51. Austrian Chemistry Olympiad
National competition

Theoretical Exam
26 May 2025

Name

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Problem 1 (I. Stadler-Ulitsch) **5 Points**

Radioactive and Inorganic

A. All About Radon

Radon is an invisible, odourless, radioactive noble gas. The air we breathe outdoors, indoors, and especially in underground caves contains a mixture of radon and its decay products. Radon thus contributes to the natural radiation exposure of humans and, due to its short-lived decay products, is responsible for approximately 10 % of all bronchial carcinomas.

The decisive nuclide is radon-222. It is produced by alpha decay from a parent nucleus, decays with a half-life of 3.8 days, and after several decays eventually forms lead-206.

1.1 State the number of α and β^- decays between Rn-222 and Pb-206.

α-decays	β^--decays

1.2 Write the equation for the formation of Rn-222 from its parent nucleus.

1.3 Calculate the mass of the Rn-222 atom, whose nuclear binding energy is 1714 MeV. Give your result in atomic mass units (u) to three decimal places and show which values or constants you use.

In a residential space, the Rn-222 concentration resulted in an activity of A = 50 Bq per cubic meter of air.

1.4 Calculate the number of Rn-222 atoms in one cubic meter of air.

Polonium-210 also belongs to the uranium-radium series and represents the actual health concern. It has a half-life of 138.4 days.

1.5 Calculate how long it takes for 85.5% of a given amount of ^{210}Po to decay.

B. Inorganics from period 4

An important alloy of **gallium** with an element from a transition group (electron configuration …d^3…s^2) has a molar mass of 222.54 g/mol and is used as a superconductor with a critical temperature of 16.8 K.

1.6 Give the empirical formula of the alloy.

In the 1990s the ability to produce high-quality GaN crystals via hydride vapor phase epitaxy led to the first commercially available blue LEDs. In the lab gallium nitride can be synthesized at 1050 °C from gallium and ammonia.

1.7 Provide a balanced equation for this synthesis of GaN.

Germanium was discovered in 1886 by the German chemist Clemens Winkler, who first noticed a deficit of 6.44% (m/m) among the components previously identified in argyrodite. As the name suggests, argyrodite contains silver as well as another element – but not lead – in a 4 : 3 ratio.

1.8 Provide the molar mass of argyrodite.

1.9 Give the empirical formula of argyrodite and show through calculation the agreement with the given data.

Germanium(IV) fluoride reacts with water to form Germanium(IV) oxide and hexafluorogermanic acid, in which the oxidation state of germanium remains unchanged.

1.10 Write a balanced equation for this reaction.

In contrast, when **arsenic**(III) oxide reacts with water, triprotic arsenious acid is formed. Passing hydrogen sulfide into a solution of this acid yields yellow orpiment (246 g/mol), a lemon-yellow compound that transforms into a red modification at 170 °C, which sublimates well below its boiling point, forming dimers in the gas phase.

1.11 Write the balanced equation for the formation of arsenious acid.

1.12 Write the balanced equation for the synthesis of yellow orpiment.

1.13 Write the formula of the molecules in the gas phase of the red modification.

C. Finally, a comparison

1.14 Which of the three discussed elements…

… has the highest first ionization energy? ☐ Ga ☐ Ge ☐ As
… has the largest atomic radius? ☐ Ga ☐ Ge ☐ As
… has the strongest metallic character? ☐ Ga ☐ Ge ☐ As
… has the first seven ionization energies (eV)? (eV)
6 – 21 – 31 – 63 – 86 – 113 – 141 ☐ Ga ☐ Ge ☐ As

Problem 2 (N. Langer) **7 Points**

Χρῶμα

Chromium has a density of $\rho = 7.14$ g/cm^3. The atomic radius is 1.25 Å. Chromium crystallizes in a regular cubic system – either body-centered or face-centered.

2.1	*Determine in which of the two lattice types chromium crystallizes an provide a transparent calculation supporting your conclusion*

Razor blades are made from an iron-chromium alloy. 0.1331 g of such a blade was dissolved in diluted sulfuric acid, forming iron(II) and chromium(III) ions. In the resulting solution, the iron was titrated with permanganate solution (c = 0.0205 mol/L). Volume used: 20.08 cm^3. The chromium ions did not react under these conditions.

