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General Information

Instructions

- You have three hours to solve the problems.
- Write all calculations and everything else 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 legible answers written **on the question sheets** can be considered. You may use the back page if you require more space. Indicate this in the respective answer box.
- This exam has **9** problems.

Viel Erfolg!

Bonne chance!

Buona fortuna!

Good luck!

Theoretical Final Exam 2025

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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	$R = 8.314\,462\,\mathrm{J\,mol^{-1}\,K^{-1}}$
Atomic mass unit	$u = 1.660\,539\,066\,60 \times 10^{-27}\ \mathrm{kg}$
Proton mass	$m_{p^+} = 1.672\,621\,923\,69 \times 10^{-27}\ \mathrm{kg}$
Neutron mass	$m_{n^0} = 1.674\,927\,498\,04 \times 10^{-27}\ \mathrm{kg}$
Electron mass	$m_{e^-} = 9.109 \times 10^{-31}\ \mathrm{kg}$
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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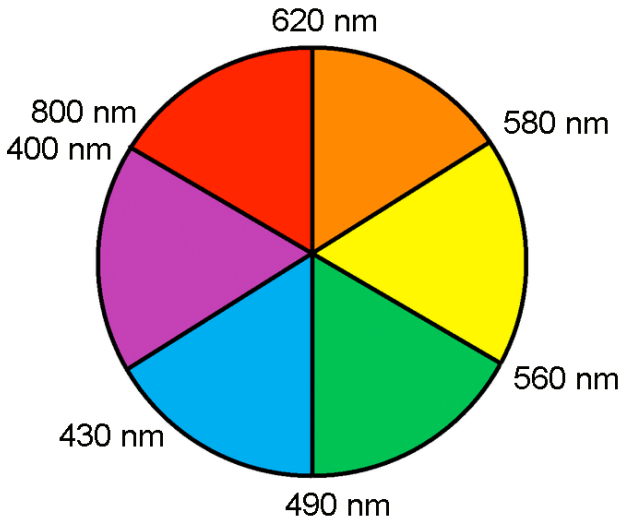
Formulae and Equations

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	$Q = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$
Relationship between 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	$\mathrm{pH} = \mathrm{pK}_a + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$
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	$V = \frac{4\pi}{3}R^3$

For calculations 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 the task, consider all gases ideal throughout this exam.



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

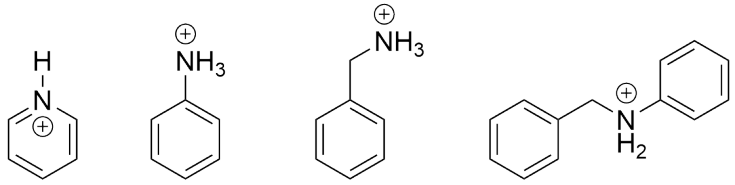
Name of participant: _____

Problem	Title	Maximum Points	Achieved Points	Tasks
Q1	On the Purification of Amines	17.5 pt		6
Q2	Perovskite Solar Cells	16.5 pt		8
Q3	Simple Complexes and Metallocenes	15.0 pt		9
Q4	Dating Fossile Bones Through Kinetics of Amino Acid Racemisation	20.0 pt		9
Q5	Boxes for Electrons	21.0 pt		10
Q6	Thermal Contraction of Rubber	16.0 pt		9
Q7	Carbocation Intermediate	20.5 pt		10
Q8	Can You See Me?	19.5 pt		14
Q9	Landiolol - a Cardioselective Beta-Blocker	16.0 pt		12
Total		163.5 pt		87

On the Purification of Amines

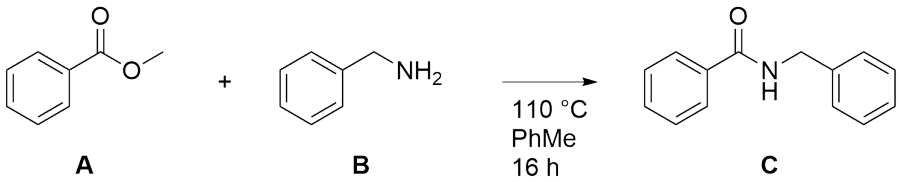
17.5 pts

Amines are ubiquitous in chemistry. Therefore, a tremendous amount of research has been done surrounding this class of compound. They are however known to be quite challenging to purify. They can act as acids and bases of various strength. This both offers opportunities and challenges to the synthetic chemist, who invariably develops a very strong and vocal opinion on amines after only a few experiments.



pK_a	5.2	4.6	9.3	3.8

Here are the pK_a values of some amines. For this problem, the effects of substituents on the rings upon the pK_a may be neglected.



A **B** **C**

Consider the reaction shown above, where 1 mol of **A** and 4 mol of **B** are mixed to obtain **C** . After the reaction appeared to be complete, the warm organic phase was washed *three times* with 1 L of 1 mol L^{-1} HCl solution each time. Then the aqueous phases were combined.

1.1 **Calculate** the pH of the combined aqueous phases. 3.0 pt

You may assume the following: The product **C** does not enter the aqueous phase, while all unreacted **B** did so. The reaction yield was 100%.

SOLUTION:

Effectively, the aqueous phase is a 1M solution of benzylamine HCl salt.

$10^{-pK_A} = K_A = 5.011 \cdot 10^{-10}$

$K_A = \frac{[H_3O^+] \cdot [RNH_2]}{[RNH_3^+]}$ which simplifies to $K_A = [H_3O^+]^2$

From this: $pH = -\log(\sqrt{5.011 \cdot 10^{-10}}) = 4.650$

3 pt maximum: 1 pt for the relationship between pK_a and K_a, 1 pt for the definition of K_a and 1 pt for the correct pH value

0.5 pt may be awarded if e.g. pH=pKa-log(conc) is used and the correct numbers used, a further 0.5 pt if a comment is added that the result cannot be correct

1.2 You find the pH in the combined aqueous phases to be 8.53. **Calculate** the yield of the reaction in %. 3.0 pt

You may assume the following: The product **C** does not enter the aqueous phase, while all unreacted **B** does.

SOLUTION:

The problem requires the Henderson-Hasselbalch equation to be solved:

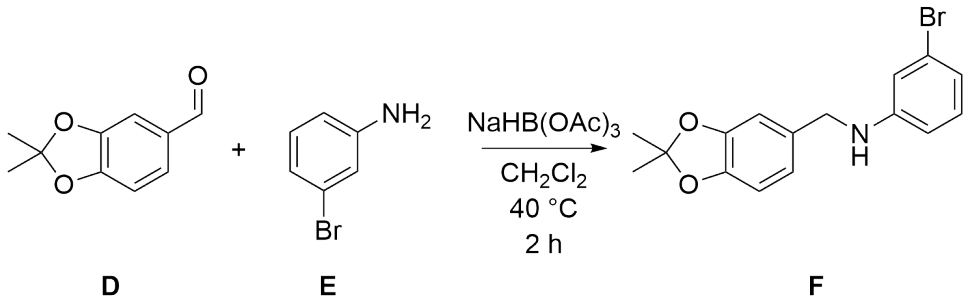
$$pH = pK_A - \log \frac{HA}{A^-}$$

so $8.53 = 9.30 - \log(x)$ to $x = 5.89$

There will be 3 mol or 1 mol / l of protonated species so $\frac{3}{5.89} = 0.51$

0.51 mol of benzylamine dissolved in water, giving a **yield of 49%.**

3 pt maximum: 1 pt for stating the HH equation, 1 pt for solving it and 1 pt for normalizing to get the final result



D **E** **F**

We now turn our attention to the above reaction between 125 mmol of **D** and 200 mmol of **E** to yield **F**.

For purification of the product **F**, it was decided to extract the organic phase with a buffer solution of *formic acid* (HCOOH, pK_a = 3.80) and its sodium salt (HCOONa). A buffer was prepared so that the pH = 4.20. The aim of this is to limit the amount of **F** being washed away in its protonated form, while maximising the amount of **E** removed from the reaction mixture.

1.3 **Calculate** the maximal yield and purity of **F** that is isolated after one extraction. 3.0 pt

SOLUTION:

For 100% yield, there will be 75 mmol of **E** and 125 of **F** in solution.
pK_a for **E** is 4.60, for **F** is 3.90
at 4.25, ca 69% of **E** and 31% of **F** get protonated
$0.69 \cdot 75\ mmol = 51.8\ mmol$ **E** plus $0.33 \cdot 125\ mmol = 38.8\ mmol$ of **F** dissolve
Thus, 125-38.8 = 86.2 mmol F stay in the organic phase, $\frac{86.2}{125} = 0.69$
Yield: 69% of theory
75 -51.8 = 23.2 mmol of **E**, $\frac{86.2}{23.2+86.2} = 0.79$
Purity = 79 mol%

3 pt, 1 pt each for each Henderson Hasselbach equation, leading to a correct HA/A or other value derived therefrom
0.5 pt for each purity and yield calculation

1.4 **Calculate** the minimum amount of formate species n_{HCOOH}, n_{HCOONa} in mmol in the buffer required so that the pH does not deviate more than 0.05 units from 4.20 during workup. 5.0 pt

You may assume the following: 100% yield. All protonated species will enter the aqueous phase without affecting the protonation equilibrium. $NaHB(OAc)_3$ and its reaction products can be ignored.

SOLUTION:

In the buffer: at pH 4.20, $\frac{HA}{A} = 0.4$, at pH 4.25, $\frac{HA}{A} = 0.35$
from $\frac{0.4}{1.4} - \frac{0.35}{1.35} = 0.026$ we get that only 2.6% (exact value $\frac{5}{189}$) of the buffer may get deprotonated.
For 100% yield, there will be 75 mmol of **E** and 125 of **F** in solution.
pK_a for **E** is 4.60, for **F** is 3.90
at 4.25, ca 69% of **E** and 31% of **F** get protonated
$0.69 \cdot 75\ mmol = 51.8\ mmol$ **E** plus $0.33 \cdot 125\ mmol = 38.8\ mmol$ of **F** dissolve
$51.8 + 38.8 = 90.6\ mmol$
$90.6\ mmol / \frac{5}{189} = 3424.7\ mmol$
3424 mmol of formate is required in total
at pH 4.25, HA/A of the buffer is 0.35
3424.7/1.35= 2536.8
2536.8 * 0.4 = **887.9 mmol HCOOH**
2536.8* 1 = **2536.8 mmol HCOONa**
5 pt, 1 point each for the amount of dissolved **E**/**F** (can be taken from above)
1 pt for determination of total buffer strength
1 pt each for correct conversion into species

The solution of **F** is then concentrated so that a concentration of 0.8 mol L^{-1} is established. Then, a stream of H_2S is passed through the solution until it was saturated. The solubility of H_2S is 0.58 mol L^{-1}. After stirring for a few hours, beautiful translucent crystals start forming. The crystals are **F** · H_2S with a solubility constant K_S = 0.256 mol^2 L^{-2}.

1.5 **Calculate** the yield of this crystalization process. 2.0 pt
You may assume the following: the solubility of H_2S includes H_2S and its deprotonated forms.
SOLUTION:
K_L=0.256, [F]=0.80 mol / l, [H_2S] = 0.58 mol / l
the pKa of H_2S is irrelevant, the precipitation drives the equilibrium
0.256 = [F][H2S], while $\frac{F}{H_2S} = \frac{0.8}{0.58} = 1.38$
thus $K_L = [F] \cdot \frac{[F]}{1.38}$ solves to $0.256 = 0.725 \cdot [F]^2$
where $[F] = 0.59$ mol / l
$\frac{0.59}{0.80} = 0.74$, or 74% stay in solution, **26% yield**
3 pt maximum.
1 pt for stating correct equilibrium. without solvent, precipitate
1 pt for correct numerical result and mathematical manipulation

1.6 **Calculate** how many times the above procedure must be repeated to isolate at least 80% of all **F** initially contained in the solution. Each repetition consists of adjusting the concentration followed by the introduction of H_2S. 1.5 pt
Note: *If you obtained no result in the above task, you may assume a theoretical yield of 40% for the crystallisation.*
SOLUTION:
Simple taks of solving $0.2 = 0.74^x$ for x, which yields x=5.3, hence **6 repetitions**.
2 pt, 1 pt for sensible mathematics treatment of the problem, 0.5 pt for correct result if in keeping with the previous task.

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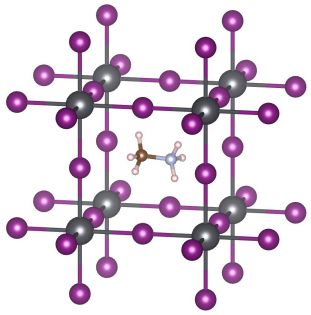
Perovskite Solar Cells — 16.5 pts

Perovskite solar cells are thin-film photovoltaic devices utilizing perovskite materials for efficient sunlight-to-electricity conversion. Methylammonium Lead Iodide ($MAPbI_3$, MA = $CH_3NH_3^+$) is a key material in this context, valued for its high efficiency and cost-effectiveness. Its ideal band gap for photovoltaic applications, strong light absorption, and efficient charge transport make it widely used in achieving high-performance solar cells.

Unit Cell

2.1 Below, you find a structural representation of $MaPbI_3$. **Assign** the Lead (Pb) and the Iodine (I) atoms as either the gray or purple atom. 2.0 pt



Structural representation of $MAPbI_3$.

Explain your reasoning.

SOLUTION:

Purple: Iodine
Gray: Lead
Reasoning: Each MA is surrounded by corner sharing PbI_6 octahedra which results in Iodine being purple and Lead being gray.
Purple: Iodine 0.5 pt and Gray: Lead 0.5 pt. Either 1 pt for correct assignment of both or 0.5 pt if only one was chosen (it is a 50:50 chance, but you never know). 1 pt for the reasoning. There are multiple ways to explain (by calculation and graphically using the provided structure and the sum formula.

2.2 **Select** the correct coordination number for the Pb ion. 1.0 pt

SOLUTION:

6
1 pt assigned when correct, if not, 0 pt.

2.3 The cell constants and angles for the full $MAPbI_3$ unit cell are listed in the table below. Based on the given data, **choose** the appropriate crystal system. 1.0 pt

a = 8.8392 Å
b = 8.8392 Å
c = 12.6948 Å
α = 90°
β = 90°
γ = 90°

SOLUTION:
Tetragonal
1 pt for correct assignment.

2.4 **Calculate** the density ρ in kg cm^{-3} of the structure using $Z = 4$ for the calculation, where Z represents the number of formula units in the unit cell. 3.0 pt
SOLUTION:

$\rho = \frac{M_r \cdot Z}{V_{\text{Unit Cell}} \cdot N_A}$
$M_r = 619.98 \frac{\text{g}}{\text{mol}}$
Z = 4 (given)
$V_{\text{Unit Cell}} = a \cdot b \cdot c$ = 8.8392 Å · 8.8392 Å · 12.6948 Å
$V_{\text{Unit Cell}}$ = 992.51 Å^3
$\rho = \frac{619.98 \frac{\text{g}}{\text{mol}} \cdot 4}{992.51^3 \cdot N_A}$
$\rho = 4.14 \cdot 10^{-4}$kg/cm^3
3 pt maximum: 1 pt for the correct formula for ρ, 1 pt for calculating V, 1 pt for the final result

Synthesis and Degradation

Methylammonium iodide (MAI) is synthesized using 24 mL of methylamine (MA) solution and 10 mL of hydroiodic acid (HI) solution. The two solutions are mixed in a round-bottom flask and stirred at 0 °C for 120 minutes to obtain a white solution. The solution is then evaporated at 80 °C for 120 minutes, producing a white precipitate. The precipitate is washed several times with diethyl ether until it becomes colorless, forming a white crystalline powder. The solution is then filtered and desiccated in a vacuum oven at 60 °C for 24 hours.

