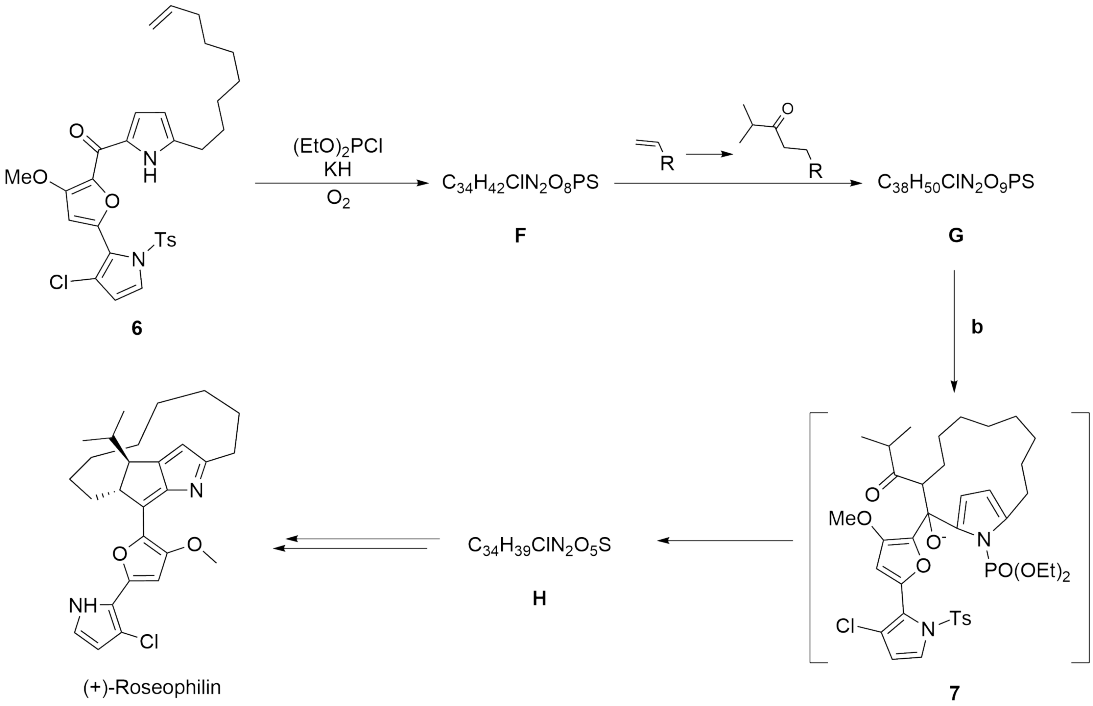
$C_{16}H_{14}ClNO_4S$
D



$C_{17}H_{14}ClNO_6S$
E

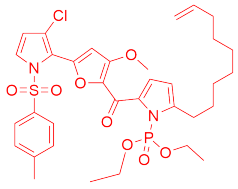
2.0 pts per correct structure. 4.0 pts total.

In the last steps of the total synthesis, **6** is further converted and undergoes an olefin metathesis, going from **F** to **G** (as shown above the arrow). **G** is then treated with **b** to give the intermediate **7**, which reacts to form **H**. In two last steps, (+)-roseophilin is synthesised.

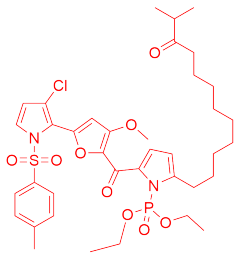

MeO
O
N
H
Ts
N
Cl
6
(EtO)2PCl
KH
O2
C34H42ClN2O8PS
F
R
O
R
C38H50ClN2O9PS
G
b
MeO
O
O-
N
PO(OEt)2
O
Cl
N
Ts
7
C34H39ClN2O5S
H
N
O
O
NH
Cl
(+)-Roseophilin

10.6 **Draw** the structures of **F**, **G** and **H**. 6.0 pt

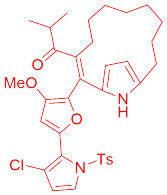
SOLUTION:



$C_{34}H_{42}ClN_2O_8PS$
F



$C_{38}H_{50}ClN_2O_9PS$
G



$C_{34}H_{39}ClN_2O_5S$
H

2.0 pts per correct structure. 6.0 pts total.

10.7 **Select**, for the given reagents, whether or not they are suitable for the conditions under **b**. 3.0 pt

Reagent	Suitable	Not suitable
$NaBH_4$	☐	☐
LDA	☐	☐
MeMgBr	☐	☐
OsO_4	☐	☐
KO^tBu	☐	☐
Ferrocene ($Fe(C_5H_5)_2$)	☐	☐

SOLUTION:

Conditions	Suitable	Not suitable
$NaBH_4$	☐	☒
LDA	☒	☐
MeMgBr	☐	☒
OsO_4	☐	☒
KO^tBu	☒	☐
Ferrocene ($Fe(C_5H_5)_2$)	☐	☒

0.5 pts for each correct tick. 0.0 pts per row, if none or more than one boxes are ticked. 3.0 pts total.

10.8 **Explain**, what the driving force(s) of the reaction from intermediate **7** to **H** is/are. 2.0 pt

SOLUTION:

1. **Enthalpy:** the bond strength of P−O / P=O in the phosphate ester that is cleaved is enormous.
2. **Entropy:** one particle decays into two. $\Delta n > 0$

1.5 pts for the argument of bond stability. 0.5 pts for the argument of entropy. 2.0 pts total.

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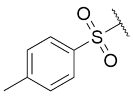
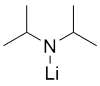
Q10-9

English (Official)



Ts

THP



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