2.2	*Give balanced, indexed (ionic) equations for the dissolution of iron, the dissolution of chromium, and the titration reaction.*
2.3	*Calculate the mass fractions of iron and chromium in the alloy.*

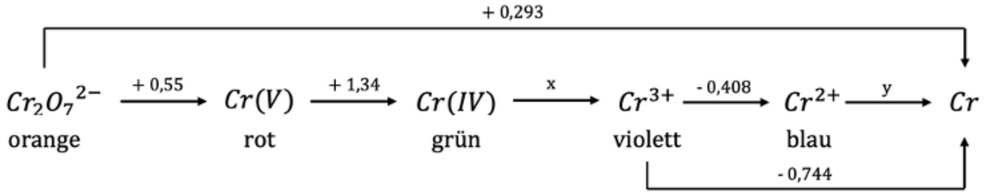
Metallic chromium coatings can be produced by electrolysis. An electrolytic cell was filled with 100 L of a solution containing 230 g/L of "anhydrous chromic acid" (CrO_3). Electrolysis was then carried out at a current of 1500 A for 10 hours. The chrome plated objects served as the cathode, while the anode remained unchanged. The mass increase at the cathode was 670 g, and gases were formed at both the cathode and the anode.

2.4 Give the formulae of the gases formed.

Cathode: Anode:

2.5 Calculate the percentage current efficiency for the described process.

Compounds or ions of chromium exhibit a multicolored appearance (χρωμα – color). The standard reduction potentials can be clearly represented in a Latimer diagram (all data refer to pH = 0):



2.6 Calculate x and y using the diagram.

In analytical chemistry, the redox system dichromate/chromium(III) ($E°(Cr_2O_7^{2-}/Cr^{3+}) = +1.33$ V) is often used.

2.7 Calculate the ***change*** *in potential when the pH value is increased by 1 (T = 298 K), assuming the chromium species concentrations remain constant.*

In coordination chemistry, numerous chromium complexes are known, such as $K_3[Cr(CN)_6]$, which absorbs light with $\lambda = 376$ nm.

2.8 State the name and the color of the compound.

2.9 Calculate the ligand field splitting Δ_0 of the complex.

Hexaaquachromium(III) complexes exhibit a special type of structural isomerism. When anhydrous chromium(III) chloride is dissolved, the dark green triaquachromium(III) chloride trihydrate **1** is first formed, which transforms into a green isomer **2**, then into a light blue-green **3**, and finally into a violet **4.** During this process, the electrical conductivity of the solution increases.

2.10 Write the formulae of compounds ***1 to 4*** *and state the specific name of this type of isomerism.*

1 **2**

3 **4**

Name the type of isomerism:

Problem 3 (W. Faber) **7 Points**

The Mohr Method

The titration according to Mohr (Carl Friedrich Mohr, 1806 - 1879) is a method for determining the concentration of chloride and bromide ions. The solution to be analyzed is titrated with silver nitrate solution, whereby silver chloride or silver bromide precipitates are formed. Potassium chromate is used as an indicator. At the equivalence point, excess silver ions form a colored silver chromate precipitate, the formation of which indicates the end point of the titration.

The solubility products are given for this task:

$$K_{\mathrm{sp}}(\mathrm{AgBr}) = 5.35 \cdot 10^{-13}$$

$$K_{\mathrm{sp}}(\mathrm{Ag_2CrO_4}) = 1.12 \cdot 10^{-12}$$

$$K_{\mathrm{sp}}(\mathrm{AgOH}) = 1.52 \cdot 10^{-8}$$

2.00 mL of a K_2CrO_4 solution (c = 0.3 mol/L) are added to 50.00 mL of a sample solution with a bromide ion concentration of 0.200 mol/L, the pH is adjusted to 7.00 by adding a buffer and the solution is made up to 100.00 mL. This solution is titrated with a silver nitrate solution (c = 0.100 mol/L).

3.1	*Calculate the maximum volume of silver nitrate solution that can be added before the first silver bromide precipitate forms. As this volume is probably very small, the change in volume of the solution in the titration flask can be neglected in this calculation.*

For all further subtasks, it can be assumed that approximately all silver ions react with bromide ions as long as the bromide ions have not yet been consumed.

3.2	*60.00 mL of the silver nitrate solution are added to the sample solution. Calculate the concentration of bromide ions in this solution.*

3.3 When 100.05 mL of silver nitrate solution is added, the equivalence point is just exceeded. Calculate the concentration of silver ions in this solution. Then show by calculation whether Ag_2CrO_4 precipitate has already formed.