2.5 **Write** the balanced equation of the synthesis of MAI under the conditions given in the introductory text. 1.0 pt
SOLUTION:
$CH_3NH_2 + HI \longrightarrow CH_3NH_3I$
1 pt for the reaction equation

To make the perovskite thin film, a two-step process is applied. First, a solution of PbI_2 (0.4 g in 2 mL of DMF) is coated onto a thin polymer layer. Using the spin coating technique, it is spun at 100 °C for 10 minutes. Next, a solution of MAI (0.01 g in 2 mL of DMF) is added to the PbI_2 layer. After that, the film is heated and spun again at 100 °C for another 10 minutes. During this process, the color of the film changes from light yellow to dark brown.

2.6 a) **Write** the balanced equation of the synthesis of $MAPbI_3$ from MAI and PbI_2 under the conditions given in the introductory text. 1.5 pt
b) **Assign** the oxidation states of lead (Pb) and iodine (I) in the product and starting materials.

SOLUTION:

$CH_3NH_3I + PbI_2 \longrightarrow CH_3NH_3PbI_3$

C: -3
H: +1
N: -3
I: -1
Pb: +2

1.5 pt maximum, 1 pt for the reaction equation, 0.5 pt for the oxidation numbers

2.7 $MAPbI_3$ degrades when it comes into contact with water. **Write** the balanced chemical reaction for the reaction of $MAPbI_3$ with water. 2.0 pt

SOLUTION:

Hydrolysis (backward reaction of the synthesis):

$CH_3NH_3PbI_3 + H_2O + O_2 \longrightarrow PbI_2 + CH_3NH_3I \longrightarrow PbI_2 + CH_3NH_2 + HI$

"In the presence of H_2O and O_2, the $MAPbI_3$ perovskite film degrades into CH_3NH_3I and PbI_2. Then, CH_3NH_3I further decomposes into CH_3NH_2 and HI."
https://doi.org/10.1016/j.solener.2023.03.021
But I see how many different reactions can also happen like:

Oxidation, forming PbO:

$CH_3NH_3PbI_3 + O_2 \longrightarrow PbO + CH_3NH_3I + I_2$, in this case water would be like the solvent

Formation of Lead Hydroxide $CH_3NH_3PbI_3 + H_2O + O_2 \longrightarrow Pb(OH)_2 + I_2 +$ CH_3NH_3I followed by further degradation

1.5 pt maximum for the reaction equation including the degradation of CH_3NH_3I.
1 pt for the reaction without the degradation of CH_3NH_3I.

Band gaps

The band gap of a compound is defined as the difference in energy between the valence band and the conduction band of a solid material. The range of the band gap describes of the range electron energies that cannot be adopted.

2.8 The band gap of $MAPbI_3$ is between 1.55 eV and 1.64 eV. 5.0 pt

a) **Calculate** the corresponding wavelengths λ in nm of light absorbed at 1.55 eV and 1.64 eV.

SOLUTION:

$E = \frac{h \cdot c}{\lambda}$

$\lambda = \frac{h \cdot c}{E}$

E = 1.55 eV $\cdot 1.06 \cdot 10^{-19} \frac{J}{eV} = 2.48 \cdot 10^{-19}$ J

$\lambda_{(1.55\,eV)} = \frac{h \cdot c}{E} = \frac{h \cdot c}{2.48 \cdot 10^{-19} J} = 800.53$ nm

E = 1.64 eV $\cdot 1.06 \cdot 10^{-19} \frac{J}{eV} = 2.63 \cdot 10^{-19}$ J

$\lambda_{(1.55\,eV)} = \frac{h \cdot c}{E} = \frac{h \cdot c}{2.63 \cdot 10^{-19} J} = 756.6$ nm

3 pt maximum: 1 pt for the formula of E, 1 pt for each λ

b) **Reason** how this affects the utilization of this compound in solar cells.

SOLUTION:

The rather small band gap lets the compound absorb light in the visible range, which is readily available from the sun. A larger band gap would lead to a smaller fraction of sunlight being absorbed. A smaller band gap would lead to waste of energy, as the excess energy of light over the band gap is lost in waste heat.

2 pt maximum: 1 pt if not extensive

Simple Complexes and Metallocenes 15.0 pts

Simple Complexes

Let's consider the complex $[Co(NH_3)_4Cl_2]Cl$.

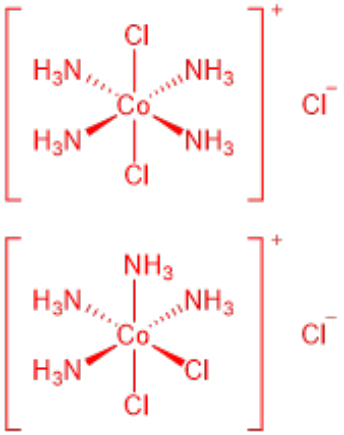
3.1 **Determine** the oxidation state of the central metal ion in $[Co(NH_3)_4Cl_2]Cl$. 1.0 pt

SOLUTION:

+III, 1.0 pt

3.2 **Draw** all stereoisomers and **describe** the relationship between the stereoisomers of $[Co(NH_3)_4Cl_2]Cl$. 2.5 pt

SOLUTION:



Relationship: diastereomers
Also accepted: cis-trans isomers

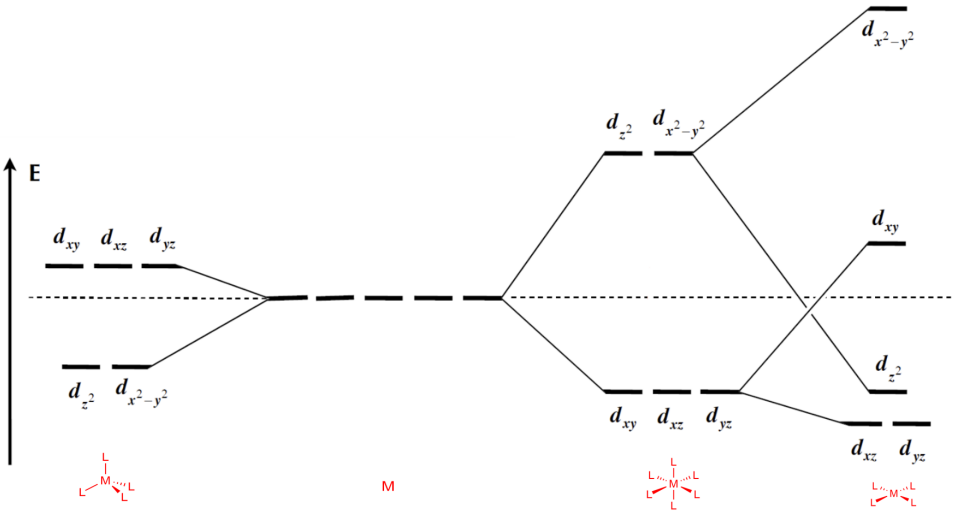
2.5 pt maximum: 1 pt for each structure, 0.5 pt for diastereomers

3.3 **Determine** the d^n electron configuration of $[Co(NH_3)_4Cl_2]Cl$. 1.0 pt

SOLUTION:

Co: [Ar] $3d^7\ 4s^2$
Co^{3+}: [Ar] $3d^6$
d^6 configuration 1.0 pt

Many properties of transition metal complexes, such as visible light absorption and magnetism, are determined by the way the degeneracy of the d-orbitals is lifted when the ligands are added to the central metal. The new energy levels can be predicted through the ligand field splitting model, where the complex geometry and the nature of the ligands is considered.



Overview of different common crystal field splittings for different geometries.

The spectrochemical series shows which ligands and metal ions generate a weaker or stronger splitting.

Ligand:

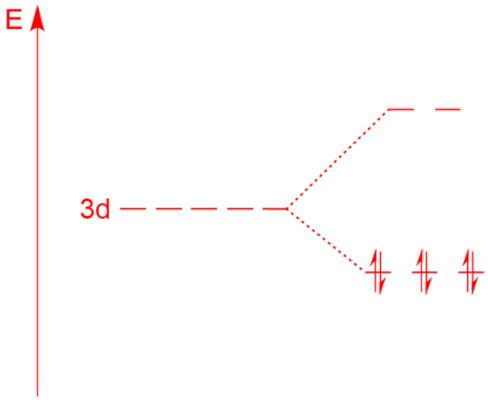
$$O_2^{2-} < I^- < Br^- < S^{2-} < \mathbf{S}CN^- < Cl^- < N_3^- < F^- < NCO^- < OH^- < ONO^- < C_2O_4^{2-} \approx H_2O < \mathbf{N}CS^- < CH_3CN < NH_3 < NO_2^- < PPh_3 < CN^- < CO$$

Metal ion:

$$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Cu^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+} < Rh^{3+} < Ir^{3+} < Pt^{4+}$$

3.4 a) **Draw** the energy diagram for $[Co(NH_3)_4Cl_2]Cl$ and **fill** in the d-electrons. 3.0 pt
b) **Select** whether the complex is high-spin or low-spin and **explain** your choice.
c) **Select** the correct magnetic properties for the complex.

SOLUTION:



a) Figure above, only right hand side of the diagram gives points (free ion not needed) 1.0 pt

b)
☒ low-spin
☐ high-spin
0.5 pt correct box

Explanation:
strong splitting of NH_3 and Co^{3+} causes low-spin
1.0 pt correct explanation (0.5 pt if only one factor mentioned)

c)
☒ diamagnetic
☐ paramagnetic
☐ not clearly any of the above
0.5 pt

Now consider two other ammine cobalt complexes, $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$. You have isolated both, one sample is orange and absorbs light at 475 nm, while the other is purple.

3.5 **Assign** the correct color to each complex and **explain** your answer. 2.0 pt

SOLUTION:

Complex	Colour	Explanation
$[Co(NH_3)_6]Cl_3$	orange 0.5 pt	orange colour means absorbance of blue light (430 nm - 490 nm), shorter wavelength absorbed means higher energy photon absorbed and therefore stronger splitting: No chloride ligand present 0.5 pt
$[Co(NH_3)_5Cl]Cl_2$	purple 0.5 pt	purple colour means absorbance of yellow light (560 nm - 580 nm), longer wavelength absorbed means lower energy photon absorbed and therefore weaker splitting: Chloride ligand causes weaker splitting 0.5 pt

3.6 **Calculate** the crystal field splitting Δ of the orange complex in $kJ\,mol^{-1}$ under the assumption that the crystal field splitting is responsible for the color. 0.5 pt

SOLUTION:

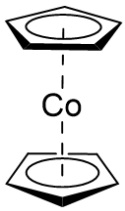
$\Delta = \frac{hc}{\lambda}$, $\Delta = 4.182 \cdot 10^{-19} J$

$4.182 \cdot 10^{-19}\,J \cdot N_A = 251.8\,kJ \cdot mol^{-1}$

final answer 0.5 pt

Metallocenes

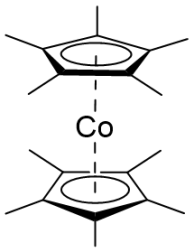
Cobaltocene ($CoCp_2$), another cobalt complex, is composed of a cobalt-ion packed between two planar cyclopentadienyl anions, just like a sandwich. The complex is neutral and stable, but should be kept under an inert atmosphere.



Structure of cobaltocene, $CoCp_2$.

3.7	**State** the oxidation state of the central atom and **determine** the total valence electron count of cobaltocene. **SOLUTION:** +II, 1.0 pt 19 electrons (6+6+7), 1.0 pt	2.0 pt

3.8	**Predict** the reactivity of cobaltocene. **SOLUTION:** (strong) reducing agent (similar to alkali metals) 1.0 pt	1.0 pt



Structure of decamethylcobaltocene, $CoCp^*_2$.

3.9	**Predict** the change in reactivity compared to cobaltocene. **Explain** your answer.	2.0 pt

SOLUTION:

stronger reducing agent, due to the methyl groups donating electron density (σ-effect), stabilizing the Co^{3+} center after oxidation

explanations using the destabilisation of $CoCp^*_2$ can be accepted too.

2.0 pt

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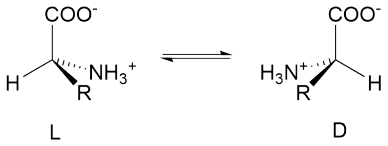
English (Official)

Dating Fossile Bones Through Kinetics of Amino Acid Racemisation — 20.0 pts

Only L-stereoisomers of amino acids (L-amino acids, see figure below) usually occur in the proteins of living organisms - although some D-amino acids are present in certain bacteria. The full isomerisation reaction of an L-amino acid into an D-amino acid includes a step with the creation of an enolate intermediate, however overall it can be simplified to:

$$\text{L—amino acid} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{D—amino acid}$$

with rate constants k_1 and k_2 . The figure below shows the respective 3-dimensional structures of the L- and D-stereoisomers of an amino acid.



For amino acids which have only one stereogenic centre, L- and D-amino acids are present in equal amounts under conditions of chemical equilibrium, so a system containing exclusively L-amino acids is thermodynamically unstable: the amino acid racemisation reaction will, after a period of time which is characteristic of each amino acid, eventually convert pure L-amino acids into a racemic mixture (i.e. one in which the D- and L-enantiomers are present in equal amounts).

4.1 For the forward racemisation reaction 3.0 pt

$$\text{L}-\text{amino acid} \longrightarrow \text{D}-\text{amino acid}$$

of an amino acid with only one stereogenic centre, **indicate** if the changes of enthalpy $\Delta_r H$, of Gibbs free energy $\Delta_r G$, and of entropy $\Delta_r S$ are respectively greater than zero ($>$), equal to zero ($=$), or smaller than zero ($<$) when going from an initial state with 100% L-amino acid (0% D-amino acid) to a final state with 50% L-amino acid and 50% D-amino acid. **Explain** each of your answers.

SOLUTION:

$\Delta_r H = 0$: the same chemical bonds are broken and then re-created during the reaction.

It is mentioned in the introduction of the present question that under conditions of chemical equilibrium L- and D-amino acids are present in equal amounts. It follows that the direct reaction when there is an excess of L-amino acid over D-amino acids must be thermodynamically favorable and that $\Delta_r G < 0$.

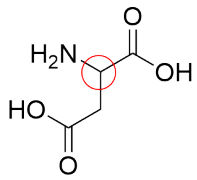
Finally $\Delta_r G = \Delta_r H - T\Delta_r S$ combined with the previous results for $\Delta_r G$ and $\Delta_r H$ implies $\Delta_r S > 0$. This can be justified as going from a relatively organised system (with a selection of L- amino acids only) to a less organised system where the two chemical structures present in the universe may be found.

3 pt maximum, 1 pt for each correct classification with a sound reasoning. 0 pt if the reasoning is wrong or missing. Only 0.5 pt if the increase of S is justified only through the $\Delta_r G = \Delta_r H - T\Delta_r S$ equation, without a narrative interpretation.

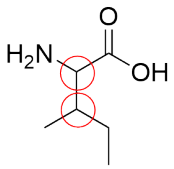
4.2 Based on the chemical formulas given below for the amino acids **Asp**, **Ile** and **Ala**, clearly **mark** the carbon atoms which are stereogenic centers with a $*$. For each of these three amino acids, **indicate** if the rate constant k_1 of the forward isomerisation reaction from the L- to the D- stereoisomer of the amino acid is expected to be equal to the rate constant k_2 of the reverse reaction, or if it is not possible to predict the relationship between k_1 and k_2. In each case, **explain** why. 3.0 pt

SOLUTION:

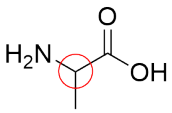
Asp



Ile



Ala



When there is only one chiral carbon atom (**Asp** and **Ala**), the rate constants $k_1 = k_2$ so that, at equilibrium, when the respective concentrations of the L- and D-amino acids are equal, the quantity of each amino-acid produced or consumed by the reactions over time are the same.
When there are two chiral carbon atoms **(Ile**, for instance), the respective equilibirum concentration of each of the four stereoisomers depends on two isomerisation reactions, so the relationship between k_1 and k_2 may not be predicted without additional information.
3 pt maximum: 0.5 pt per correct stereogenic center, minus 0.5 pt for an incorrect stereogenic center (no negative overall points for the stereogenic centers). 0.5 pt for each answer about the relation between k_1 and k_2 with a proper explanation.

