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

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 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

SOLUTION:

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

Tap water is a mixture and not a compound, as many ions are dissolved inside

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

SOLUTION:

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

I. Is described by a chemical reaction: $4\,Fe + 3\,O_2 + 2\,H_2O \longrightarrow 4\,FeOOH$ or $4\,Fe + 3\,O_2 + 6\,H_2O \longrightarrow 4\,Fe(OH)_3$
II. Is described by a chemical reaction: $Fe + 2\,HCl \longrightarrow FeCl_2 + H_2$
III. Is a phase transition -> purely physical
IV. Burning of wood is described by a chemical reaction: $(C_6H_{10}O_5)_n + 6\,nO_2 \longrightarrow 6\,nCO_2 + 5\,nH_2O$
V. Pressurizing a cooking pot consists of evaporization of water and pressure increase due to heat and confined volume -> purely physical

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

SOLUTION:

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

From the periodic table we read $M_{CuSO_4 \cdot 5\,H_2O} \approx 249.7\,g/mol$ and compute from this $n_{CuSO_4 \cdot 5\,H_2O} = m/M \approx 0.020\,mol$. Using Avogadro's number we obtain $1.2 \cdot 10^{22}$ particles which we still have to multiply by 21 atoms/particle to arrive at $2.5 \cdot 10^{23}$ atoms.

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

SOLUTION:

- ☐ 17%
- ☐ 4%
- ☐ 31%
- ☒ 67%

From the periodic table we find the molar mass $M_{C_4H_7OH} = 72.1\,\text{g/mol}$ and $M_{C_4} = 48.04\,\text{g/mol}$. The fraction multiplied by 100% gives $\%w_C \approx 67\%$.

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

SOLUTION:

- ☐ 6
- ☒ 18
- ☐ 12
- ☐ 48

Cd is located in the fifth row in the periodic table, meaning that there are five shells available. The first shell doesn't contain p-electrons, and the fifth shell p-electrons are not filled yet (higher in energy). So the total amount of p-electrons is 18, with 6 from each of the second, third and fourth shell.

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

SOLUTION:

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

As the charge is not provided, it could be any element/ion (ionized, e.g. Na^+).

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

SOLUTION:

- ☐ Kr
- ☒ Br^-
- ☐ Rb^+
- ☐ F^-

With a fixed nuclear charge, the radius grows with the number of electrons. Comparing elements with the same number of electrons, anions have larger radii as the charge of the nucleus is smaller than for the neutral element with the same number of electrons or even the cation.

1.8 Consider the hypothetical equilibrium: 1.5 pt

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

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:

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

SOLUTION:

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

The equilibrium constant is defined as

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

so in our case

$$K_c = \frac{[\mathrm{C}][\mathrm{D}]^{3/2}}{[\mathrm{A}][\mathrm{B}]^2}$$

which means that looking at the reverse reaction inverts the constant: $K_{c,reverse} = \frac{1}{K_c}$. The changed stoichiometry has to be accounted for by squaring it.

1.9 Consider the gas-phase equilibrium: 1.0 pt

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

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

SOLUTION:

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

Using Le Chatelier's principle, we identify the driving force to be the temperature decrease, which is counteracted by the equilibrium shifting towards the reactants (as the forward reaction is endothermic, the backward reaction is exothermic). Looking at the definition

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

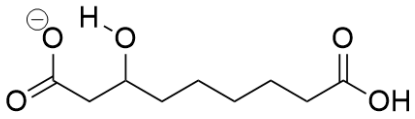
we see that K_c thus must decrease.

Carboxylic, Amino and Lewis acids

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

SOLUTION:

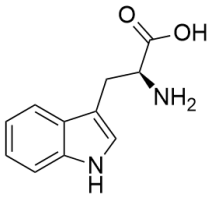
Left carboxyl group is most acidic. This is due to an inductive effective effect from the hydroxy group (electron withdrawing) as well as the stabilisation of the negative charge through a six membered ring with an H bond.



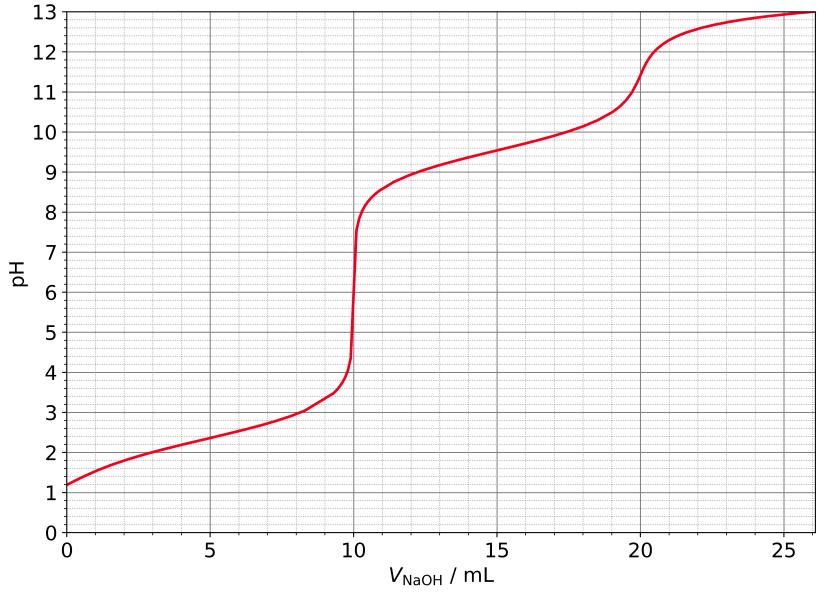
2.0 pt total.

- 1.0 pt for the correct proton
- 1.0 pt for a chemical reasoning

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

SOLUTION:

The pK_a of tryptophan are 2.38 (COOH) and 9.44 (NH_3). Values between 2.2-2.6 and 9.4-9.6 are acceptable :).

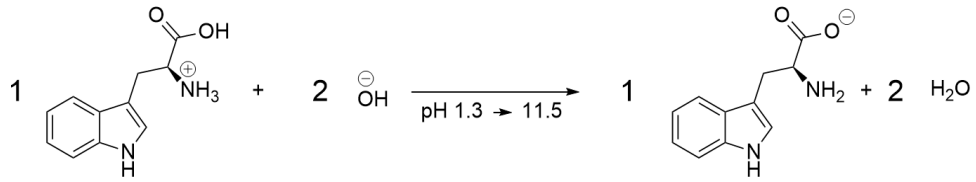
1.0 pt total.

- 0.5 pt per correct value (only numbers were asked, no assignment to the functional groups).

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.

SOLUTION:



2.0 pt total.