The pH value must be kept stable during this titration, as some of the chromate is converted into dichromate in an acidic solution. The so-called “chromate-dichromate equilibrium” is responsible for the pH dependency:

$$2\ H^+ + 2\ CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad K = 4.20 \cdot 10^{14}$$

Water as a solvent is not taken into account in the equilibrium constant.

3.4	*Calculate what percentage of the chromate added before the titration is still present as chromate at the pH value of 7.00 before the start of the titration.*

To increase the relative chromate concentration, it would be helpful to increase the pH value, but this could lead to the formation of silver hydroxide. Assume a silver ion concentration of $2.00 \cdot 10^{-5}$ mol/L.

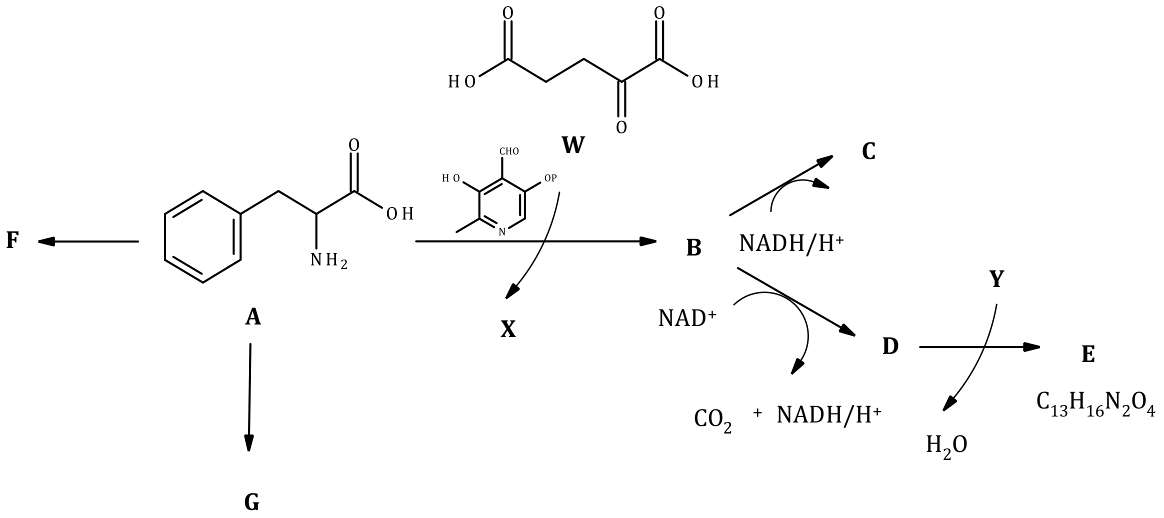
3.5	*Calculate the pH value from which the formation of a silver hydroxide precipitate can be expected.*

Problem 4 (M. Scherl) **12 Points**

Biochemistry and Organic Syntheses

A. Pathobiochemistry in metabolism: Phenylketonuria

Phenylketonuria (PKU) is an inherited metabolic disorder that impairs the processing of the amino acid phenylalanine **A**. Without treatment, this accumulates in the body and can cause severe neurological damage. However, with early screening and a targeted diet, the disorder can be effectively controlled so that those affected can lead a largely normal life. Here are some metabolic pathways:



- Reaction **A** → **F** is catalysed by a decarboxylase
- **F** is a neurotransmitter
- **X** is produced by hydroysis of **Y**.
- The reaction **A** + **W** → **B** + **X** requires an enzyme and a vitamin as a cofactor.
- **A** → **G** (a canonical amino acid) requires phenylalanine hydroxylase as an enzyme.