For relatively low extent of racemisation (small D/L ratios), the racemisation process can be considered as an irreversible first-order reaction, and k_1 may be written as

$$\ln(1 + [\mathrm{D}]/[\mathrm{L}]) - \ln(1 + [\mathrm{D}]_0/[\mathrm{L}]_0) = k_1 t$$

where $[\mathrm{D}]$ and $[\mathrm{L}]$ denote the respective concentrations of the D- and L-amino acids at time t and $[\mathrm{D}]_0$ and $[\mathrm{L}]_0$ denote the respective initial concentration. This equation can be used to obtain an order of magnitude for the time scale of the racemisation process.

For the historical conditions of Egypt, k_1 could be established as $9.9 \cdot 10^{-5}$ year^{-1} for the amino acid **Asp**.

4.3 Using the equation above and assuming that the initial concentration of D-**Asp** is zero, **calculate** the time $t_{1/2}$ in years required for the racemisation reaction to proceed halfway towards the equilibrium state. 2.0 pt

SOLUTION:

Half-way towards the equilibrium starting from a null concentration of D means 25% D- and 75% L- (not 50% D- and 50% L- which is the equilibrium situation itself). Thus:

$$[\mathrm{D}]_0/[\mathrm{L}]_0 = 0 \qquad [\mathrm{D}]/[\mathrm{L}] = 25\%/75\% = 1/3$$

so

$$t = \frac{\ln(1+1/3) - \ln(1)}{k_1} = 2905\,\text{years}$$

2 pt maximum: 0.5 pt for using $[\mathrm{D}]/[\mathrm{L}] = \frac{1}{3}$ at halfway towards equilibrium, 1 pt for the analytical solution and 0.5 pt for the numerically correct result of t. Cascade mistakes if a wrong $[\mathrm{D}]/[\mathrm{L}] \neq \frac{1}{2}$ was are awarded up to 1.5 pt

The full kinetic equation for the racemisation of the amino acid **Asp**, which takes into account the reverse reaction, has been established as:

$$2k_1 t = \ln\left[\frac{1+[\mathrm{D}]/[\mathrm{L}]}{1-[\mathrm{D}]/[\mathrm{L}]}\right] - \ln\left[\frac{1+([\mathrm{D}]_0/[\mathrm{L}]_0)}{1-([\mathrm{D}]_0/[\mathrm{L}]_0)}\right]$$

4.4 For the cases where $[D]_0/[L]_0 = 0$, **determine** an equation to provide the ratio ($[D]/[L]$) as a function of time. Using the value of k_1 provided in task **4.3** and the template below, **represent** on a chart the results at the times $t = 0, 2500, 5000, 7500$ and 10000 years. 2.0 pt

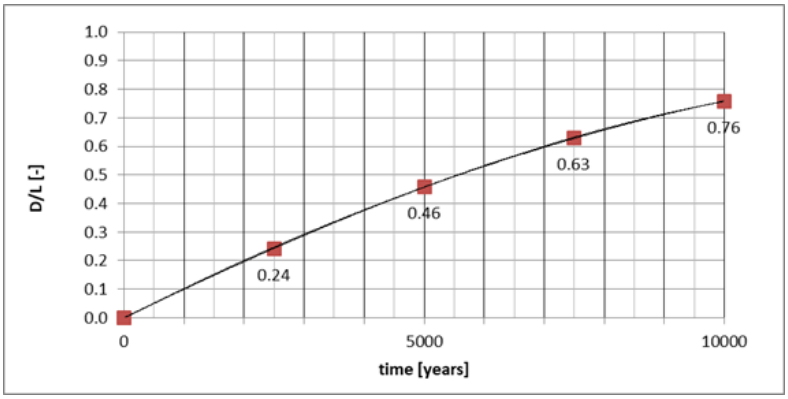
Note: *If you couldn't find an equation for* $[D]/[L]$ *as a function of* t*, you may use the equation* $[D]/[L] = kt - (k^3t^3)/3 + (2k^5t^5)/15$ *to prepare the chart.*

SOLUTION:

With $[D]_{0/}[L]_0 = 0$, the equation can be rearranged to yield

$$[D]/[L] = \frac{\exp(2k_1t) - 1}{\exp(2k_1t) + 1}$$

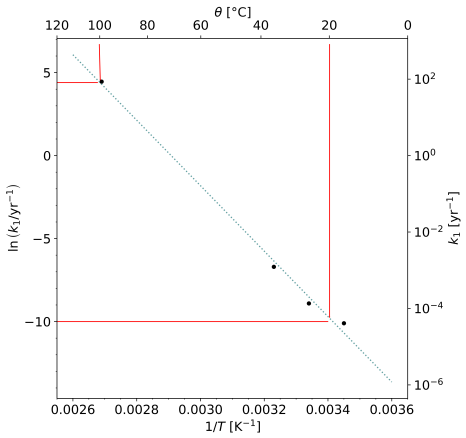
This allows to produce the chart below.



2 pt maximum: 1 pt for the equation, 1 pt for the chart.

4.5 Assuming that the average annual temperature for the region of Egypt is 26.3 °C, **calculate** the ratios $\frac{k_{T=27.3\,°C}}{k_{T=26.3\,°C}}$ and $\frac{k_{T=25.3\,°C}}{k_{T=26.3\,°C}}$ to find the sensitivity (% variation) of k_1 for **Asp** to an imprecision of 1 °C in the measurements, using the chart below and the Arrhenius law. 5.0 pt

SOLUTION:



The slope m of the curve on the chart corresponds to $\ln(k)/(1/T)$ and can be measured (graphically) as

$$m = \frac{(4.4\ -\ (-10.0))}{(\frac{1}{(100+273.15)} \cdot 1000 - \frac{1}{(20+273.15)} \cdot 1000)} = -19.7 \cdot [1000/\mathrm{K}] = -19'700\mathrm{K}^{-1}$$

The Arrhenius law can be expressed as $\ln(k) = \ln(A) - \frac{1}{T}\frac{E_A}{R}$
so the slope $m = \frac{E_A}{R}$ and $E_A = R \cdot m = 163'786\,\mathrm{J/mol}$.
Comparing the relative values of k for $T = 299.45\,\mathrm{K} (= 26.3\,°\mathrm{C}), 300.45\,\mathrm{K}$ and $298.45\,\mathrm{K}$ by replacing E_A in the Arrhenius law yields:

$$\frac{k_{T=27.3\,°C}}{k_{T=26.3\,°C}} = \frac{A\exp(-E_A/(R \cdot 300.45\,\mathrm{K}))}{A\exp(-E_A/(R \cdot 299.45\,\mathrm{K}))} \approx 124.5\%$$

$$\frac{k_{T=25.3\,°C}}{k_{T=26.3\,°C}} = \frac{A\exp(-E_A/(R \cdot 298.45\,\mathrm{K}))}{A\exp(-E_A/(R \cdot 299.45\,\mathrm{K}))} \approx 80.2\%$$

The empirical pre-exponential factor A does not need to be measured on the chart as it cancels out when the relative values of k are compared at different temperatures.
4 pt maximum: 1 pt for reading the slope from the plot, 1 pt to set the relation between the slope and E_A, 1 pt for using the Arrhenius law to calculate the ratio $\frac{k_T}{k_{T=26.3\,°C}}$ without the factor A , 2 pt for the correct values of the two fractions (1 pt each if within 10% of the respective values given above, 0.5 pt if within 20%, 0 pt if the difference is bigger).

4.6 Using the relation provided in task **4.4** for t as a function of $[D]/[L]$ (with $k_1 = 9.9 \cdot 10^{-5}$ year^{-1}) and assuming $[D]_0$ of **Asp** is zero, **determine** the age range in years considering an average temperature $T = 26.3\,^{\circ}C$, for a bone sample found in the region of Egypt with a $[D]/[L]$ ratio of 0.6. The bounds are determined by an imprecision of $1.0\,^{\circ}C$ from the average temperature. 2.0 pt

Note: *If you couldn't solve task **4.5**, assume* $\frac{k_{T=27.3\,^{\circ}C}}{k_{T=26.3\,^{\circ}C}} = 120\%$ *and* $\frac{k_{T=25.3\,^{\circ}C}}{k_{T=26.3\,^{\circ}C}} = 80\%$

SOLUTION:

For the case where $[D]_0/[L]_0 = 0$, the relation in task 4.4

$$2k_1 t = \ln\left[\frac{1+[D]/[L]}{1-[D]/[L]}\right] - \ln\left[\frac{1+([D]_0/[L]_0)}{1-([D]_0/[L]_0)}\right]$$

can be simplified and re-arranged to

$$t = \frac{\ln\left[\frac{1+[D]/[L]}{1-[D]/[L]}\right]}{2k_1}$$

Replacing with the numerical values yields:
mean value for $t_{0.6} = 7001$ years
lower bound for $t_{0.6} = 5625$ years
upper bound for $t_{0.6} = 8728$ years
2 pt maximum: 1 pt for the equation, 0.5 pt for the mean value of t and 0.5 pt for the values of the lower and the upper bounds (0.25 pt each, allow for 10% variation to the given answer due to the admitted imprecision on the $\frac{k_T}{k_{T=26.3\,^{\circ}C}}$ ratios measured in task **4.5**).

4.7 **Compare** the usefulness of the method of amino acid racemisation dating with that of radiocarbon dating, given the following data: 2.0 pt

- Radiocarbon dating has a 0.3% precision with samples aged up to $10'000$ years and a 10% precision up to $50'000$ years. After that, the method is no longer useful.
- The method of amino acid racemisation has a hypothetical boundary of [D]/[L] < 0.95, as the precision decreases as the ratio approaches 1.0.

SOLUTION:

Under 10000 years, the ^{14}C method is obviously much more precise than the **Asp** datation method. In the example of task **4.6**, the ^{14}C method would yield 7001 ± 21 years (0.3% incertitude) which is clearly lower than the calculated lower and upper bounds for the **Asp** method.

It can also be observed that even one degree variation between the average annual temperatures is already a major assumption that needs to be checked for each geographical region. Higher variation means of course higher incertitude for the **Asp** datation method.

This issue is even more critical if the **Asp** racemisation method is used for a range from 10000 years to 50000 years, for which it is obviously challenging to obtain paleontological proofs of the mean annual temperatures. If this had not been the case, the **Asp** datation method could have had some scientific and archaelogical value for confirming the ages obtained by ^{14}C. Indeed, considering for example the conditions of Egypt, the same formula as in task **4.6**

$$t = \frac{\ln\left[\frac{1+[\mathrm{D}]/[\mathrm{L}]}{1-[\mathrm{D}]/[\mathrm{L}]}\right]}{2k_1}$$

yields for the [D]/[L] ratio = 0.95 (hypothetical maximum value for the racemization method) $t_{mean} = 18503$ years, $t_{T=27.3\,^\circ\mathrm{C}} = 14864$ years (a variation of -3639 years), and $t_{T=25.3\,^\circ\mathrm{C}} = 23065$ years (a variation of 4563 years). This is of course a quite wide incertitude, however it is still comparable with the assumed 10% error on ^{14}C dating, which would be 1850 years for $t = 18503$ years. Thus the **Asp** racemisation method could have been used to confirm ^{14}C dating for ages beyond 10000 years, if there was not the likely fatal issue of proving that the mean annual temperature remains within a defined and relatively small range of temperature, such as $\pm 1\,^\circ$C.

- 0.5 for showing with a calculation that the ^{14}C method is more precise than the **Asp** method below 10000 years
- 0.5 for stating that the 1 degree variation range for the temperature is already a major hypothesis
- 0.5 for showing that the **Asp** method has a range of incertitude comparable to the ^{14}C method beyond 10000 years
- 0.5 for stating the significant issue with the assumption of 1 degree temperature variation range for periods from 10000 years to 50000 years ago

2.0 pt in total.

4.8 **Assess** a method based on **Ala** against the radiocarbon dating method. 0.5 pt
The **Ala** racemisation rate is much slower than **Asp**, approximated to $k_{\textbf{Ala}} = 3.466 \times 10^{-5}$ year^{-1} for the same conditions as before.

SOLUTION:

Finally, the same formula as above applied to Ala (in the conditions of Egypt, as an example) with $k_{\text{ala}} = 3.466 \cdot 10^{-5}$ year^{-1} yields for the [D]/[L] ratio = 0.95 (hypothetical maximum value for the racemisation method) $t_{mean} = 52854$ years. The datation method based on Ala racemisation remains therefore somewhat interesting for archaelogy: in spite of all the challenges created by the temperature parameter, it can provide a rough estimate of the age of fossils over 50000 years when the ^{14}C method is not applicable anymore.

0.5 for calculating the maximum age possible with the **Ala** method in the conditions of Egypt and stating that it has some archaeological interest over 50000 years since the ^{14}C method is not available.

4.9 **Justify** why the effect of temperature on the ages obtained with the **Ala** racemisation may or may not be expected to be the same as for the **Asp** racemisation. 0.5 pt

SOLUTION:

The incertitude due to temperature variation should not be readily calculated as for **Asp**: indeed the activation energy is specific to each racemisation reaction (eg $93 \cdot [1000/\text{kJ/mol}]$ for **Ala** in the litterature vs $163 \cdot [1000/\text{kJ/mol}]$ for **Asp** as per Bada, 1985) so that the effect of temperature may not be assumed to be the same for **Ala**. This is due to the exponential term in the Arrhenius equation including both E_A and T.

0.5 for explaining that the E_A for **Ala** racemisation may not be expected to be the same as the E_A for the **Asp** racemisation, and that this implies that the effect of the temperature variation on the racemisation reaction rate may not be expected to be the same either.

Boxes for Electrons — 21.0 pts

The dynamics of π-electrons in a chain of conjugated double bonds can be modeled with the simple "particle in a box" model. The model assumes a one-dimensional box in which the electrons are confined and subjected to a constant potential. This leads to distinct energy levels for the electrons, given by

$$E(n) = \frac{n^2 h^2}{8 m_e L^2}$$

where $n = \{1, 2, 3, \dots\}$ is the principal quantum number of the electron, h is Planck's constant, m_e is the mass of the electron and L is the length of the one-dimensional box.

In the ground state, the π-electrons occupy the lowest possible energy states (orbitals). Remember that according to Pauli's principle maximum two electrons are permitted in an orbital. The highest occupied orbital is called HOMO and the lowest unoccupied orbital is called LUMO. Interactions between electrons will be neglected in the entire problem.

1D-Boxes

In the following, we will consider linear conjugated alkenes such as 1,3,5-hexatriene:

$$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$$

The system can be approximated as a one-dimensional box with length $L = \left(k - \frac{1}{2}\right) \cdot 2.4\,\text{Å}$, where k corresponds to the number of double bonds, so in this case $k = 3$.

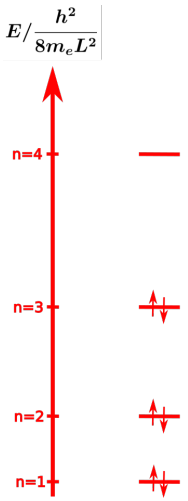
5.1 **Determine** the number n_π of π-electrons in 1,3,5-hexatriene. 1.0 pt

SOLUTION:

$n_\pi = 6$ as there are two π-electrons contained in each double bond.

5.2 **Add** the energy levels for $n = 1, 2, 3, 4$ to the molecular orbital diagram template provided below and **fill in** the π-electrons for 1,3,5-hexatriene. **Indicate** the principal quantum number n of the orbitals with labels. 2.0 pt

SOLUTION:



1 pt for the energy levels in adequate spacing:
- 0.5 pt for the labels on the axis (n or n^2 are fine)
- 0.5 pt for the electrons

5.3 **Determine** the wavelength λ in nm that is required to excite an electron from the HOMO to the LUMO in 1,3,5-hexatriene, assuming they behave as particles in a box. 2.0 pt

SOLUTION:

First we have to use the provided formula to obtain the length as $L \approx (3 - \frac{1}{2}) \cdot 2.4\,\text{Å} = 6\,\text{Å}$.