- 1.0 pt for the coefficients (0.25 pt per coefficient)
- 1.0 pt for the correct Lewis formula (0.5 pt per box)

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

SOLUTION:

From the titration curve: 20 mL NaOH solution & diprotic

From the text: 1.000 M NaOH solution

$0.02\ \text{L} * 1\ \text{mol L}^{-1} = 0.02\ \text{mol}$ # amout of titrant * concentration of titrant = amount of NaOH

$\frac{0.02\ \text{mol}}{2} = 0.01\ \text{mol} = 10\ \text{mmol}$ # amount of NaOH / 2 (diprotic) = amount of tryptophan

2.0 pt total

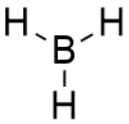
- 1.0 pt for mathematical consideration
- 1.0 pt for result.
- if the division by 2 (diprotic) is missing
  - max 1.0 pt when task 2.3 correct
  - up to 2.0 pt when task 2.3 incorrect ⇒ consistency in their thinking

There exists another acid-base concept by Lewis. A Lewis acid possesses an empty orbital, through which

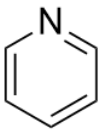
it can accept an electron pair from a Lewis base. A Lewis base possesses a filled orbital (often a lone pair, sometimes a π bond), whose electron pair can be donated to a Lewis acid.

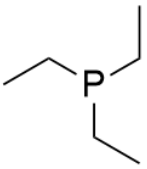
2.5 **Indicate** for the following ions and molecules whether they are Lewis acids or Lewis bases. 3.0 pt

SOLUTION:



Lewis acid	Lewis base	Lewis acid





Lewis acid	Lewis base	Lewis base

3.0 pt total
- 0.5 pt for correct assigned property
- 0.0 pt if multiple answers are given.

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

SOLUTION:

Using $M_{H_2O} = 18\,\text{g/mol}$ we get $n_{H_2O} \approx 2\,\text{mol}$.

0.5 pt for $1.9\,\text{mol} \leqslant n_{H_2O} \leqslant 2.1\,\text{mol}$

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

SOLUTION:

Using the ideal gas equation

$$pV = nRT$$

we get

$$p = \frac{n_{H_2O}RT}{V} = \frac{2\,\text{mol} \cdot 8.3145\,\text{J mol}^{-1}\,\text{K}^{-1} \cdot 393.15\,\text{K}}{0.0063\,\text{m}^3}$$

so

$$p \approx 1\,037\,729\,\text{Pa}$$

1.5 pt for $1'000'000\,\text{Pa} \leqslant p \leqslant 1'050'000\,\text{Pa}$

- 1.0 pt if formula correctly rearranged, but p incorrect (also units)
- 0 pt for just ideal gas equation.

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

SOLUTION:

It is important to note that an over-pressure of $\Delta p_{\text{max}} = 2\,\text{bar}$ means an over-pressure against the ambient pressure that is already $p_0 = 1\,\text{bar}$, so we have to calculate with $p = 3\,\text{bar}$

$$n_{\text{max}} = \frac{pV}{RT} = \frac{3 \times 10^5\,\text{Pa} \cdot 0.0063\,\text{m}^3}{8.3145\,\text{J mol}^{-1}\,\text{K}^{-1} \cdot 398.15\,\text{K}}$$

which yields

$$n_{\text{max}} \approx 0.57\,\text{mol}$$

2 pt for $0.55\,\text{mol} \leqslant n_{\text{max}} \leqslant 0.60\,\text{mol}$

- 0.5 pt if formula correctly rearranged, but n_{max} incorrect (also units)
- 0 pt for only ideal gas law
- -0.5 pt if the over-pressure was not accounted for and the calculation was done for $p = 2\,\text{bar}$

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

SOLUTION:

Using that pressure defines force per area, we get that the force acting on the lid is given by

$$F = p_{\text{explode}} A$$

with the area

$$A = \pi R^2 = 0.01\pi \approx 0.031\,\text{m}^2$$

we get

$$F = 3000\pi \approx 9400\,\text{N}$$

The force acting for $t_{\text{open}} = 0.01\,\text{s}$, leads to an acceleration $a = \frac{F}{m}$ which results in the initial speed of

$$v_{\text{ini}} = t_{\text{open}} \cdot a = t_{\text{open}} \frac{F}{m_{\text{lid}}} = 1\pi \approx 3.1\,\text{m/s}$$

Now, using gravitation, we have to solve the equations

$$v_{\text{ini}} = t_{\text{fly}} \cdot g$$

$$h = v_{\text{ini}} \cdot t_{\text{fly}} - \frac{1}{2} g t_{\text{fly}}^2$$

which yields

$$t_{\text{fly}} = \frac{v_{\text{ini}}}{g} \approx 0.31\,\text{s}$$

and finally (by the second equation above)

$$h \approx 5\,\text{m}$$

Alternatively, after finding v_{ini} one can use energy conservation

$$\frac{1}{2} m v_{\text{ini}}^2 = mgh \Rightarrow h = \frac{1}{2g} v_{\text{ini}}^2$$

4 pt for $4.75\,\text{m} \leqslant h \leqslant 5.25\,\text{m}$, also if found through energy conservation

If partially correct:

- 1 pt for equations of force (with or without correct numerical value)
- +2 pt for equations of initial velocity (with or without correct numerical value)
- +1 pt for equations of height (with or without correct numerical value), either energy conservation or kinematics is fine

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

SOLUTION:

$$C_{31}H_{64} + 47\,O_2 \longrightarrow 31\,CO_2 + 32\,H_2O$$

1 pt

- 0.5 pt if correctly balanced reaction, but wrong products (for example if reacted to $C + H_2$
- 0 pt if coefficients are incorrect

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

SOLUTION:

$$r = k[C_{31}H_{64}]\,[O_2]^{47}$$

From the exponents we read that the reaction proceeds first order with respect to $C_{31}H_{64}$ and 47^{th} order for O_2. The overall order is then 48.
1 pt if consistent with the previous task. Rate law with partial pressures or activities is also correct

- 0.5 pt for rate law expression
- 0.5 pt for the reaction orders (consistent with the rate law), 0 pt if any incorrect

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

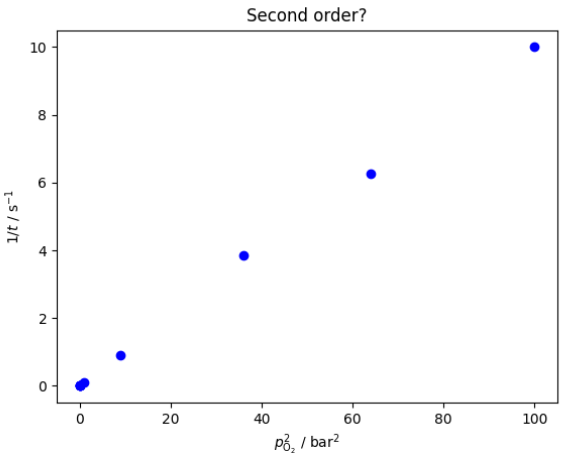
4.3 Judging from the data in the table above, **estimate** the experimental reaction order for O_2 (it's a whole number). 2.0 pt

SOLUTION:

The time required to burn the candle is related to the reaction rate by

$$t \propto \frac{1}{r}$$

Fast students might directly see that they deal with a second order reaction from the first and last data point (decrease of partial pressure by factor 10 leads to decrease of reaction rate by factor 100. Otherwise they can also invert the other data points and get that the reaction is of **second** order.
If they wish, they can also make a plot:



We see a linear dependence -> Second order in the first regime.