*4.1 Draw the structures of **B** – **G**, **X** and **Y***

4.2 Write down the correct enzyme class for the following reactions.

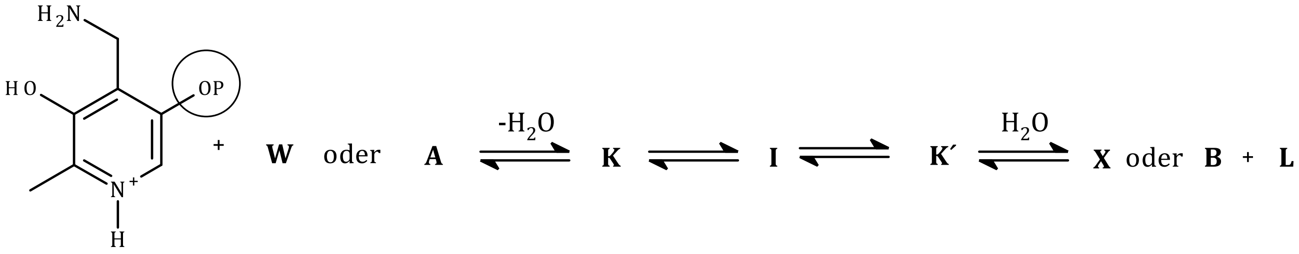
A → F: ______________________________

A → G: ______________________________

B → C: ______________________________

A → B: ______________________________

The conversion of **A + W → B + X** takes place in several steps as a catalytic cycle, whereby this reaction sequence also occurs, in which one of the two starting materials (you have to decide which one) is converted:

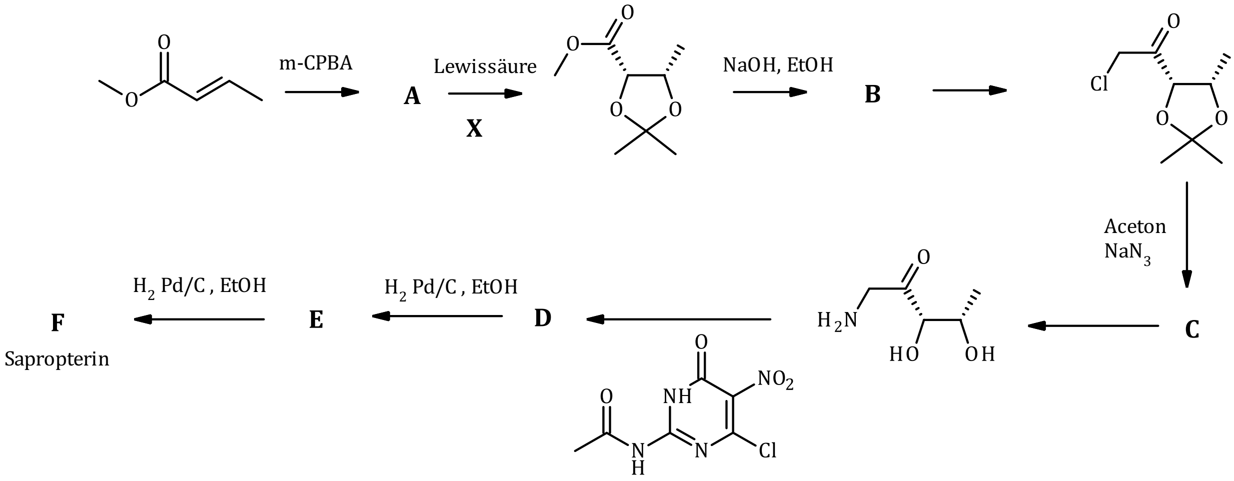


4.3 Name the circled functional group and draw the complete structure of "-OP" at physiological pH.

*4.4 Draw the structures **K**, **I**, **K´** und **L**.*

B. Synthesis or Sapropterine

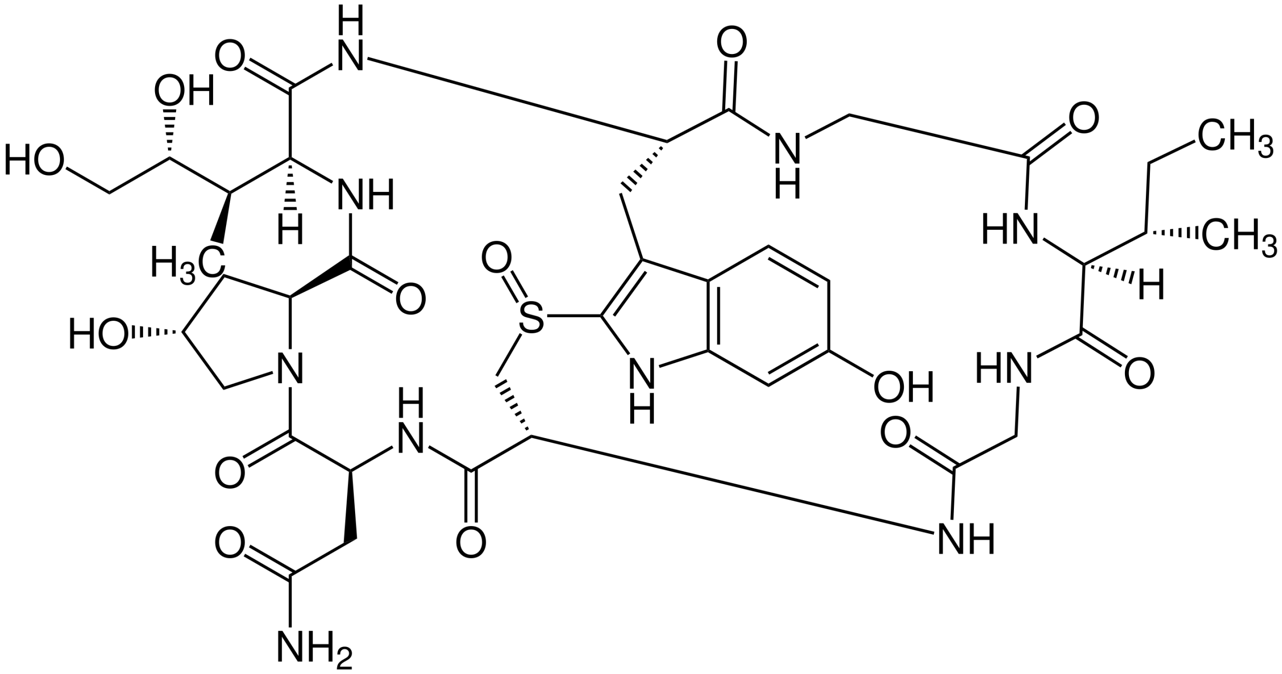
Sapropterin is a synthetic analog of tetrahydrobiopterin, an important co-factor for enzymes that break down phenylalanine. It is used to treat certain forms of phenylketonuria (PKU) in which residual phenylalanine hydroxylase activity is present. By taking it, the phenylalanine level in the blood can be lowered and the dietary requirements for PKU patients may be eased.



- m-CPBA = *meta* -chloro perbenzoic acid
- Formation of **E:** an additional heterocycle is formed.
- Formation of **F:** the less stable double bound reacts.

4.5	*Draw the structures of **A** – **F** and the reagent **X** considering the correct stereochemistry.*

C. The Poison of the Death Cap Mushroom – Amanitine



4.6	*Circle all peptide bonds in the given structure. Indicate the number of amino acids in the present oligopeptide..*
	number:
4.7	*Label the canonical amino acids in the structure of amanitine with their names (3-letter abbreviation).*

D. D. Farnesole - structure elucidation and synthesis

Farnesole was named after the Farnese acacia tree (*Vachellia farnesiana*) around 1905, as the substance was identified in the essence of its flowers. In this example, several paths - structure elucidation and synthesis - lead to the structure of farnesol.

Structure elucidation: Farnesole was subjected to ozonolysis and worked up with dimethyl sulphide. This yielded the three substances **A**, **B** and **C** in a ratio of 2 : 1 : 1..

A ^1H and a ^{13}C NMR spectrum of each of the three substances were recorded in CD_3OD.

A: δ ^1H [ppm]: 9.6, 1H (t, 6.65 Hz); 2.9, 2H (td, 7.41 Hz, 6.65 Hz); 2.7, 2H (t, 7.41 Hz); 2.1, 3H (s).

δ ^{13}C [ppm]: 29.8; 35.6; 37.5; 200.0; 206.5.

B: δ ^1H [ppm]:2.1, 6H (s)

δ ^{13}C [ppm]: 30.7; 206.7.

C: δ ^1H [ppm]: 9.5, 1H (t, 6.03Hz); 3.8, 2H (6.03 Hz).

δ ^{13}C [ppm]: 63.9; 201.4.