Identifying the HOMO with $n = 3$ and the LUMO with $n = 4$, we get the energy difference as

$$\Delta E = (4^2 - 3^2)\frac{h^2}{8m_eL^2} \approx 1.17 \cdot 10^{-18}\,\text{J}$$

This corresponds a wavelength of

$$\lambda = \frac{hc}{\Delta E} \approx 1.70 \cdot 10^{-7}\,\text{m} = 170\,\text{nm}$$

2 pt for $165\,\text{nm} \leqslant \lambda \leqslant 175\,\text{nm}$:
- 0.5 pt for the length L
- 1 pt for ΔE
- 0.5 pt for the corresponding λ

5.4 1,3,5-hexatriene also absorbs light at $\lambda = 74\,\text{nm}$. **Explain** why and **support** your explanation with a calculation. 2.0 pt

SOLUTION:

The wavelength $\lambda = 74\,\text{nm}$ corresponds for example to the transition $n = 3 \rightarrow n = 5$.

2 pt for providing a correct transition:

- only 1 pt if only stated that it's another transition

5.5 Using the model developed, **develop** a formula for the dependence of the wavelength $\lambda(k)$ required to excite the HOMO-LUMO transition on the number of double bonds k. 2.0 pt

SOLUTION:

Realizing that the HOMO-LUMO transition of a molecule with k double bonds is the transition between the k^{th} and the $(k+1)^{\text{th}}$ energy level, we find that

$$\Delta E_k = ((k+1)^2 - k^2)E_{1,k} = (2k+1)E_{1,k}$$

with $E_{1,k} = \frac{h^2}{8m_e L_k^2}$ the lowest energy level in the molecule.

This can be plugged into the formula for the wavelength

$$\lambda(k) = \frac{hc}{\Delta E_k}$$

to get the full formula:

$$\lambda(k) = \frac{8m_e c L_k^2}{(2k+1)h} = \frac{8m_e c\left((k-\frac{1}{2})(2.4\,\text{Å})^2\right)^2}{(2k+1)h}$$

2 pt for the correct formula with sound reasoning:

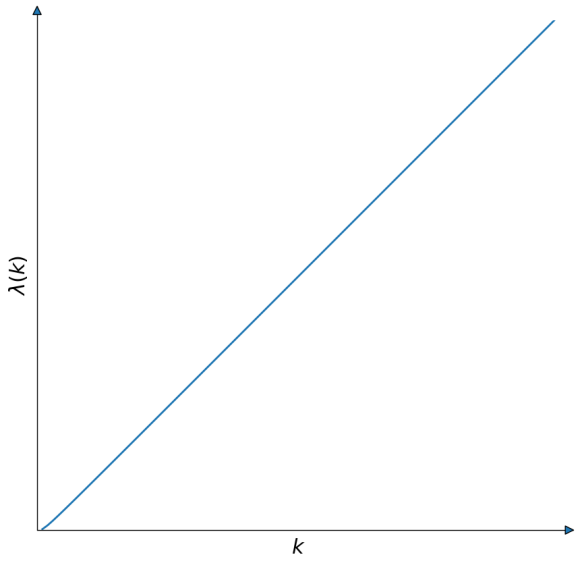
- 1 pt for getting the energy in terms of $E_{1,k}$
- 1 pt for deriving the final formula from this
- only 1.5 pt if L_k is not written out explicitly

5.6 For molecules with many double bonds, qualitatively **sketch** the relationship of the HOMO-LUMO transition wavelength $\lambda(k)$ against the number of double bonds k in the template below. 1.0 pt

Note: *If you could not determine the formula for $\lambda(k)$ in the previous task, assume* $\lambda(k) = \frac{k^2-k+0.25}{2k+1} \cdot 190\,\text{nm}$.

SOLUTION:

From the formula found in the previous task, we find that the relationship for large k becomes linear. The function plotted from $k = 0$ to $k = 99$ is shown in the following figure:



1 pt if a line with the correct shape (monotonically increasing, maybe smaller slope at low k values, linear asymptote); 0.5 pt something incorrect but linear asymptote clearly visible

5.7 **Determine** the number of conjugated double bonds k required for a linear molecule to absorb light at $\lambda = 2140\,\text{nm}$ through the HOMO-LUMO transition within the model developed. **Support** your answer with a calculation. 2.0 pt

Note: *If you could not determine the formula for $\lambda(k)$ you may use the alternative provided in the previous task.*

SOLUTION:

At $\lambda = 2140\,\text{nm}$ we are pretty well in the linear regime. Here we use for example $\lambda(10) \approx 816\,\text{nm}$ and $\lambda(20) \approx 1761\,\text{nm}$ to obtain the parameters a, b of the linear approximation $\lambda(k \gg 1) \approx a + b \cdot k$. Assuming a linear relationship we get $b = \frac{\lambda(20)-\lambda(10)}{20-10} \approx 94.5\,\text{nm}$ and $a = \lambda(10) - 10 \cdot b \approx -129\,\text{nm}$. So we get

$$\lambda(k) \approx k \cdot 94.5\,\text{nm} - 129\,\text{nm}$$

which easily inverts to

$$k(\lambda) \approx \frac{\lambda - a}{b}$$

and we get

$$k(\lambda = 2140\,\text{nm}) = 24$$

2.0 pt for $k = 24$:

- 1 pt for getting the idea that the linear relationship can be applied
- Also full mark if the quadratic equation is setup and solved. Note that it is not required though
- Only 1 pt if just tried out and guessed correctly

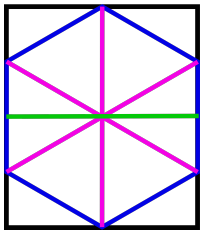
2D-Boxes

So far we have been limited to linear molecules that can be approximated with a one-dimensional box. In the following we will try to extend the model to two dimensions so we can derive the molecular orbital diagram of benzene (C_6H_6).

5.8 Given the C–C bond length $L_B = 1.4\,\text{Å}$ in benzene and the template below, **determine** the minimal required side lengths L_x (horizontal) and L_y (vertical) in Å for the rectangular box to accommodate the benzene molecule as it's shown. 2.0 pt

SOLUTION:

As benzene forms an equilateral hexagon, with inner angles of $120°$, we can see that the triangles formed by the pink diagonals (figure below) are also equilateral. Thus the height of the rectangle is given by $L_y = 2L_B = 2.8\,\text{Å}$ and the width by $L_x = 2\sqrt{(1.4\,\text{Å})^2 - (0.7\,\text{Å})^2} \approx 2.42\,\text{Å}$ (using Pythagoras with half of the green line in the figure below).



2 pt for the correct result, L_x, L_y exchanged also gives full mark

- 1 pt for $L_x = 2.4\,\text{Å}$
- 1 pt for $L_y = 2.8\,\text{Å}$

The energy levels for an electron in a two-dimensional box with side-lengths L_x, L_y are given by

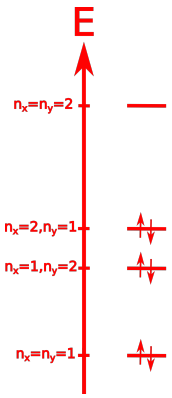
$$E(n_x, n_y) = \frac{h^2}{8m_e}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right)$$

where n_x, n_y denote the principal quantum numbers.

5.9 **Draw** the energy diagram of benzene (up to the LUMO) within the discussed model into the template provided below. **Indicate** the principal quantum numbers n_x, n_y on the energy axis. **Fill** the orbitals with the π-electrons. 3.0 pt

Note: *If you cold not determine L_x, L_y in the previous task, assume $L_x = 2.0\,Å$ and $L_y = 2.5\,Å$.*

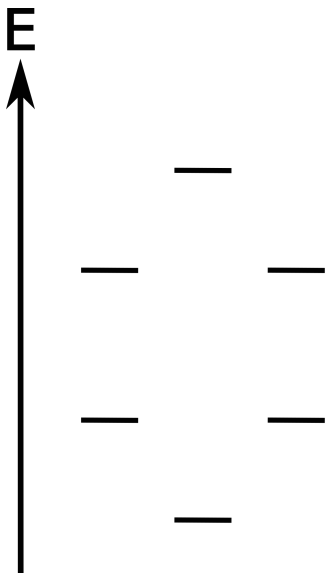
SOLUTION:



2 pt overall:

- 1 pt for the energy levels with appropriate spacing
- 0.5 pt for the electrons
- 0.5 pt for the principal quantum number assignment (consistent with the previous task!)

The molecular orbital diagram of benzene without the crude approximations employed looks a bit different:



5.10 **Highlight** and **explain** the differences between the actual molecular orbital diagram of benzene and the one derived from our simplified model. 4.0 pt

SOLUTION:

We notice two major differences: One is the degeneracy of the HOMO, which we introduced by our box having $L_x \neq L_y$ and the other is the degeneracy of the LUMO (which is completely different in our model), which appears because in our model box the 6-fold symmetry axis of benzene is not preserved. What we would obtain with a square box would largely resemble the MO diagram of cyclobutadiene.

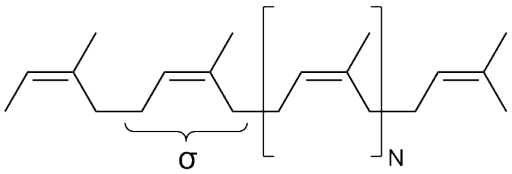
4 pt maximum:

- 2 pt for the degeneracy of the HOMO, that could be solved by taking a square instead of a rectangular box
- 2 pt for the degeneracy of the LUMO ($n_x = n_y = 2$), points awarded for any reference of the symmetry that is not preserved
- -1 pt for an incorrect addition (minimum 0 pt)

Thermal Contraction of Rubber

16.0 pts

Most materials expand in volume upon heating. This is commonly explained as molecules begin to vibrate and move faster, resulting in an increased distance between the individual molecules. Rubber, however exhibits the special property that it contracts when heated. This question aims to explain this observation with fundamental statistical thermodynamics.

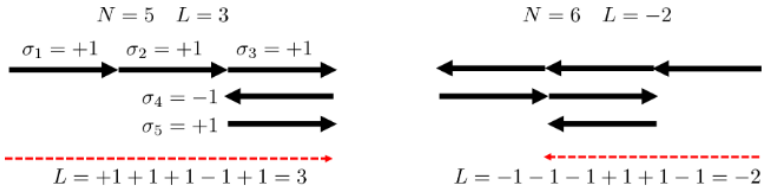


Structure of polyisoprene, the material of which rubber is made. The length of the repeating unit (indicated segment) is treated as $\sigma = 1$ if it is aligned towards to the right direction and $\sigma = -1$ if it is aligned to the left direction.

Rubber consists of polymeric materials (for example polyisoprene, shown above), consisting of $N \gg 1$ repeating units. For simplification, we model a rubber band in one dimension, where the N segments σ_i of length 1 can point only in $\pm x$ direction. The end-to-end length of the rubber band is then given by

$$L = \sum_{i=1}^{N} \sigma_i = \sigma_1 + \sigma_2 + \cdots + \sigma_N,$$

so we distinguish between positive and negative length. Two examples to illustrate the model are provided below.



Examples for $(N, L) = (5, 3)$ and $(6, -2)$.

6.1 **State** the set of all possible values for the end-to-end length L of a rubber band consisting of $N = 5$ segments. 1.0 pt

SOLUTION:

The minimal length would be $-N$ and the maximal length would be N, where all segments point in the same direction. As flipping a segment induces a change of 2 in length, the possible values are then given by

$$L \in \{-N, -N+2, \dots, N-2, N\}$$

so

$$L \in \{-5, -3, -1, 1, 3, 5\}$$

1 pt for the correct solution, 0.5 pt if negative values forgotten, 0 pt for $\{-5, -4, \dots, 4, 5\}$. Also 0.5 pt if just the general values $\{-N, -N+2, \dots, N\}$ are stated.

The entropy of a system can be quantified using the Boltzmann equation:

$$S(L, N) = k_B \ln(\Omega(L, N)),$$

where $\Omega(L, N)$ corresponds to the number of distinct configurations, given a fixed value for the length L and number of particles N.

For example in the figure above, for $(N, L) = (5, 3)$ there exist $\Omega_{5,3}(N = 5, L = 3) = 5$ possible configurations, of which one is shown.

6.2 **State** the number of possible configurations $\Omega_{7,-7}(N = 7, L = -7)$. 1.0 pt

SOLUTION:

Clearly, all seven segments have to point to the negative direction to reach $L = -7$. As the segments are indistinguishable, there thus only exists one configuration, so $\Omega_{7,-7} = 1$.

1 pt for the correct solution

6.3 **Determine** the number of possible configurations $\Omega_{6,4}(N = 6, L = 4)$. 1.0 pt

SOLUTION:

One segment has to point to the negative direction while the other five segments point to the positive direction. There are $\Omega_{6,4} = 6$ possible positions for the segment that points to the negative direction.

1 pt for $\Omega_{6,4} = 6$, no reasoning required

6.4 Using the Stirling approximation: $\ln(N!) \approx N\ln(N)$, **show** that 3.0 pt

$$S(N,L) = k_B\left[N\ln(N) - \frac{N+L}{2}\ln\left(\frac{N+L}{2}\right) - \frac{N-L}{2}\ln\left(\frac{N-L}{2}\right)\right]$$

Hint: *If the order is not of concern,*

$$\binom{N}{n} = \frac{N!}{n!(N-n)!}$$

different possibilities exist to drawing n samples from N objects.

SOLUTION:

Define n_+ to be the number of segments that point in $+$ direction and thus contribute $+1$ to L and n_- to be the number of segments that point in the $-$ direction and thus contribute -1 to L. From this we obtain the equations

$$\begin{cases} n_+ + n_- = N \\ n_+ - n_- = L \end{cases}$$

which imply

$$n_\pm = \frac{N \pm L}{2}$$

From the formula sheet, we get

$$\Omega = \binom{N}{n_+} = \frac{N!}{n_+!(N-n_+)!} = \frac{N!}{n_+!n_-!}$$

and plugging in the results for n_+, n_- gives

$$\Omega(N,L) = \frac{N!}{(\frac{N+L}{2})!\,(\frac{N-L}{2})!}$$

Finally, we plug $\Omega(N,L)$ into the formula for the entropy $S(L,N)$ and get

$$S(L,N) = k_B\ln\left(\frac{N!}{(\frac{N+L}{2})!\,(\frac{N-L}{2})!}\right) = k_B\left[\ln(N!) - \ln\left(\left(\frac{N+L}{2}\right)!\right) - \ln\left(\left(\frac{N-L}{2}\right)!\right)\right]$$

which implies the provided equation through the Stirling approximation.

3 pt maximum: 1 pt for the system of equations with n_+, n_-, 1 pt for using the N choose k formula and 1 pt for the mathematical rearrangement into the desired formula.

6.5 For a fixed value of N, **determine** all values L_{min} and L_{max} for which the entropy $S(N, L)$ is minimal/maximal. 2.0 pt

SOLUTION:

Taking a look at $S = k_B \ln(\Omega)$ and knowing that the logarithm is a monotonically increasing function, we find that the smaller the value of Ω, the smaller the entropy. For $L_{\text{max}} = -N, N$ we have only one possible configuration each, which means that they have the smallest entropy.