2 pt for correct solution
- 1 pt for getting that $r \propto \frac{1}{t}$

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

SOLUTION:

The theoretical reaction order assumes that all molecules are required for the transition state. Looking at the sheer number of O_2 molecules needed, we see that this doesn't make sense and the reaction should proceed stepwise, rather than concerted.
1 pt for finding that all many too many molecules would have to be present in the RDS.
- 0 pt for reasoning with limiting reagents

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

SOLUTION:

This is much more difficult, as we can only consider the wax that is actually in a state where it can react (melted and close enough to the flame). A way to "change its concentration" would be to change the radius of the wick and approximate the concentration of $C_{31}H_{64}$ to be proportional to the area $A = \pi r^2$.

2 pt for a solution that could actually work

- 1 pt for anything other that's reasonable but wouldn't work
- 1 pt if correct solution but also something that wouldn't work

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

SOLUTION:

$2\,Ag^+ + Cd \longrightarrow 2\,Ag + Cd^{2+}$

1 pt only if all correct, 0 pt if wrong way around

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

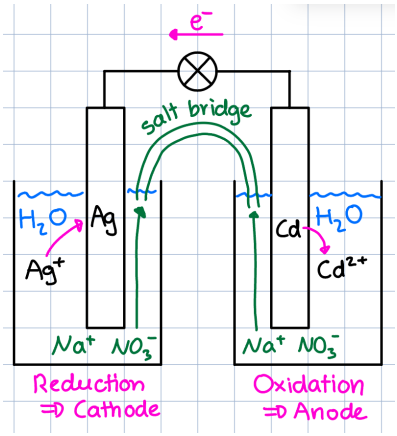
SOLUTION:

$U = E^\circ(Ag/Ag^+) - E^\circ(Cd/Cd^{2+}) = 0.80 + 0.4 = 1.2\,V$

1 pt for correct value (consistent with previous task -> if there reaction wrong way around and the value is negative also award 1 pt)

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

SOLUTION:



1 pt for correct solution
- 0.5 pt for the correct assignment of anode/cathode
- 0.5 pt for the correct electron flow

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

SOLUTION:
- CH_4 : $-IV$
- CO : $+II$
- CO_2 : $+IV$
- HCHO : 0
- HCOOH : $+II$
- HOOCCOOH : $+III$
- CH_3OH : $-II$

0.25 pt for each correct assignment, no punishment if incorrect

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

SOLUTION:

The reactions with a negative standard reduction potential rule out their products ($HOOCCOOH, HCOOH, CO, HCHO$), and the reactants with a positive standard reduction potential rule out their reactants ($C, HCHO, CH_3OH, CO$). This leaves us with CO_2 and CH_4 as possible candidates. Combination of the reactions:

$$\begin{aligned} CO_2 + 2\,H^+ + 2\,e^- &\longrightarrow CO + H_2O & E^\circ &= -0.11\,V \\ CO + 2\,H^+ + 2\,e^- &\longrightarrow C + H_2O & E^\circ &= 0.52\,V \\ C + 4\,H^+ + 4\,e^- &\longrightarrow CH_4 & E^\circ &= 0.13\,V \end{aligned}$$

we get

$$CO_2 + 8\,H^+ + 8\,e^- \longrightarrow CH_4 + 2\,H_2O$$

with a standard reduction potential of $E^\circ_{\text{overall}} = \frac{1}{8}(2 \cdot -0.11 + 2 \cdot 0.52 + 4 \cdot 0.13)\,V = 0.1675\,V \approx 0.17\,V$

This concludes that CH_4 is most stable and thus $-IV$ is the most stable oxidation state for C.

4.0 pt if correct result **with reasoning**

- 1.0 pt for narrowing down to CO_2 **and** CH_4
- 1.0 pt for setting up the total reaction
- 1.0 pt for the calculation (last step)
- 1.0 pt for the final result (consistently with the previous task)
- There is an alternative solution by sketching the Frost diagram or just calculating the n_{E° values for each oxidation state. If applied correctly, full points are awarded too.

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 $1.5\,V$.

SOLUTION:

Overall reaction:

$$CO_2 + 2\,H_2 \longrightarrow CH_4 + O_2$$

To judge whether our cell can provide the potential to drive the reaction, we use the potential from the previous task $E^\circ_{\text{overall}} = 0.1675\,V$ and combine it with the standard reduction potential of the oxygen reduction reaction

$$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O, \quad E^\circ = 1.23\,V$$

we get a potential of $E^\circ_{CO_2,\,\text{red}} = 0.1675 - 1.23\,V \approx -1.06\,V$.

Comparing this with the voltage of the cell ($1.2\,V$), we see that the voltage is enough to drive the reaction.

2.25 pt if everything correct and **reasoned**

- 0.5 pt for the correct overall reaction
- 1.5 pt for the calculation of the cell potential
- 0.25 pt for the conclusion consistently with the result from the second task

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

SOLUTION:

SF_6: octahedral, NO_3^- Trigonal planar, Me_3SiCl Tetrahedral

0.5 pt per correct choice, 0 pt if multiple boxes are checked

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

SOLUTION:

IF_3

IF_5

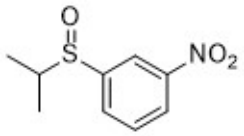
IF_7

0.5 pt for correct sum formula, 0.5 pt for correct structure

0.5 pt for wrong sum formula with corresponding sensible structure

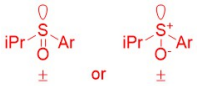
0.5 pt if structure and sum formula dont match, and one of both is correct

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

SOLUTION:
chiral



1 pt for correct structure, 1 pt for correct assignment of chirality
1 pt if a symmetrical structure is drawn and assigned as symmetrical, 0 pt if chiral is chosen and a symmetrical structure is drawn

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

SOLUTION:

From the definition of the solubility product

$$K_s^{CaCO_3} = [Ca^{2+}] \cdot [CO_3^{2-}]$$

and realizing that $[Ca^{2+}] = [CO_3^{2-}]$ we get

$$K_s^{CaCO_3} = [Ca^{2+}]^2 \Rightarrow [Ca^{2+}] = [CO_3^{2-}] = \sqrt{K_s^{CaCO_3}} \approx 2.5 \cdot 10^{-2}\,\text{mol/L}$$

1.0 pt for $0.023\,\text{mol/L} \leqslant c_{Ca^{2+}} = c_{CO_3^{2-}} \leqslant 0.026\,\text{mol/L}$

- 0.5 pt for each concentration (even though they are equal)
- 0.5 pt if $\sqrt{K_s^{CaCO_3}}$ there, but numerical result wrong

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

SOLUTION:

From the definition of the solubility product

$$K_s^{Ag_2CO_3} = [Ag^+]^2 \cdot [CO_3^{2-}]$$

and realizing that $[Ag^+] = 2 \cdot [CO_3^{2-}]$ we get

$$K_s^{Ag_2CO_3} = \frac{1}{2} \cdot [Ag^+]^3 \Rightarrow c_{Ag^+} = \left(4K_s^{Ag_2CO_3}\right)^{1/3} \approx 0.19\,\text{mol/L}$$

and

$$c_{CO_3^{2-}} = \frac{1}{2} c_{Ag^+} \approx 0.096\,\text{mol/L}$$

1.0 pt if $0.17\,\text{mol/L} \leqslant c_{Ag^+} \leqslant 0.21\,\text{mol/L}$ and $0.08\,\text{mol/L} \leqslant c_{CO_3^{2-}} \leqslant 0.11\,\text{mol/L}$

- 0.5 pt for each value
- 0.5 pt if calculation correct, but numerical values wrong
- 0 pt for just definition of solubility product

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

SOLUTION:

In the two saturated solutions we have the individual concentrations

$$[\mathrm{Ag^+}]_1 = [\mathrm{Br^-}]_1 = \sqrt{K_s^{\mathrm{AgBr}}}$$
$$[\mathrm{Ag^+}]_2 = [\mathrm{Cl^-}]_2 = \sqrt{K_s^{\mathrm{AgCl}}}$$

Upon mixing them, the concentration of the anions get divided by two, whereas the cation concentration corresponds to the mean

$$[\mathrm{Ag^+}]_{\mathrm{mix}} = \frac{[\mathrm{Ag^+}]_1 + [\mathrm{Ag^+}]_2}{2} = \frac{\sqrt{K_s^{\mathrm{AgBr}}} + \sqrt{K_s^{\mathrm{AgCl}}}}{2}$$
$$[\mathrm{Br^-}]_{\mathrm{mix}} = \frac{\sqrt{K_s^{\mathrm{AgBr}}}}{2}$$
$$[\mathrm{Cl^-}]_{\mathrm{mix}} = \frac{\sqrt{K_s^{\mathrm{AgCl}}}}{2}$$

To check if there will be precipitation of AgBr (AgCl will not prepipitate, as larger solubility product), we compute the solubility product as

$$[\mathrm{Ag^+}]_{\mathrm{mix}}[\mathrm{Br-}]_{\mathrm{mix}} = \frac{\sqrt{K_s^{\mathrm{AgBr}}} + \sqrt{K_s^{\mathrm{AgCl}}}}{2}\frac{\sqrt{K_s^{\mathrm{AgBr}}}}{2} = \frac{K_s^{\mathrm{AgBr}} + \sqrt{K_s^{\mathrm{AgBr}} K_s^{\mathrm{AgCl}}}}{4} \approx 1.6{\cdot}10^{-5}\ \mathrm{mol^2/L^2}$$

which is larger than K_s^{AgBr}. Thus AgBr will precipitate from the solution.
Analog calculations could be done to find that AgCl will not percipitate from the solution, but this should be clear anyway as it is more soluble.

2 pt for correct conclusion with proper reasoning

- 1 pt if conclusion wrong, but good reasoning
- 1 pt if calculation only done for AgCl and conclusion that it does not precipitate
- 0 pt if no reasoning

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

SOLUTION:

To solve the task, we setup the system of equations:

$$K_s^{CaBr_2} = [Ca^{2+}]\,[Br^-]^2$$
$$K_s^{CaCl_2} = [Ca^{2+}][Cl^-]^2$$
$$\frac{1}{2}[Ca^{2+}] = [Cl^-] + [Br^-]$$

Rearranging the first two equations we get

$$[Br^-] = \sqrt{\frac{K_s^{CaBr_2}}{[Ca^{2+}]}}$$
$$[Cl^-] = \sqrt{\frac{K_s^{CaCl_2}}{[Ca^{2+}]}}$$

and plugging this into the third equation we obtain

$$\sqrt{\frac{K_s^{CaBr_2}}{[Ca^{2+}]}} + \sqrt{\frac{K_s^{CaCl_2}}{[Ca^{2+}]}} = 2[Ca^{2+}]$$

which we need to square to get

$$\frac{K_s^{CaBr_2}}{[Ca^{2+}]} + 2\frac{\sqrt{K_s^{CaBr_2}K_s^{CaCl_2}}}{[Ca^{2+}]} + \frac{K_s^{CaCl_2}}{[Ca^{2+}]} = 4[Ca^{2+}]^2$$

That can then be directly solved as:

$$[Ca^{2+}] = \left[\frac{1}{4}\left(K_s^{CaBr_2} + K_s^{CaCl_2} + 2\sqrt{K_s^{CaBr_2}K_s^{CaCl_2}}\right)\right]^{1/3}$$

and gives

$$c_{Ca^{2+}} \approx 4.73\,\text{mol/L}$$

5 pt for correct result with calculations shown

- 0.5 pt for each of the initial equations (totals to 1.5 pt)
- 0.5 pt for each of the expressions for $[Br^-], [Cl^-]$ (totals to 1.0 pt)
- 1.0 pt for putting everything together
- 1.0 pt for the final analytical expression
- 0.5 pt for $4.6\,\text{mol/L} \leqslant c_{Ca^{2+}} \leqslant 4.9\,\text{mol/L}$

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

SOLUTION:

$$\frac{3}{2}H_2 + \frac{1}{2}N_2 \rightleftharpoons 1\ NH_3$$

1 pt for reaction equation, also if not with equilibrium arrows ($\rightleftharpoons$)

- 0 pt if not with coefficient 1 for ammonia

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

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

SOLUTION:

☐ Endothermic
☒ Exothermic
☐ Neither of the above

1.0 pt for correct answer

- 0 pt for multiple answers or wrong answer

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

SOLUTION:

- Two molecules of gas are consumed. High pressure is required to push the equilibrium to the right side (and increase the reaction rate).
- The high temperature is applied for purely kinetic reason: It would simply take too long for the equilibrium to set at room temperature. (Extra, not required: The need for high temperature is mainly accounted for by the strong N≡N bond that needs to be broken).