The smaller the value of $|L|$, the more possible configurations there are, as there are many ways to bend a lot. However, $L = 0$ is not attainable for every N, which is why we have to distinguish the two cases

$$L_{\text{min}} = \begin{cases} 0 & \text{if N even} \\ \pm 1 & \text{if N odd} \end{cases}$$

Alternatively one could determine the derivative with respect to L to find the maximum at $L_{\text{max}} = 0$:

$$\frac{\mathrm{d}S}{\mathrm{d}L} = \frac{1}{2}\left[\ln\left(\frac{N+L}{2}\right) - \ln\left(\frac{N-L}{2}\right)\right] = -\frac{1}{2}\ln\left(\frac{N+L}{N-L}\right)$$

2 pt for the correct solution, doesn't matter which way it was solved. Minus 0.5 pt if not distinguished between N odd and even

6.6 Because the segments in polyisoprene interact only very weakly, we may assume that the enthalpy for different arrangements (values of the length L) remains constant: $\Delta H = 0$. Using the free energy $G = H - TS$, qualitatively **describe** the relationship between the force F required on the rubber band in order to stretch/contract it to a given length L and the number of segments N. 2.0 pt

SOLUTION:

The force is provided by the change in free energy as the length of the rubber band is changed. As H is constant, this only depends on the temperature T and on the entropy term S, of which we know the dependence on the number of segments N through the provided formula.

From this we can see that the closer L gets to $\pm N$, the larger the required force F will be. Also, the required force will increase linearly with the temperature T, as the entropy term gets more weight.

Mathematical derivation (**not required**)

The force is equal to the change in free energy as the length is changed, or in mathematical terms the derivative:

$$F = \frac{\partial A}{\partial L} = -T\frac{\partial S}{\partial L} = \frac{k_B T}{2}\ln\left(\frac{N+L}{N-L}\right)$$

The derivation of the derivative is shown in the previous solution (alternative).

2 pt maximum; 1 pt for the relationship that the force is provided by the change of free energy when the length is varied, 1 pt for realizing that the (absolute value of the) force increases as L approaches $\pm N$.

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Q6-5

English (Official)

A mathematical derivation of the formula for F from the previous task and inversion to $L(T, f, N)$ should yield the length L depending on the applied force:

$$L = N \tanh\left(\frac{F}{k_B T}\right) = N \frac{e^{\frac{F}{k_B T}} - e^{-\frac{F}{k_B T}}}{e^{\frac{F}{k_B T}} + e^{-\frac{F}{k_B T}}}$$

6.7 **Determine** and **interpret** the limit where the force applied to the rubber band approaches $+\infty$. 2.0 pt

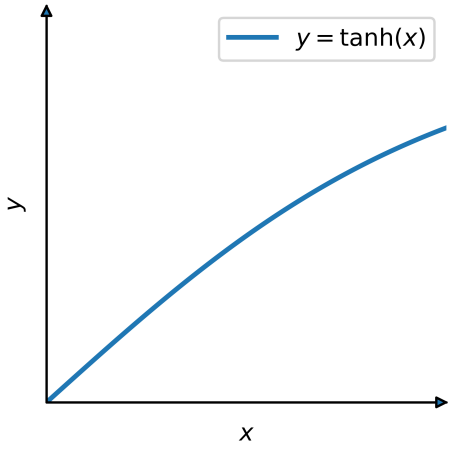
SOLUTION:

At infinite force applied, a completely stretched out chain is expected:

$$\lim_{F \to +\infty} L(T, F, N) = N$$

2 pt maximum: 1 pt for the limit N and 1 pt for some words telling that infinite force means full stretch

The temperature dependence of the length L of the rubber band when a fixed force F is applied can be described through analysis of the graph of the $\tanh(x)$ function:



6.8 **Reason** mathematically why for a fixed force $F > 0$ we have a negative thermal expansion ($|L|$ becomes smaller as the temperature rises). 3.0 pt

SOLUTION:

From the provided graph of $\tanh(x)$ it should be quickly visible, that the function is monotonically increasing. As $1/x$ is strictly monotonically decreasing, this implies that $\tanh(1/x)$ is monotonically decreasing, infering that also

$$L = N \tanh\left(\frac{F}{k_B T}\right)$$

is monotonically decreasing (as F, k_B, T are all positive). Therefore the rubber band will contract upon heating when the applied force F remains constant.
Alternatively (**not required**), one could use derivatives:

$$\frac{\partial L}{\partial T} = \frac{N}{\cosh^2\left(\frac{F}{k_B T}\right)}\left(-\frac{F}{k_B T^2}\right) < 0$$

as the terms N, F, k_B, T^2 and $\cosh^2\left(\frac{F}{k_B T}\right)$ are all greater than zero.

3 pt maximum: 1 pt for stating something like that the graph is monotonically increasing, 1.5 pt for making the connection that $\tanh(1/x)$ therefore must be decreasing, 0.5 pt for stating that the other constants are positive
Full mark for the alternative solution involving the derivative (1 pt for the derivative expression, 1.5 pt for solving it, 0.5 pt for highlighting the positive constants)

6.9 **Explain** the negative thermal expansion (that smaller $|L|$ values are more favorable at higher temperature) in thermodynamic (phenomenological) terms. 1.0 pt

SOLUTION:

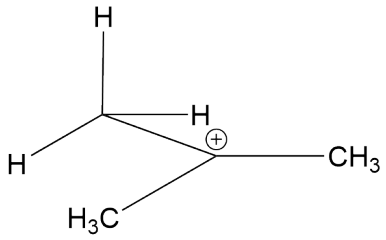
The thermodynamic behaviour is determined by minimizing the free energy $F = H - TS$. This means that as the temperature prows higher, more weight is given to the entropy term TS, which in turn is higher for smaller $|L|$ thanks to more possible configurations. This manifests in the negative thermal expansion of rubber bands.

Carbocation Intermediate

20.5 pts

Introduction

In this problem we're going to deal with reactions involving a common unstable intermediate, which is the carbocation. Although elusive for long, the study of carbocations earned George Olah the Nobel Prize in 1994.



7.1 For the molecule in the figure above, **predict** the hybridization of the carbon that bears the positive charge. 0.5 pt

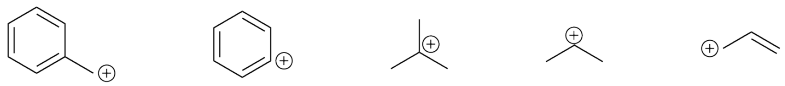
SOLUTION:

sp^2

There are only 3 bonds around the carbocation and no lone pair, which indicate it requires three sp^2 orbitals for bonding and one leftover p orbital that stays empty. This gives it a flat, trigonal planar shape.

Carbocations are unstable because they do not obey the octet rule. However, they can be stabilized either by resonance or an effect called hyperconjugation, in which the σ-bond of the neighbouring C–H and C–C bonds donate their electron density to the carbocation.

7.2 **Compare** the stability of the following carbocations, with either (>) or (<) sign to indicate the more stable carbocation. 2.5 pt



1 **2** **3** **4** **5**

SOLUTION:

3 < 1

4 < 5

4 > 2

5 < 1

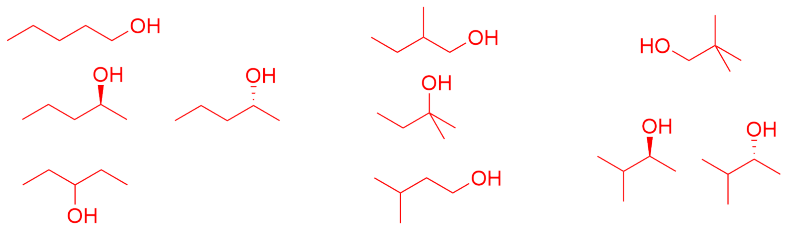
1 > 2

0.5 pt per correct assignment.
Phenyl carbocation is very unstable because the positive charge cannot be shared with the benzene ring. Unlike other carbocations, where nearby electrons can help stabilite the charge, the structure of benzene prevents this, making the phenyl carbocation much less stable.

Carbocations can be produced by elimination of water from alcohols under acidic conditions. Usually H_2SO_4 is employed because it also has dehydrating properties, which promote the formation of carbocations.

7.3 From the chemical formula $C_5H_{12}O$, **determine** how many isomers n_{isom} (including stereo- and regioisomers) are alcohols and **draw** their structures. 2.5 pt

SOLUTION:

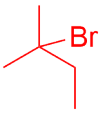


8 regioisomers of which 2 are chiral (have enantiomers), which makes a total of 10 isomers.
If all the linear chain alcohols are drawn, 1 pt. If all the methyl-containing alcohols are drawn along with all the linear chain alcohols, 1.5 pts. In case the enantiomer is not mentioned but all isomers has been drawn, 2 pts.

Interestingly, 2-methylbutan-2-ol and 3-methylbutan-2-ol yield the same cationic intermediate and thus also the same product when treated with HBr.

7.4 **Draw** the structures of the intermediate and the product of the reaction with HBr mentioned above. 1.0 pt

SOLUTION:

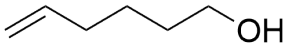
Intermediate	Product
	

0.5 pt for each correct structure

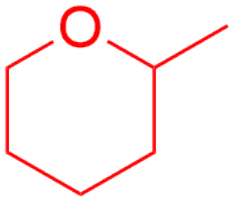
Reactions

Carbocations may react with nucleophilic moieties that exist in the same molecule, giving rise to a cyclic product through an intramolecular reaction.

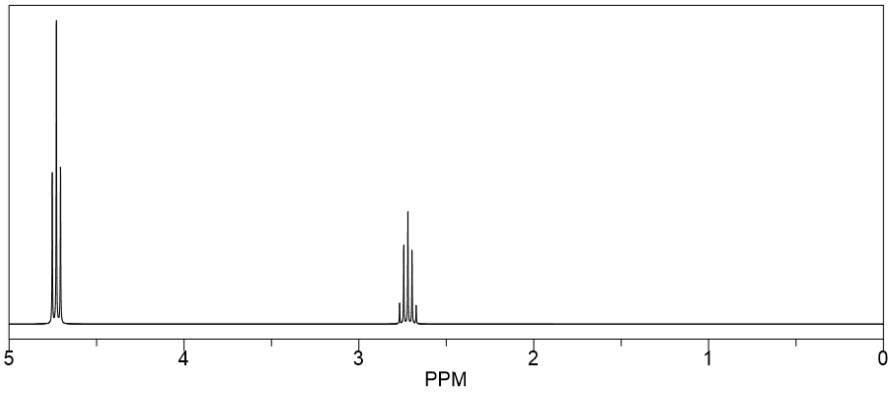
7.5 **Draw** the structure of the major product when the compound shown below is treated with H_3PO_4. The OH group is observed to be present in the carbocation intermediate and the product has been determined to be a heterocyclic compound. 1.0 pt



SOLUTION:

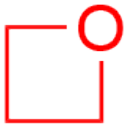


Cyclic building blocks are very common in organic reactions, both as intermediates and precursors. Here is an ^{1}H-NMR spectrum of a simple cyclic ether **A** with $\%w(\mathrm{C}) = 62.0\%$ and $\%w(\mathrm{H}) = 10.3\%$.



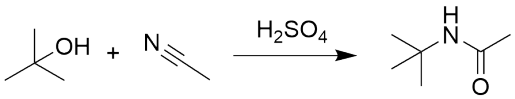
7.6 **Draw** the structure of the organic compound **A** based on the NMR spectrum and data given. 2.0 pt

SOLUTION:



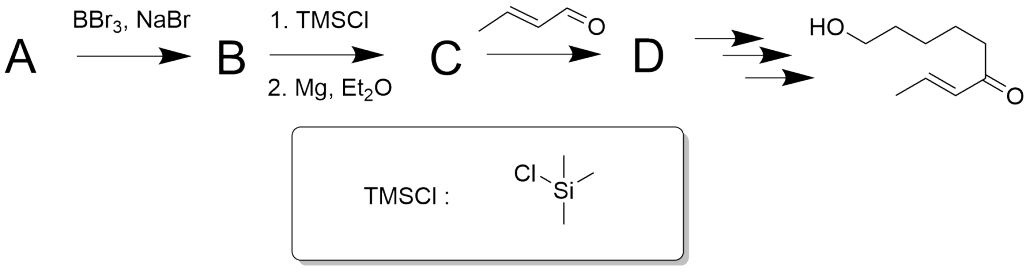
2 pt for the correct structure, 1 pt for just the molecular formula C_3H_6O.

Another reaction that utilizes a carbocation intermediate was discovered by John J. Ritter in 1948. In the Ritter reaction, an amide is generated through nitrile attack on a carbocation, followed by hydrolysis and keto-enol tautomerization.

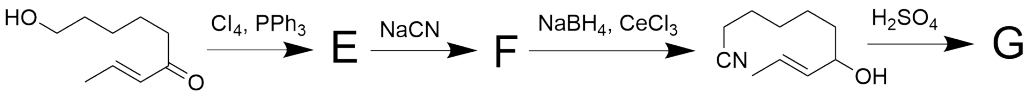


With this reaction in mind, let's synthesize a fascinating cyclic amide from the cyclic ether **A** encountered previously.

Compound **A** is treated with BBr_3 to generate a haloalcohol **B**, which is protected by a silyl derivate and converted into a very famous reagent in organic synthesis **C**. The scientist who first discovered this reagent was awarded with Nobel Prize in Chemistry in 1912. After that, **C** is reacted with an aldehyde to generate product **D**, which will be transformed further more.

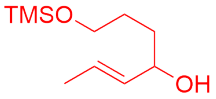
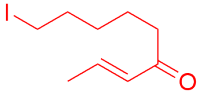
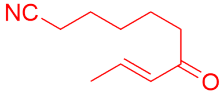
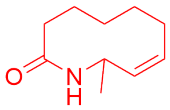


After deprotection and homologation, the compound is subjected to the Appel reaction using carbon tetraiodide (CI_4) to yield **E**, which then undergoes an S_N2 reaction, providing **F**. The alcohol obtained through Luche reduction of **F** then produces a heterocyclic compound **G** through the Ritter reaction, which was catalyzed by H_2SO_4.



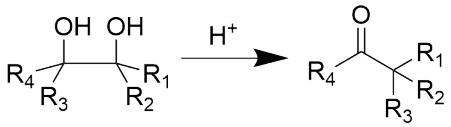
7.7 **Draw** the structures of compounds **B-G**. 6.0 pt

SOLUTION:

B 	C 	D 
E 	F 	G 

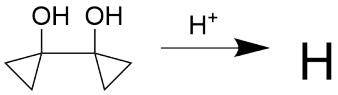
1 pt for each correct structure. 0.5 pt if something insignificant is missing. Cascade mistakes are to be punished only for the initial mistake.

Another reaction that involves a carbocation is the pinacol rearrangement and it goes as follows:

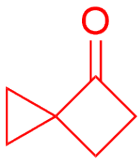


In a first step, the alcohol is protonated, yielding a carbocation through the elimination of water. The adjacent hydroxyl group then donates its lone pair, forming a C=O bond and causing an alkyl shift to form a quarternary center.

7.8 **Draw** the structure of the product **H** in the following transformation. 1.0 pt

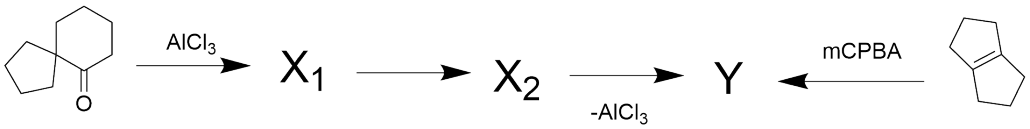


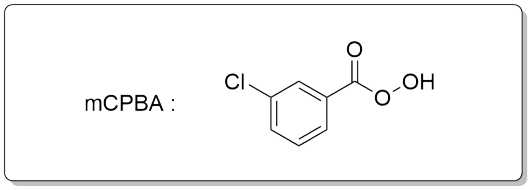
SOLUTION:



If the structure has a ketone functional group, 0.5 pt. If the structure has a four-membered ring and a three-membered ring, 0.5 pt.