2.0 pt for both arguments

- 1 pt for identifying that net gas particles are lost and thus higher pressure is required to shift the equilibrium to the right
- 1 pt for identifying high temperature pushing the reaction rate

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

SOLUTION:

$$\Delta G = \Delta H - T\Delta S = -46\,\text{kJ/mol} - 673.15\,\text{K} \cdot -124\,\text{J/(mol K)} \approx +37\,\text{kJ/mol}\,NH_3$$

1 pt for $37\,\text{kJ/mol} \leqslant \Delta G \leqslant 38\,\text{kJ/mol}\,NH_3$

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

SOLUTION:

We have $\Delta G = -RT\ln(K_c)$ on the formula sheet, which can be rearranged to

$K_p = K_c = e^{-\frac{\Delta G}{RT}} \approx 1.2{\cdot}10^{-3}$, for $\Delta G = 37\,\text{kJ/mol}$ or $2.8{\cdot}10^{-2}$ for $\Delta G = 20\,\text{kJ/mol}$

2 pt for $1.1 \cdot 10^{-3} \leqslant \Delta G \leqslant 1.3 \cdot 10^{-3}$ or $2.7 \cdot 10^{-2} \leqslant \Delta G \leqslant 2.9 \cdot 10^{-2}$

- 1 pt if algebraic calculation correct but numerical result wrong

8.6 Given initial pressures of $p^{\text{ini}}_{\text{H}_2} = 150$ bar and $p^{\text{ini}}_{\text{N}_2} = 50$ 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.

SOLUTION:

The equilibrium pressures are given as (derived from the reaction equation):

$$p_{\text{H}_2} = p^{\text{ini}}_{\text{H}_2} - \frac{3}{2} p_{\text{NH}_3}$$

$$p_{\text{N}_2} = p^{\text{ini}}_{\text{N}_2} - \frac{1}{2} p_{\text{NH}_3}$$

The equilibrium constant in terms of pressure reads

$$K_p = \frac{p_{\text{NH}_3}}{p^{3/2}_{\text{H}_2} p^{1/2}_{\text{N}_2}}$$

and can be rearranged to

$$p^2_{\text{NH}_3} = p^3_{\text{H}_2} p_{\text{N}_2} K_p^2$$

into which we can insert the equilibrium pressures of the starting materials to get

$$p^2_{\text{NH}_3} = \left(p^{\text{ini}}_{\text{H}_2} - \frac{3}{2} p_{\text{NH}_3}\right)^3 \left(p^{\text{ini}}_{\text{N}_2} - \frac{1}{2} p_{\text{NH}_3}\right) K_p^2$$

Expansion and rearrangement yields the fourth order equation

$$\frac{p^2_{\text{NH}_3}}{K_p^2} = \left(p^{\text{ini}}_{\text{H}_2} - \frac{3}{2} p_{\text{NH}_3}\right)^3 \left(p^{\text{ini}}_{\text{N}_2} - \frac{1}{2} p_{\text{NH}_3}\right)$$

$$\frac{p^2_{\text{NH}_3}}{K_p^2} = \left((p^{\text{ini}}_{\text{H}_2})^3 - \frac{9}{2}(p^{\text{ini}}_{\text{H}_2})^2 p_{\text{NH}_3} + \frac{27}{4} p^{\text{ini}}_{\text{H}_2} p^2_{\text{NH}_3} - \frac{27}{8} p^3_{\text{NH}_3}\right) \left(p^{\text{ini}}_{\text{N}_2} - \frac{p_{\text{NH}_3}}{2} p_{\text{NH}_3}\right)$$

$$\frac{p^2_{\text{NH}_3}}{K_p^2} = (p^{\text{ini}}_{\text{H}_2})^3 p^{\text{ini}}_{\text{N}_2} - \frac{1}{2}\left((p^{\text{ini}}_{\text{H}_2})^3 + 9(p^{\text{ini}}_{\text{H}_2})^2 p^{\text{ini}}_{\text{N}_2}\right) + \frac{9 p^2_{\text{NH}_3}}{4}\left((p^{\text{ini}}_{\text{H}_2})^2 + 3 p^{\text{ini}}_{\text{H}_2} p^{\text{ini}}_{\text{N}_2}\right) - \frac{27 p^3_{\text{NH}_3}}{8}\left(p^{\text{ini}}_{\text{H}_2} - p^{\text{ini}}_{\text{N}_2}\right) + \frac{27 p^4_{\text{NH}_3}}{16}$$

And finally

$$\frac{27}{16} p^4_{\text{NH}_3} - \frac{27}{8}\left(p^{\text{ini}}_{\text{H}_2} - p^{\text{ini}}_{\text{N}_2}\right) p^3_{\text{NH}_3} + \frac{9}{4}\left((p^{\text{ini}}_{\text{H}_2})^2 + 3 p^{\text{ini}}_{\text{H}_2} p^{\text{ini}}_{\text{N}_2} - K_p^2\right) p^2_{\text{NH}_3} - \frac{1}{2}\left((p^{\text{ini}}_{\text{H}_2})^3 + 9(p^{\text{ini}}_{\text{H}_2})^2 p^{\text{ini}}_{\text{N}_2}\right) p_{\text{NH}_3} + (p^{\text{ini}}_{\text{H}_2})^3 p^{\text{ini}}_{\text{N}_2} = 0$$

SOLUTION continued:

4 pt for a correct solution
- 1 pt for expressions of equilibrium pressures in terms of initial pressures
- 1 pt for the correct definition of K_p
- 1 pt for inserting the values correctly and setting up the equation that needs to be rearranged
- 1 pt for the rearrangement to the final equation

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

SOLUTION:

As the reactants were added in stoichiometric amounts, the yield is given by

$$\text{yield} = \frac{p_{NH_3}}{2p^{ini}_{N_2}} \cdot 100\% = \frac{p_{NH_3}}{\text{bar}}\%$$

with whatever result for p_{NH_3} was obtained in the previous task (for example with the given intermediate result $p_{NH_3} = 0.01$ bar the yield would be 0.01%.