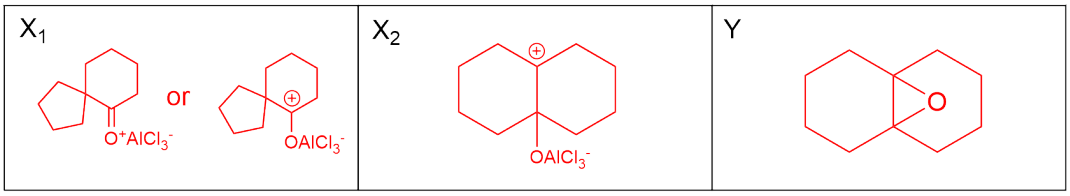
Lastly, a product of a similar transformation was subjected to a Lewis acid, which leads to a rearrangement to generate a tricyclic structure **Y**. Additionally, **Y** can be produced by the reaction of mCPBA (*meta*-chloroperoxybenzoic acid) with a bicyclic alkene as follows.





7.9 **Draw** the structures of intermediates $\mathbf{X_1}$, $\mathbf{X_2}$, and product **Y**. 3.0 pt

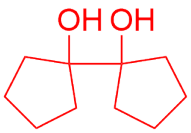
SOLUTION:



1 pt for each correct structure with charge. The total charge should be 0 and the distribution of charge should make sense. If it has a minor mistake but follows the guideline, 0.5 points.

7.10 **Draw** the precursor of the ketone, assuming it was formed through a pinacol rearrangement. 1.0 pt

SOLUTION:



If the structure has only 2 adjacent alcohol groups, 0.5 pt. If there are 2 five-membered rings, 0.5 pt

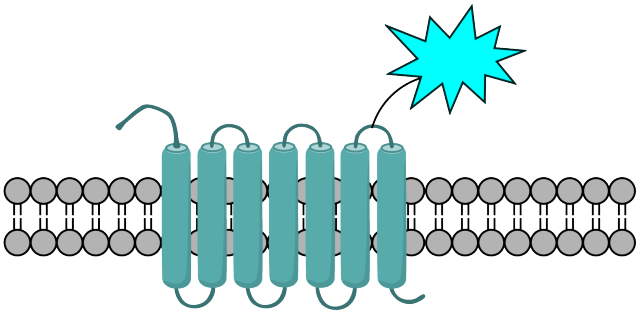
CHEMISTRY.
OLYMPIAD.CH
CHEMIE-OLYMPIADE
OLYMPIADES DE CHIMIE
OLIMPIADI DELLA CHIMICA

Q8-1

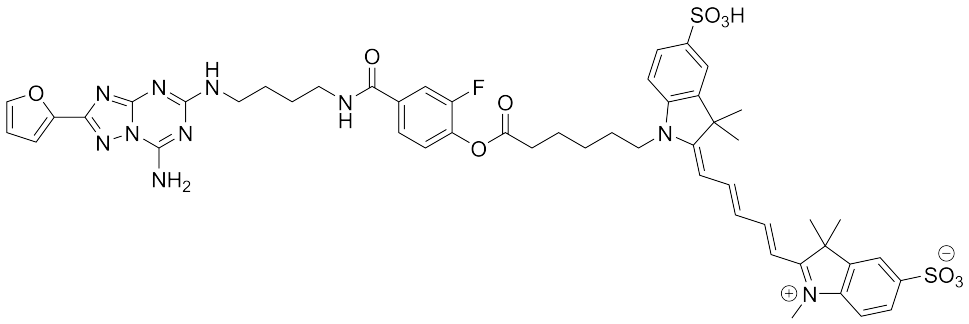
English (Official)

Can You See Me? 19.5 pts

Introduction



Seeing is believing. The fluorescent labeling of biomolecules allows scientists, among other things, to track the localisation and the dynamics of production and degradation of these molecules. Labeling methods have become better and more specific over time. In this task, you will learn about ligand-directed covalent labeling of a cell-surface receptor and the requirements of such a probe to fulfill the desired function. In this approach, a small molecule, the ligand, binds reversibly to the receptor. Upon binding, the probe can then react with nucleophilic residues of the protein, which leads to the formation of a covalent bond and thus irrversible labeling. The probe you will be analysing is shown below.

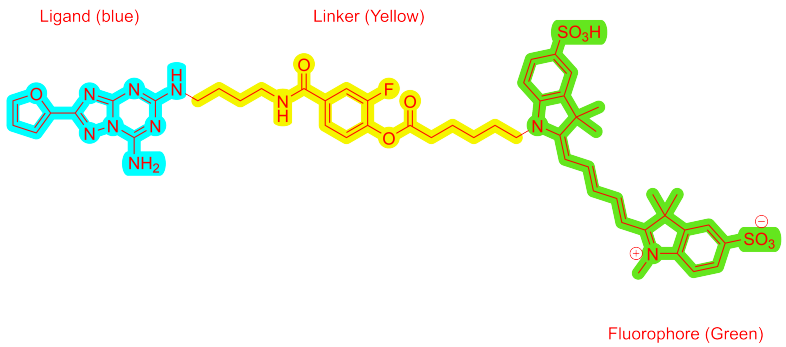


Probe Properties

The probe is composed of three parts: A ligand, a fluorophore and a linker with a reactive moiety. The ligand will bind to the receptor in a reversible fashion. The fluorophore will ultimately be the observable entity and the linker connects the two parts and contains the reactive handle, which will lead to covalent labeling.

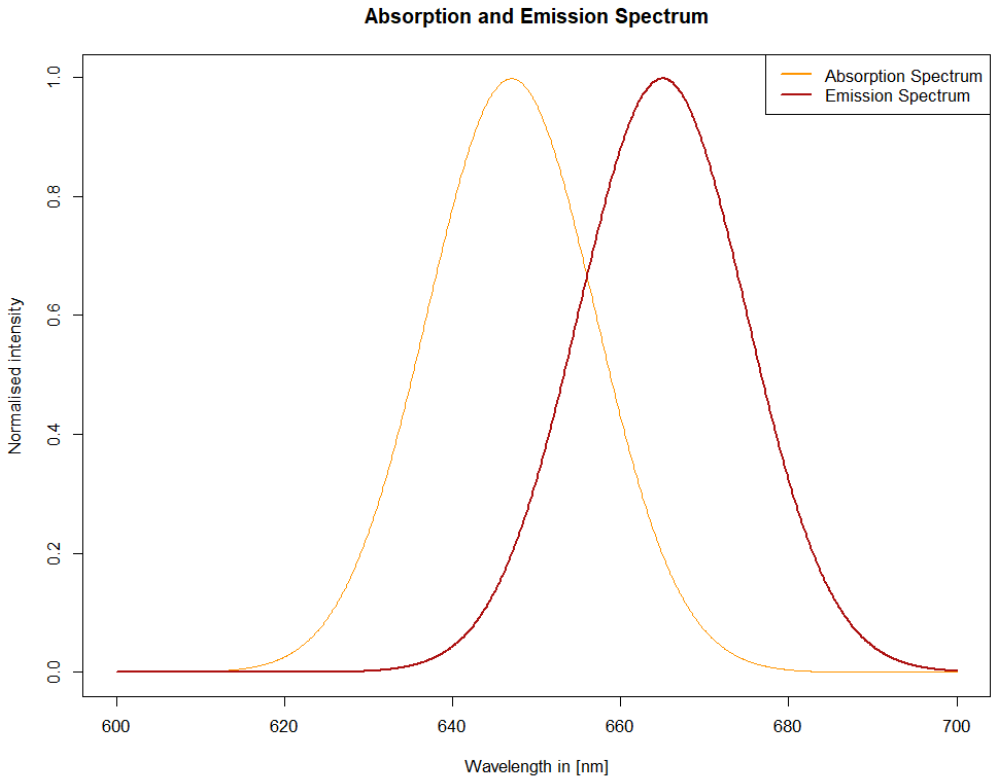
8.1 Below, the probe is shown again. **Identify** and **clearly mark** ligand (I), fluorophore (II) and linker (III) in the molecule below. 1.5 pt

SOLUTION:



0.5 pt for each correctly identified part. Be generous with the margins of the parts they indicate. Full points as long as the marked section is roughly correct. However, what will give deduction of points is, if not the whole conjugated system is marked as fluorophore, this any chemist should be able to rationalise and see, which parts are connected through conjugation. But f.ex. if the nitrogen atom of the ligand, connected to the linker is marked as linker or ligand, will both be awarded full points.

A special characteristic property of a fluorophore is the so-called Stokes shift. The Stokes shift is the difference in the maximum of the emission vs. absorption wavelength of the fluorophore. Below, the absorption and emission spectrum of our probe is shown.



Absorption and emission spectrum of our probe.

8.2 From the provided spectrum, **estimate** the Stokes shift $\Delta\lambda$ of your probe in nm. 1.0 pt

SOLUTION:

$\Delta\lambda = 20\,\text{nm}$

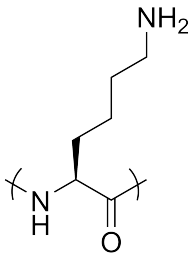
$\lambda_{abs} = 645\,\text{nm}$

$\lambda_{em} = 665\,\text{nm}$

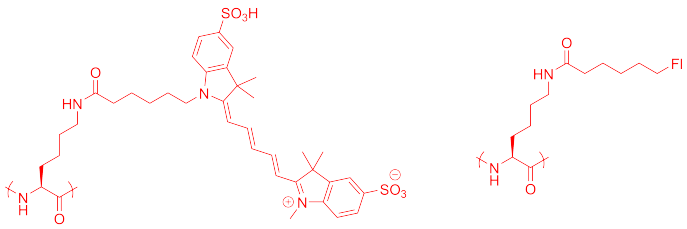
Anything ± 5 nm will be accepted with full points.

Upon binding of the ligand to the receptor, a lysine residue in the vicinity of the binding pocket can react with the probe. The lysine residue reacts with the reactive handle in the linker of the probe to form a stable covalent bond, labeling the receptor.

8.3 Below, a lysine residue is shown. **Draw** the product of the reaction between the lysine side-chain and the probe. You may use the structure below as a template to complete your drawing. Further, you may use the abbreviations -L for ligand and -Fl for fluorophore. 2.0 pt



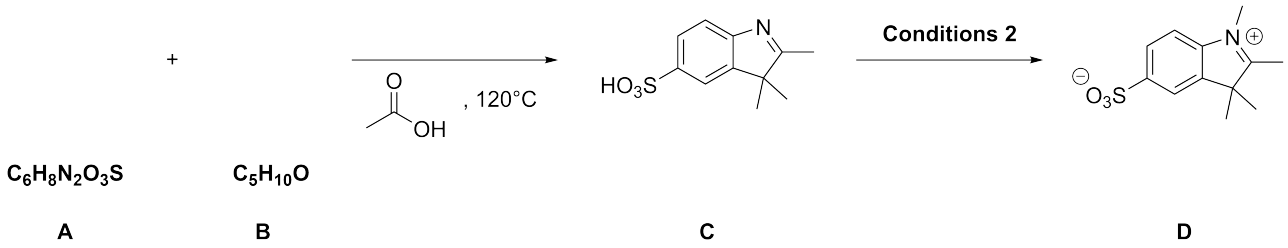
SOLUTION:



2.0 pt for correct structure. Any other suggestion may be evaluated on a case by case basis. F.ex. if a student attacks the amide bond of the linker part instead of the ester, maybe 0.5 pt could be awarded. -0.5 pt if they use the template lysine provided but don't correct for the one proton they have to loose in order to obtain a neutral amide bond.
No points if just an amide bond is drawn and the linker part, where it's connected to isn't shown!

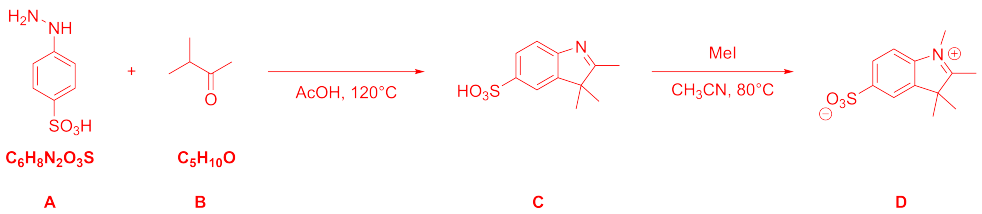
Probe Synthesis

Let's take a closer look at the synthesis of the probe. Different parts of the probe are synthesised separately and connected in the end. In the scheme below, the synthesis of one part of the probe is shown.



8.4 According to the scheme above, please **provide** the structures of compounds **A** and **B**. **Hint:** *In the transformation to compound* **C**, *a gas is released.* 2.0 pt

SOLUTION:

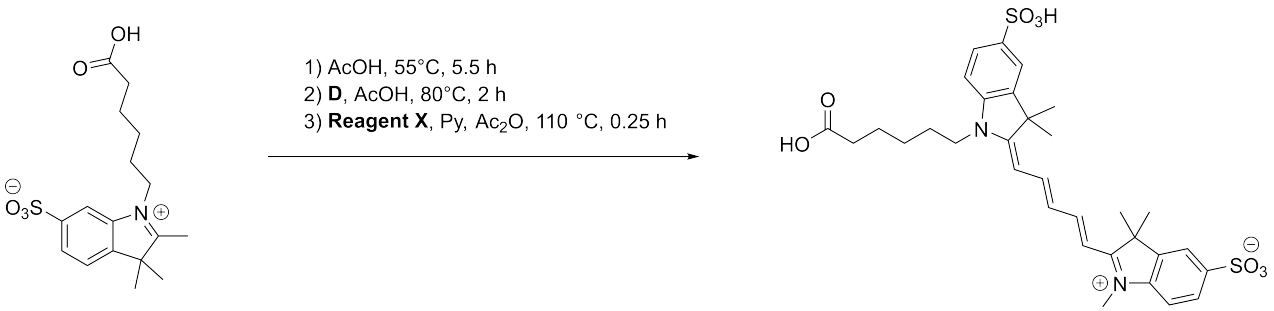


1 pt each. Other provided structures should be evaluated on a case by case basis, however, at least the sum formula provided has to be correctly respected in order for them to get any points.

8.5 From the list below, **choose** the most suitable conditions for the transformation of compound **C** to compound **D**. 1.0 pt

SOLUTION:

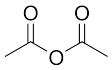
Option 3 is correct and will be awarded 1 pt. Anything else will not lead to methylation of the nitrogen and will thus be awarded no points.



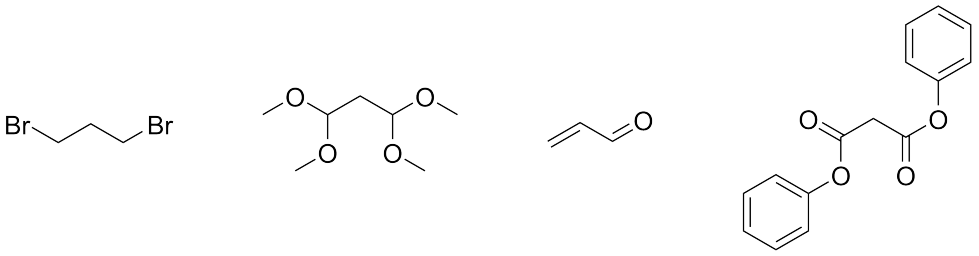
E **F**

AcOH = 

Py = 

Ac_2O = 

8.6 From the options below, **choose** a suitable **Reagent X** for the transformation of compound **E** to compound **F**. 1.0 pt

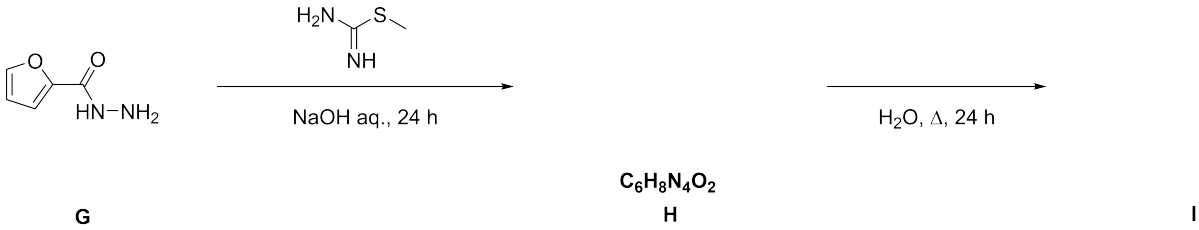


☐ ☐ ☐ ☐

SOLUTION:

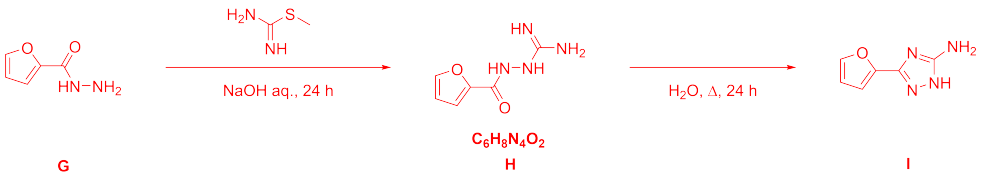
Option 2) is correct and will give 1 pt. The other options would not work already just looking at the required oxidation states of the carbon centers.

Let's take now a look at the synthesis of another part of the molecule. In the scheme below, a synthetic outline for that part is shown.



8.7 **Draw** the structures of compounds **H** and **I**. **Hint:** *In the transformation of compound* **H** *to* **I**, *one equivalent of water is lost from the molecule.* 2.0 pt

SOLUTION:



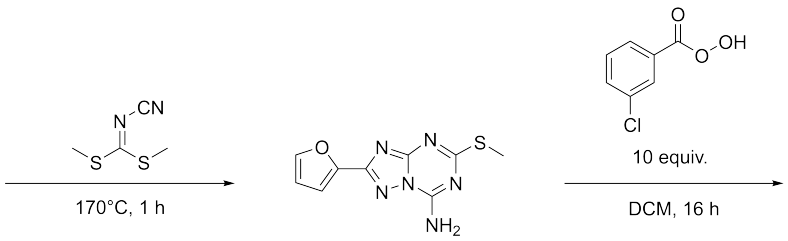
1.0 pt each. Full point is also awarded, if the previous structure was already wrong but the chemical transformation still makes sense given the conditions and as long as the chemical formula, if given, is still correct i.e. they need to loose an equivalent of water for the transformation of H to I.

8.8 What is the driving force for the transformation of compound **H** to **I**? **Select** the appropriate answer from the list below. 1.0 pt

SOLUTION:

Option 4 cannot be a driving force here, as the reaction is run in aqueous solution.

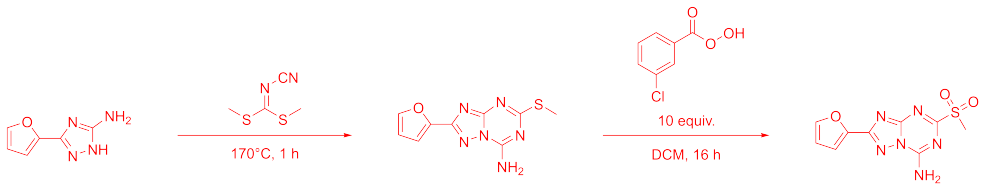
Option 3 is correct and will give 1 pt.



I J $C_9H_8N_6O_3S$ K

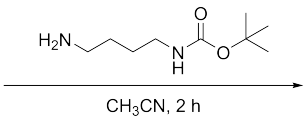
8.9 **Draw** the structure of compound **K.** 1.0 pt

SOLUTION:



I J $C_9H_8N_6O_3S$ K

1 pt for the correct structure. Other structures with f.ex. oxidation of amines may be awarded partial points and should be judged on a case by case basis. The molecular formula should still be in accordance with the one provided.

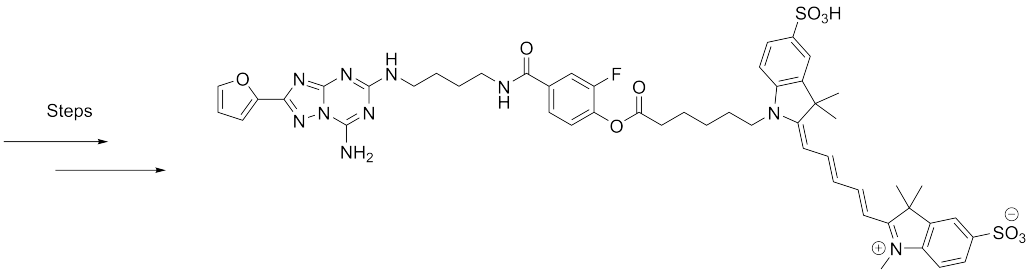


$C_9H_8N_6O_3S$

K

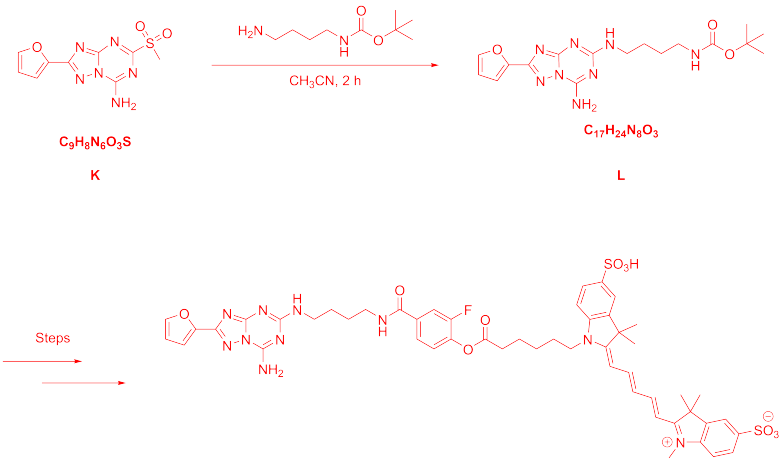
$C_{17}H_{24}N_8O_3$

L



8.10 **Draw** the structure of compound **L**. 1.0 pt

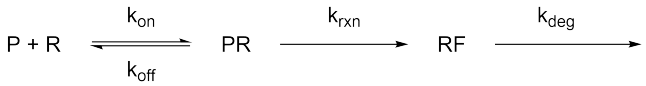
SOLUTION:



1 pt for the correct structure. Full point is also awarded, if the previous structure was already wrong but the chemical transformation still makes sense given the conditions and as long as the chemical formula, if given, is still correct.

The Labeling Reaction

Now, we'll take a closer look at the labeling reaction and what is needed in order for us to actually see the receptor. Below, a schematic representation of the labelling process is shown. In a first step, the probe, P, binds to the receptor, R, in a reversible equilibrium forming the probe-receptor complex, PR. If the probe is bound, it can also react with a close-by lysine residue in an irreversible fashion, leading to the fluorescent labeling of the receptor, RF. The cell constantly produces and degrades this receptor. The receptor, independent of whether it is labelled or not, is degraded in a zeroth-order reaction with a rate constant k_{deg}.



For the following tasks, you may use the following assumption and values:

- The receptor and probe are in a rapid equilibrium of binding, while the formation of RF from PR is much slower.
- The total receptor concentration is kept constant by the cellular regulatory processes and can be assumed to be 3 µmol L^{-1}, $[\text{R}]_{\text{tot}} = 3\ \mu\text{mol L}^{-1}$.
- The dissociation constant of the probe-receptor complex is 50 µmol L^{-1}: K_D = 50 µmol L^{-1}.
- The maximum concentration of the probe you can use is 6 µmol L^{-1}, $[\text{P}]_{\text{max}}$ = 6 µmol L^{-1}.

8.11 **Derive** an equation for the change in concentration of the labeled receptor, $\frac{\text{d}[RF]}{\text{d}t}$, using the equilibrium concentrations of [P], [R] and the given rate and equilibrium constants. 2.0 pt

SOLUTION:

The final correct expression is: $\frac{\text{d}[RF]}{\text{d}t} = k_{\text{rxn}} \cdot \frac{1}{K_D} \cdot [P] \cdot [R] - k_{\text{deg}}$

This can be derived from:

$\frac{\text{d}[RF]}{\text{d}t} = k_{rxn} \cdot K_{Eq} \cdot [P] \cdot [R] - k_{deg} = k_{rxn} \cdot [PR] - k_{deg}$

And they just assume a fast equilibrium of receptor binding, where we have

$K_{Eq} = \frac{[PR]}{[P] \cdot [R]} = \frac{1}{K_D}$

- 2.0 pt for $\frac{\text{d}[RF]}{\text{d}t} = k_{\text{rxn}} \cdot \frac{1}{K_D} \cdot [P] \cdot [R] - k_{\text{deg}}$
- -1.0 pt if the degradation term is missing
- 1.0 pt if they only have: $\frac{\text{d}[RF]}{\text{d}t} = k_{rxn} \cdot [PR] - k_{deg}$

From a different experiment, you have established that the half-life time of your receptor on the cell surface is 240 min. The formula for the half-life time of a zero-order process is given below.

$$t_{1/2} = \frac{[\mathrm{R}]_0}{2 \cdot k_{\mathrm{deg}}}$$

8.12 Considering all the information given above, **calculate** the value of k_{deg} in mol L^{-1} s^{-1}. 1.0 pt

SOLUTION:

We know already that the recycling process is zeroth order in receptor. Thus, we can use the formula for the half-life for zeroth order processes.

$t_{1/2} = \frac{[R]_0}{2 \cdot k_{deg}}$

$k_{deg} = \frac{[R]_0}{2 \cdot t_{1/2}}$, with $[R]_0$ = 3 µM

Using these equations you get a value of $1.0417 \cdot 10^{-10} M \cdot s^{-1}$

- 0.5 pt for correct formula for k_{deg} but wrong value
- 1 pt if correct value is reported

8.13 Consider the very start of the labeling reaction, just after addition of the probe. **Calculate**, in s^{-1}, the value k_{rxn} needs to have at least, so we can observe any labeling at all. 2.0 pt

In case you couldn't solve the previous questions, assume:

- $\frac{d[RF]}{dt} = \frac{k_{rxn} \cdot K_D \cdot [P]}{[R]} - k_{deg}$
- $k_{deg} = 2.00 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}$

SOLUTION:

At the very beginning:

$\frac{d[RF]}{dt} = k_{rxn} \cdot \frac{1}{K_D} \cdot [P]_{max} \cdot [R]_{tot} - k_{deg}$

Thus, this experssion has to be > 0 to observe any labeling at all:

$0 < k_{rxn} \cdot \frac{1}{K_D} \cdot [P]_{max} \cdot [R]_{tot} - k_{deg}$

We want to get a value for k_{rxn}:

$k_{rxn} > \frac{k_{deg} \cdot K_D}{[P]_{max} \cdot [R]_{tot}}$

Using this formula, we arrive at a minimal value of $2.89 \cdot 10^{-4} s^{-1}$

If they use the provided k_{deg}, they get a minimal value of: $55.56 s^{-1}$

If they use the provided formula for $\frac{d[RF]}{dt}$, they should arrive at the same conclusions and ultimately:

$k_{rxn} > \frac{k_{deg} \cdot [R]_{tot}}{K_D \cdot [P]_{max}}$

Using this equation, they get a minimal value of: $1.04 \cdot 10^{-6} s^{-1}$

If they use both the provided equation and value for k_{deg}, they get a minimal value of: $0.2 s^{-1}$

- 1.5 pt if correct formula but wrong value. Full points are awarded, if the reasoning of the student is correct but they somehow had a wrong formula in the previous part already for the change in [RF]. Please try to evaluate these on a case by case basis
- 0.5 pt if the student clearly shows that the change in [RF] needs to be > 0 at the start of the labeling reaction with all the initial concentration. Independently of whether the formula or final value of the rate constant are correct.

You have performed your labeling experiment and it seems to work. However, you're not quite satisfied with the labeling you can achieve and you would thus like to increase the initial rate of labeling.

8.14 From the options below, **choose** which strategies could be worth investigating to achieve this. 1.0 pt

SOLUTION:

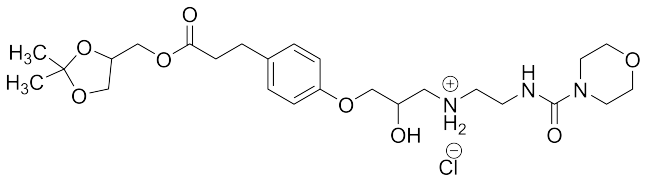
A larger fluorophore will probably not have much of an influence on the reaction rate with the probe and we can't change the solvent system, if we want the cells to survive.

Options 1 and 3 are correct and will each give 0.5 pt. For each wrong selected option: -0.5 pt. Minimal amount of points you can get is 0.

Landiolol - a Cardioselective Beta-Blocker 16.0 pts

Introduction

Every year, the food and drug administration (FDA) in the USA approves new therapeutics. In 2024, Landiolol, a beta-blocker, was approved for the treatment of supraventricular tachycardia. Landiolol was developed in Japan and already approved in Germany as a drug in 2017. As of 2024, Landiolol is the most cardioselective beta-blocker known. The structure of Landiolol is shown below.

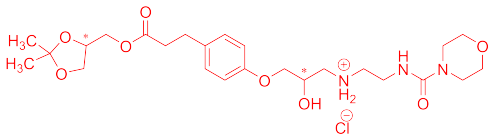


Stereochemistry

Landiolol is a chiral molecule, containing more than one stereocenter. As it is the case with almost any approved drug, Landiolol is administered as a single stereoisomer. Due to the inherent chiral nature of biological systems, different stereoisomers, even entantiomers, can have very different activity, which is why the different stereoisomers will have to be evaluated independently for their activity and possible off-target effects.

9.1 In the structure of Landiolol, **mark** all stereogenic centers with an asterisk (*). 1.0 pt

SOLUTION:



0.5 pt for each correctly indicated stereocenter. Full points are also awarded if the student clearly marks the stereocenter with something else than a star.

9.2 **Calculate** how many stereoisomers Landiolol can have. 0.5 pt

SOLUTION:

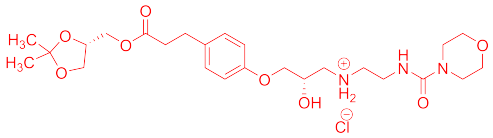
$$2^x = N_{stereoisomers} \quad (1)$$

x is the number of stereocenters. Since x = 2 in our case, the number of possible stereoisomers is 4.

1.0 pt as long as the number of stereoisomers matches the number of stereocenters the student marked in the previous question.

9.3 In the FDA-approved structure of Landiolol, all stereocenters are *S*-configured. **Draw** the structure of Landiolol with the correct stereochemistry at all stereogenic centers. **Note:** *You may abbreviate parts of the molecule, which are not relevant for stereochemistry with -R or use the template of Landiolol provided below.* 2.0 pt

SOLUTION:



During the marking process, really make sure to determine the stereochemistry of the drawn stereocenter since the students might draw the molecule slightly different than it is depicted in the solution.

1.0 pt for each correctly drawn stereocenter. No points and also no point deduction if wrong "stereocenters" are also indicated that were propagated from the previous questions.