1 pt for the correct numerical solution

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

SOLUTION:

Suggested solutions:
- Extract the product from the reaction mixture or recycle the crude mixture from the reactor
- Lower the temperature to increase the equilibrium constant
- N_2 is practically free -> Excess over H_2 (doesn't increase the yield but is economically friendly)

2 pt max, 1 pt for each reasonable solution

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

Q9-1

English (Official)

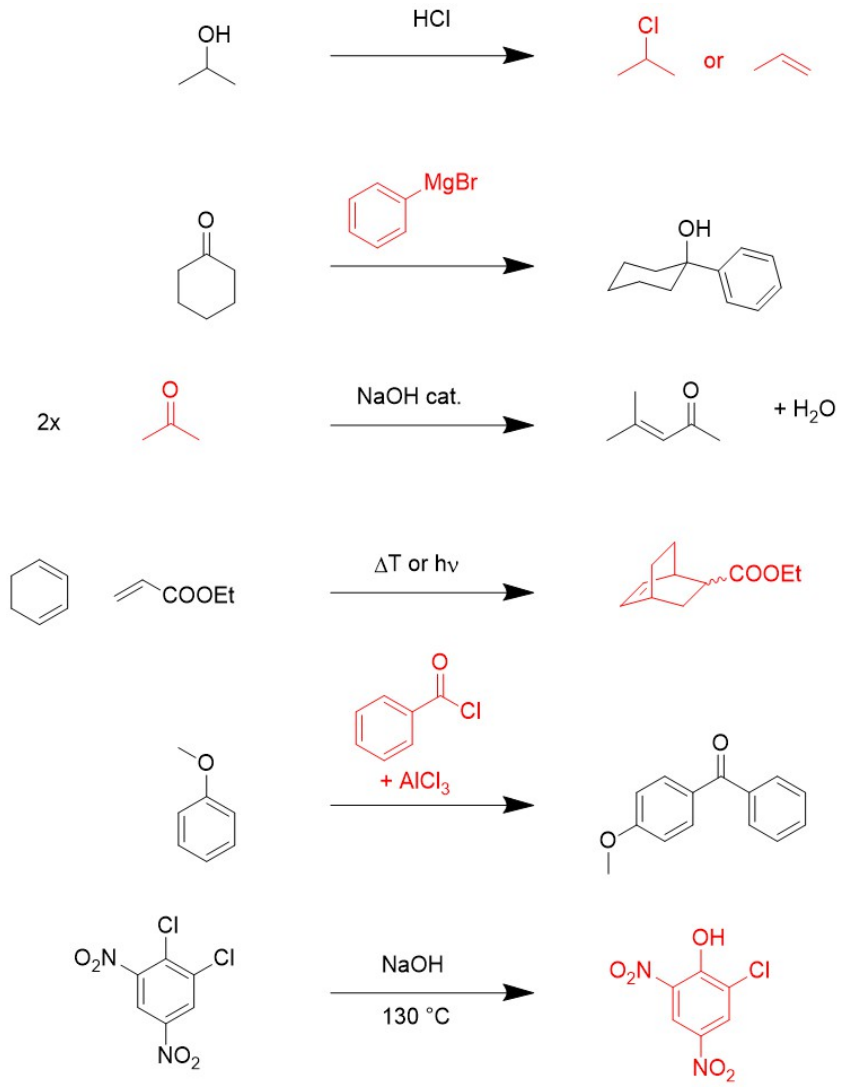
Reactions in Organic Chemistry

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

9.1b 3 pt

SOLUTION:

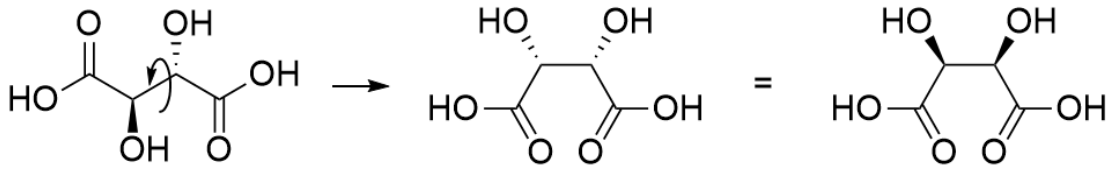


1 pt per answer. -0.5 per simple error in other wise correct structure, -0.5 for minor isomers

A & B 0.5 pt each, 0 pt if 'enantiomers' of iPrCl are given

"Hidden Achirality"

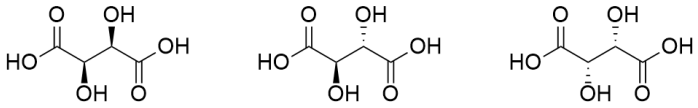
While we often think of every molecule with stereocenters as chiral, not all of them are. The exception are so called *meso*-molecules, which possess an even number of stereocenters, while being achiral. This happens when the molecule has a confomer with a mirror plane, which annilates the chirality. 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

SOLUTION:



2.5 pt
- 0.25 pt per correct marked & assigned stereocenter
- 1.0 pt for the drawing of the missing stereoisomer

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

SOLUTION:

The composition is calculated through the proportion of the angles.

1. Example

Difference of the angles = 25.4 °

The measured angle is $|\pm 12.7° | \mp 3.8°$ = 16.5°/8.9°

Proportion D-(−) $= \frac{16.5}{25.4} = 0.6496 = 65\%$

Proportion L-(+) $= \frac{8.9}{25.4} = 0.3504 = 35\%$

2.0 pt total

- 1.0 pt for correct result ±5% tolerance with logical mathematical reasoning
- 1.0 pt for mathematical resoning

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

SOLUTION:

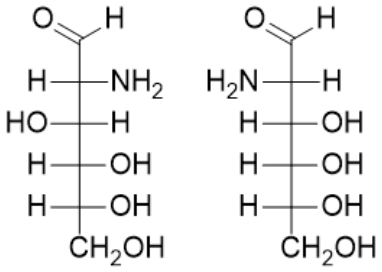
Friend C / about −12° is correct. The specific rotation of the two compunds does not influence eachother. (Despite this it can not be exactly predicted, as is depends one many factors such as concentration, measured distance, temperature...).

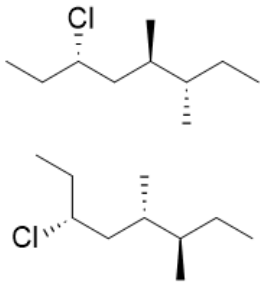
1.0 pt total

- 0.5 pt for stating Friend C /−12° is correct
- 0.5 pt for a conclusive reason

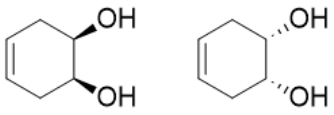
10.4 **Determine** if the following molecules are diastereoisomers, enantiomers or identical. 2.0 pt

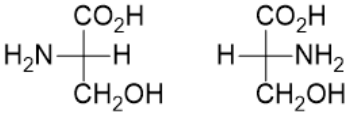
SOLUTION:





Diastereomers	Enantiomers





Identical	Enantiomers

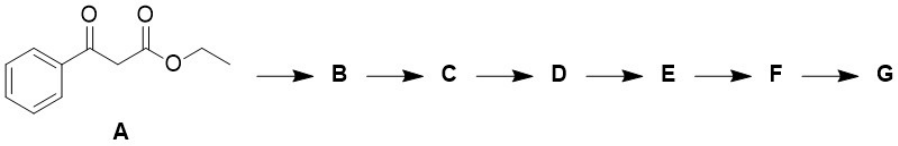
2.0 pt

- 0.5 pt per correct assigned molecule pair
- 0.0 pt if multiple answers are given

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. 0.0 pt

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.