Theoretical Final Exam 2025

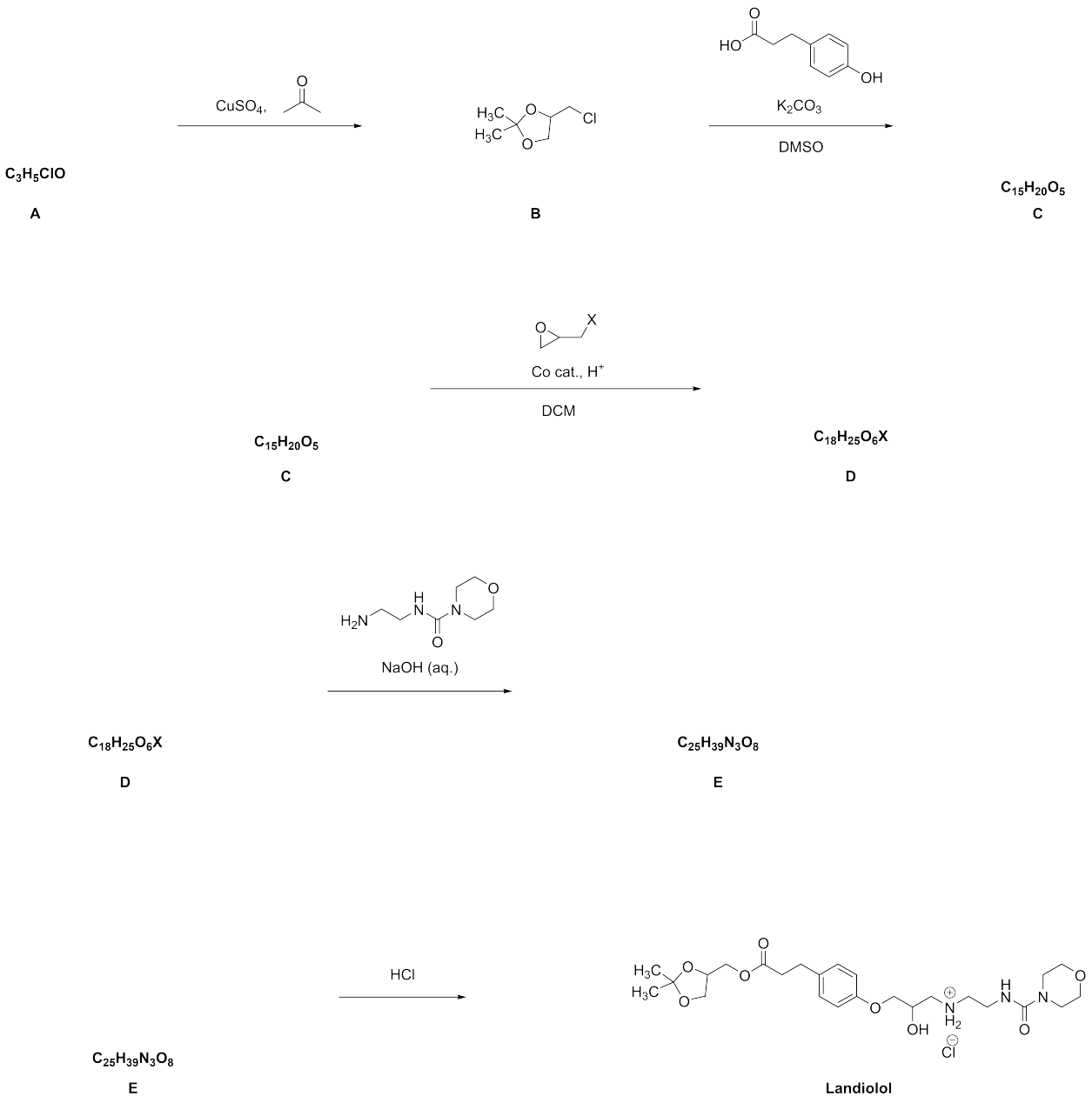
CHEMISTRY.
OLYMPIAD.CH
CHEMIE-OLYMPIADE
OLYMPIADES DE CHIMIE
OLIMPIADI DELLA CHIMICA

Q9-3

English (Official)

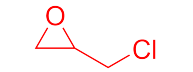
Synthesis of Landiolol

In the figure below, a synthetic strategy for Landiolol is depicted. The synthetic sequence starts from enantiomerically pure epichlorohydrin. In the following tasks, you will be asked to complete this synthetic scheme step by step.



9.4 **Draw** the structure of epichlorohydrin, compound **A**. 1.0 pt

SOLUTION:

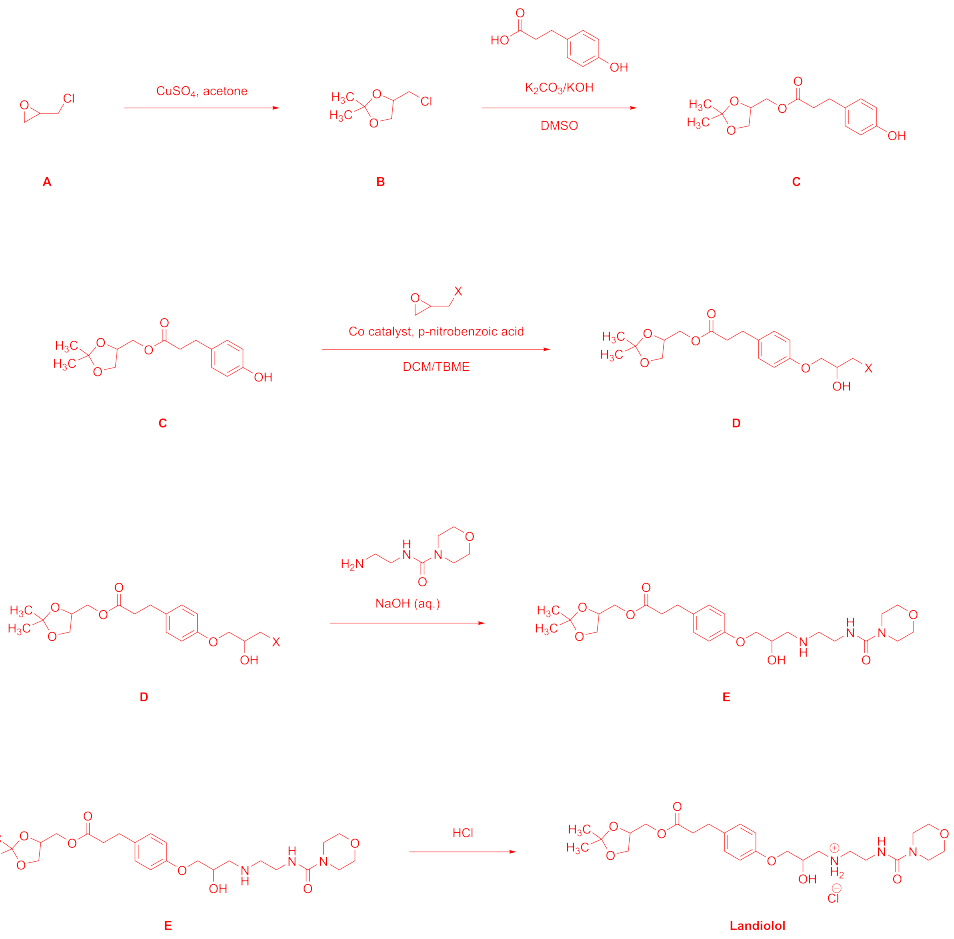


Epichlorohydrin

1.0 pt for the correct structure.

9.5 **Give** the structures of compounds **C**, **D** and **E**. 3.0 pt

SOLUTION:

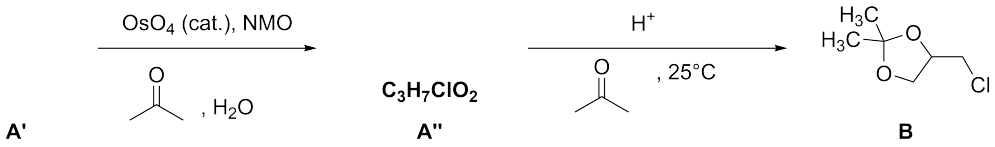


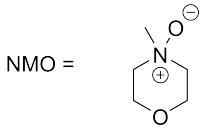
1.0 pt for each correct structure. Full point is also awarded, if the previous structure was already wrong but the chemical transformation still makes sense given the conditions and as long as the chemical formula, if given, is still correct.

9.6	For the transformation of compound **C** to **D**, **suggest** a suitable substituent **X** to enable this transformation. **SOLUTION:** Known for this transformation are: halogens (except -F), a $C_1 - C_3$ alkylsulfonic or $C_6 - C_{10}$ arylsulfonic ester. Not accepted are things like: -OMe, -OAc, -NHAc, alkyl or aryl substituents. Any other creative idea may be evaluated on a case by case basis. 1.0 pt for a correct and plausible answer.	1.0 pt

Synthesis of Individual Building Blocks

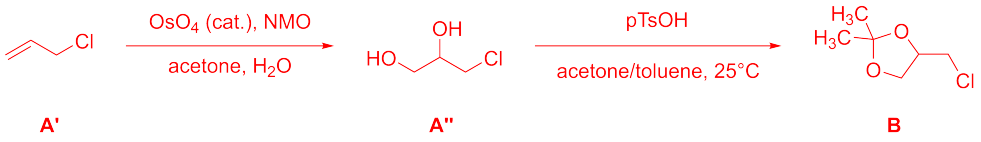
Unfortunately, your supplier of epichlorohydrin, compound **A**, has run out of stock of this chemical building block. Thus, you have to come up with a different route for compound **B**. Lucky you, one of your interns in your company has seen this coming and already come up with a possible solution. However, his notes are hard to read and you have to fill the gaps now. The synthetic scheme is shown below:





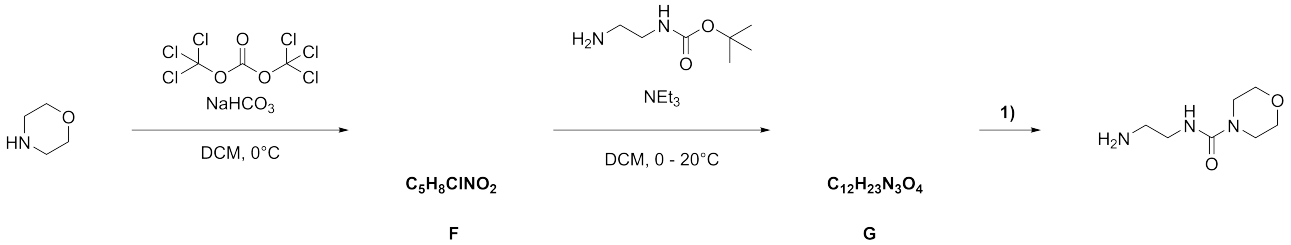
9.7 **Draw** the structures of the compounds **A'** and **A''**. **Hint:** ***A'*** *contains only one heteroatom.* 2.0 pt

SOLUTION:



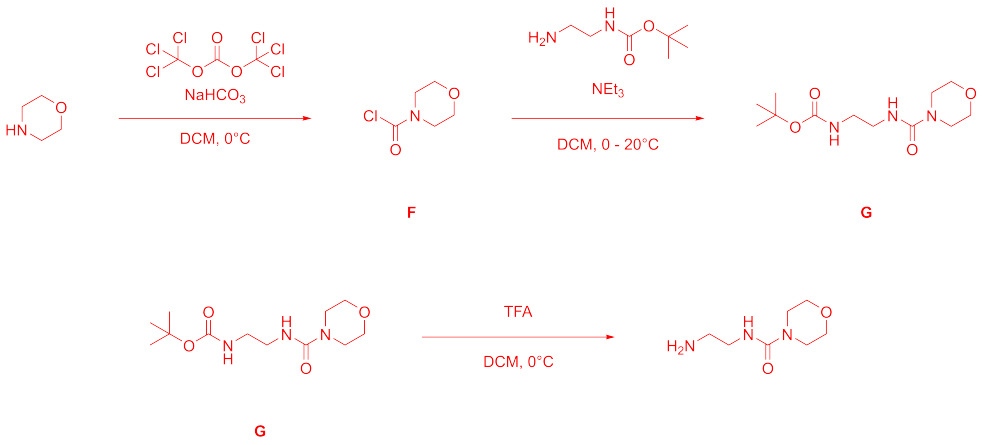
1.0 pt for each correct structure. Full point is also awarded, if the previous structure was already wrong but the chemical transformation still makes sense given the conditions and as long as the chemical formula, if given, is still correct.

Some of the reagents used in the synthetic scheme above are not available from commercial sources at reasonable prices. Thus, let's take a closer look at the synthesis of the amine used in the transformation from compound **D** to **E**. A synthetic scheme is provided below. The synthesis starts form morpholine, which is commercially available.



9.8 **Draw** the structures of the missing intermediates **F** and **G**. 2.0 pt

SOLUTION:



1.0 pt for each correct structure. Full point is also awarded, if the previous structure was already wrong but the chemical transformation still makes sense given the conditions and as long as the chemical formula, if given, is still correct.

9.9 For the transformation **1)** **select** the most suitable reaction conditions from the options below: 1.0 pt

SOLUTION:

- ☐ $LiAlH_4$, THF, -78°C
- ☐ $KMnO_4$, H_2SO_4 (aq.), 25°C
- ☒ trifluoroacetic acid, DCM, 0°C
- ☐ K_2CO_3, DMF, 80°C
- ☐ $Pd(PPh_3)_4$, benzene, 35°C

1.0 pt for the correct answer. Multiple answers are awarded 0 pt.

CHEMISTRY.
OLYMPIAD.CH
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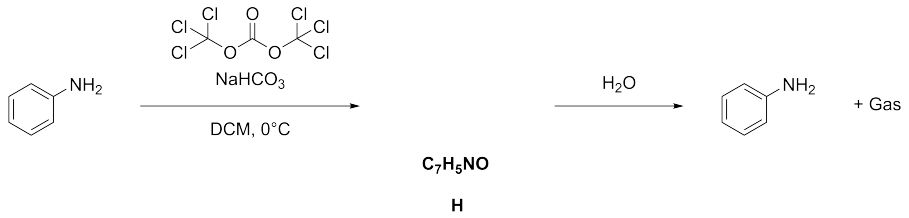
OLYMPIADES DE CHIMIE
OLIMPIADI DELLA CHIMICA

Q9-8

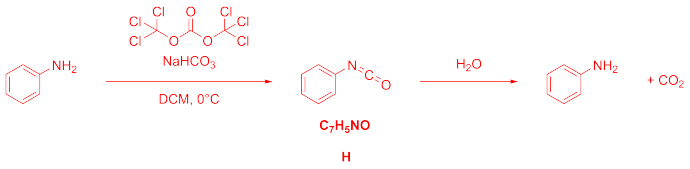
English (Official)

If instead of a secondary amine, a primary amine is subjected to the conditions for the formation of compound **F**, a slightly different product is obtained. This is illustrated in the example with aniline below. Both compound **F** and compound **H** are not stable towards moisture and will react with water under the release of a gas back to the initial amine starting material.



9.10 **Draw** the structure of compound **H**. 1.0 pt

SOLUTION:



1.0 pt for correct structure. However, if compound F was already wrong above, and the given product kind of makes sense, given what the student has written above, partial or even full points can be awarded, as long as the chemical formula is still correct.

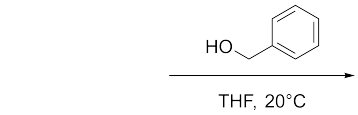
9.11 **Provide** the name or chemical formula of the gas released upon hydrolysis of compound **H**. 0.5 pt

SOLUTION:

The released gas is CO_2. They should be able to arrive at this solution already by just balancing the stoichiometric equation.

0.5 pt for correct answer.

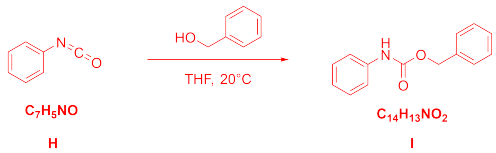
Both compound **F** and compound **H** react with a variety of nucleophiles. In case of the nucleophile being an alcohol, a stable linkage between the two moieties is formed. This type of linkage is often encountered in peptide chemistry.



C_7H_5NO (H) $\qquad$ $C_{14}H_{13}NO_2$ (I)

9.12 **Draw** the structure of compound **I**. 1.0 pt

SOLUTION:



C_7H_5NO (H) $\qquad$ $C_{14}H_{13}NO_2$ (I)

1.0 pt for correct structure.