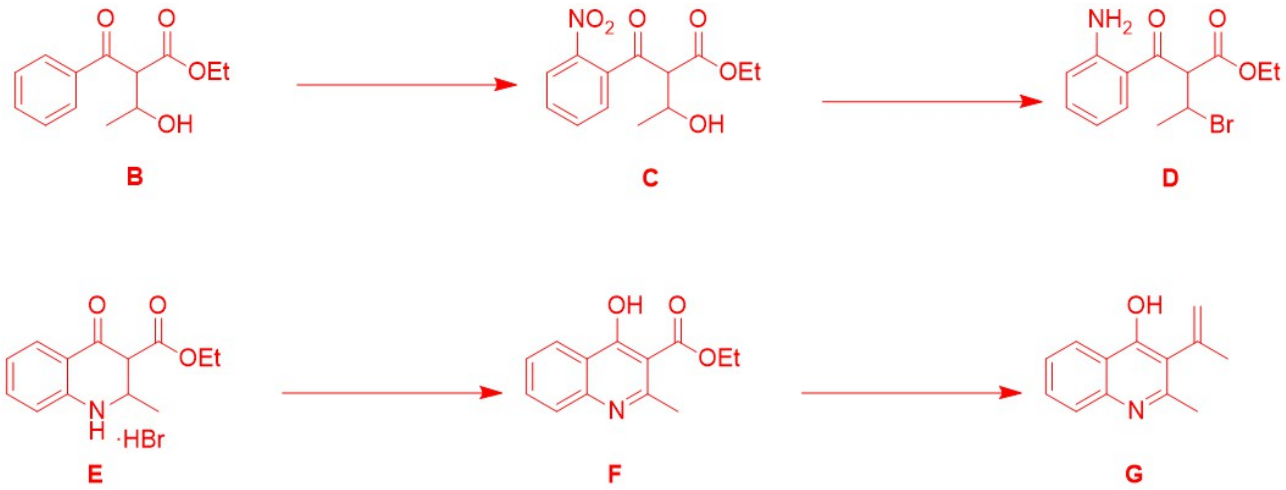


This is molecule **A**. It was reacted with NaH, leading to an aliphatic, carboanion intermediate, which in turn was reacted with acetaldehyde (ethanal) to yield the corresponding alcohol **B**, after mild acidic workup. A nitro group is then introduced in 2 position on the aromatic ring to give compound **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

11.1b 6 pt

SOLUTION:



1.5 pt for each step. -0.5 pt for each simple mistake, max 1 pt for wrong, but chemically sensible products.

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

SOLUTION:

$pK_a = -\log(K_a) = -\log(\frac{[H^+]\cdot[A^-]}{[HA]})$

$K_a = \frac{(4\cdot10^{-4})\cdot(3\cdot10^{-5})}{1.2\cdot10^{-1}} = 1.0 \cdot 10^{-7}$

$pK_a = -\log(1.0 \cdot 10^{-7}) = 7$

2.0 pt total

- 0.5 pt for K_a
- 0.5 pt for pK_a
- 1.0 pt for formula and its application.

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

SOLUTION:

Hydrogen chalkogenides get more acidic in further/higher periods. This is due to

- less electronegativity
- increased size
- longer bonds
- weaker bonds
- charge is "distributed" in a larger sphere -> stabilized

Stating that O, S, Se and Te are within the same group in the periodic table is not enough by itself. Some "chemical understanding" is necessary.

1.0 pt total

- 0.5 pt for naming the trend
- 0.5 pt for one sensible reason

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_a 12.3). 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

SOLUTION:

0.02 mol in 1 L = 0.02 mol L^{-1} = 0.02 M

$pH = pK_a + \log(\frac{[A^-]}{[HA]})$

$pH - pK_a = \log(\frac{[A^-]}{[HA]})$

$10^{pH-pK_a} = \frac{[A^-]}{[HA]}$

$10^{pH-pK_a} \cdot [HA] = [A^-]$

$[A^-] = 10^{0.6} \cdot 0.02\ M = 3.98 \cdot 0.02\ M = 0.0796\ M = 0.08\ M$

$0.08\ mol \cdot (2 \cdot 23 + 1 + 31 + 4 \cdot 16)\ g\ mol^{-1} = 0.08\ mol \cdot 142\ g\ mol^{-1} = 11.36\ g$

3.0 pt total

- 1.0 pt for result in mol
- 0.5 pt for result in g
- 1.0 pt for calculations until mol
- 0.5 for the conversion calculation to g

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

SOLUTION:

The buffer is more stable towards acids than bases. This is because it is on the basic side (pH 7.8) of the respective pK_a (7.2). The buffer tolerates a larger amount of an acid than a base.

1.0 pt total

- 0.5 pt for the statement acids
- 0.5 pt for the explanation.

SwissChO Central Exam 2025

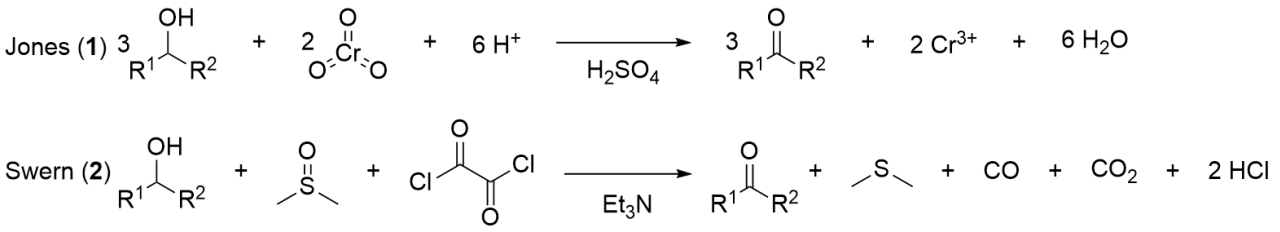
CHEMISTRY.
OLYMPIAD.CH
CHEMIE-OLYMPIADE
OLYMPIADES DE CHIMIE
OLIMPIADI DELLA CHIMICA

Q13-1

English (Official)

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

SOLUTION:

$\Delta_r H^0$ = the weighed sum of the enthalpies of formation of the reactants & products

$\Delta_r H^0 = ([-(3 \cdot -318 + 2 \cdot -587 + 6 * 73) + (3 \cdot -248 + 2 \cdot -167 + 6 \cdot -286)]/3)$ kJ mol^{-1}

$\Delta_r H^0 = [-(-1690 \text{ kJ mol}^{-1}) + (-2794 \text{ kJ mol}^{-1})]/3$

$\Delta_r H^0 = [-1104 \text{ kJ mol}^{-1}]/3$

$\Delta_r H^0 = -368 \text{ kJ mol}^{-1}$

2.0 pt total

- 1.0 pt for mathematical reasoning
- 1.0 pt for correct numerical result.
- 0.5 pt for the result -1104 kJ mol^{-1} if the last step is missing (question about 1 mole alcohol, not three)

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

SOLUTION:

$\Delta_r S^0 =$ the weighed sum of the entropies of the reactants & the products

$\Delta_r S^0 = ([-(3 \cdot 181 + 2 \cdot 587 + 6 \cdot (-25)) + (2 \cdot (-113) + 3 \cdot 200 + 6 \cdot 70)]/3)$ J mol^{-1} K^{-1}

$\Delta_r S^0 = ([-539 + 794]/3)$ J mol^{-1} K^{-1}

$\Delta_r S^0 = (255/3)$ J mol^{-1} K^{-1}

$\Delta_r S^0 = 85$ J mol^{-1} K^{-1}

2.0 pt total
- 1.0 pt for mathematical reasoning
- 1.0 pt for correct numerical result
- 0.5 pt for the result 255 kJ mol^{-1} K^{-1} if the last step is missing (question about 1 mole alcohol, not three)

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 alcohol 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 alcohol at -60°C. 2.0 pt

SOLUTION:

$\Delta G = \Delta H - T\Delta S$

$T = -60$°C $= 213$ K

$\Delta G = -112$ kJ mol$^{-1} - (213$ K $\cdot 0.523$ kJ mol^{-1}K$^{-1})$

$\Delta G = -223$ kJ

2.0 pt total
- 1.0 pt for mathematical reasoning/formula
- 1.0 pt for numerical result

	$\Delta_r H^0$/ 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

SOLUTION:

The reaction entropy ($\Delta_r S$) of the Swern oxidation is way larger than the reaction entropy of the Jones reaction. This has two obvious reasons

- During the Swern oxidation 2 equivalents of gas are formed, which have a high entropy and drive the reaction
- The Jones reaction pays a high entropy prize during the solvatisation of Cr^{3+}.

1.0 pt total

- 0.5 pt per named reason (max. two reasons)

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

SOLUTION:

2.0 pt total

- 1.0 pt for stating the reaction is very exothermic and its excess energy can facilitate its completion
- 1.0 pt for stating that this excess energy can cause a problem (side reactions, needs cooling...)

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

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

SOLUTION:

Both can be correct with the corresponding reasoning:

Reasons for Swern reaction (**2**):

- Chromium is toxic (to work with & to clean the product) & expensive
- Jones is very unselective (primary alcohol/aldehyde -> carboxylic acid) -> overoxidation

Reasons for Jones reaction (**1**):

- Dimethyl sulfide (C_2H_6S) stinks
- Swern forms lots of gases (CO and CO_2)

Other reasons are allowed.

1.0 pt total

- 1.0 pt for statement with corresponding reason
- 0.5 pt for a mismatch between statement & reason

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

SOLUTION:
Reaction order

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

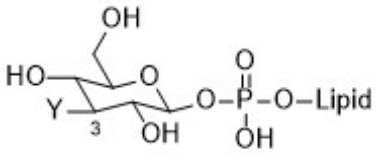
Conclusion

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

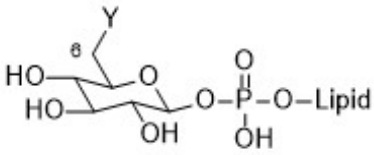
0.5 pt for correkt order,
1 pt for correct choice of conclusion

if order 2 is chosen, both at once is correct conclusion, 1 pt overall for that combination

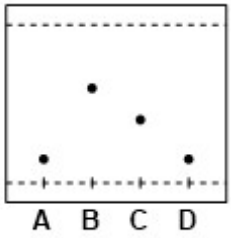
In a second experiment, compounds **C** or **D** were subjected *separately* to conditions that usually work to turn **A** to **B**, using **ALG**. **C** and **D** both were chemically modified so that **ALG** still accepts it as substrate, but cannot attach a mannose in 3 or 6 position respectively.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

SOLUTION:

☐ $--N_3$ ☒ --F ☐ --SMe ☐ --I

1 pt for correct, and only correct

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

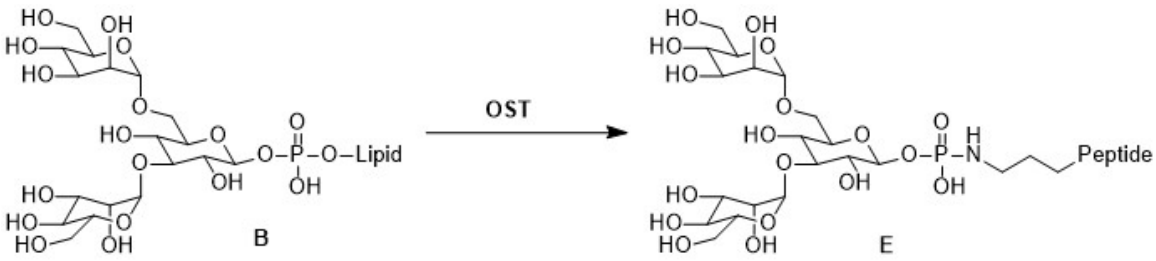
☐ The experiment failed - no conclusion
☐ Both mannose units can be added independent of eachother
☐ A mannose has to be added first at the 3-OH
☐ A mannose has to be added first at the 6-OH

SOLUTION:

☐ 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

1 pt for correct, and only correct

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

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

SOLUTION:

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

1 pt for correct result, 0.5 pt if the element, but no isotope is given

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

SOLUTION:

${}^{32}P \longrightarrow {}^{32}S^{+} + e^{-}$

1 pt for correct reaction, 0.5 for something else that is wrong, but consistent or the correct element without isotope. The electron anti-neutrino can well be ignored.

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

_____%

SOLUTION:

3.39 GBq/mL at the start

$3.39\ GBq/mL\ e^{\frac{ln(2)}{14.3days}\cdot 1day} = 3.23\ GBq/mL$ after 24 h

$2.53\ GBq/mL / 3.23\ GBq/mL = 78\%$ residual activity

$100 - 78 = 22\%$ conversion.

1 pt for corect manipulation of reactivity, 0.5 pt for realising that the conversion is 100 minus the calculated activity