In addition, farnesole was subjected to further chemical investigations to elucidate its structure:

Reaction 1: Farnesole reacted with 3 equivalents of hydrogen

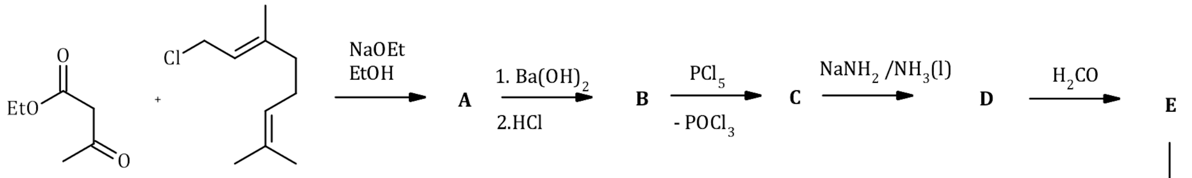
Reaction 2: Farnesole reacted with ethanoic anhydride

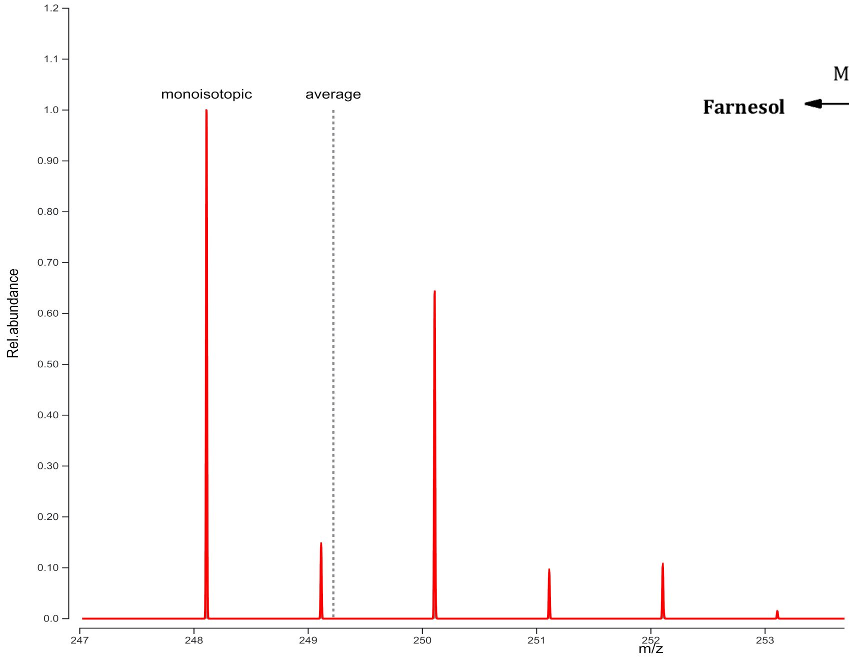
Reactions 3+4: Farnesole reacted with chromium(VI) oxide and the product with hydroxylamine.

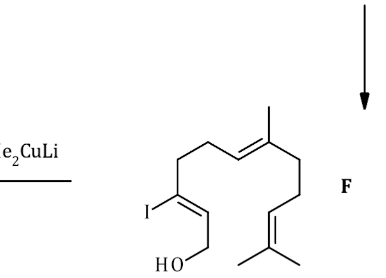
4.8 *Draw the structures of the ozonolysis producs **A, B, C**.*

4.9 *Draw the structural formulae of the reaction products **for two of the four reactions** and label them "reaction 1, 2, 3 or 4" accordingly.*

Synthesis







C: a mass spectrum is given.

D und **E** show signals in IR

D: a signal at 2260 cm^{-1}, **E**: a signal at 2155 cm^{-1} and a signal at 3300 cm^{-1} (broad).

4.10 Draw the structures of ***A-F*** *from this synthesis with the correct stereochemistry.*

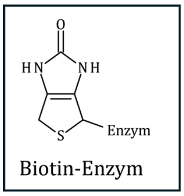
4.11 Draw the structure of farnsesole (including stereochemistry) and give the IUPAC-name.
4.12 Report the numbers of possible sterioisomers of farnesole

Problem 5 (M. Scherl) **4 Points**

Biosynthesis of Fatty Acids

Fatty acid biosynthesis is an anabolic process in the cytosol in which fatty acids are synthesised from C_2 units by stepwise elongation. In eukaryotes and many bacteria, synthesis is carried out by a multienzyme complex.

Abbreviations:		**HD**	3-hydroxyacyl-ACP-dehydratase
AC	acetyl-CoA carboxylase	**KS**	β-ketoacyl-ACP-synthase
ER	enoyl-ACP-reductase	**KR**	β-ketoacyl-ACP-reductase



Biotin-Enzym

Glg. 1: $\textbf{Hydrogencarbonat} + \textbf{ATP} \longrightarrow \textbf{A} + \textbf{B}$

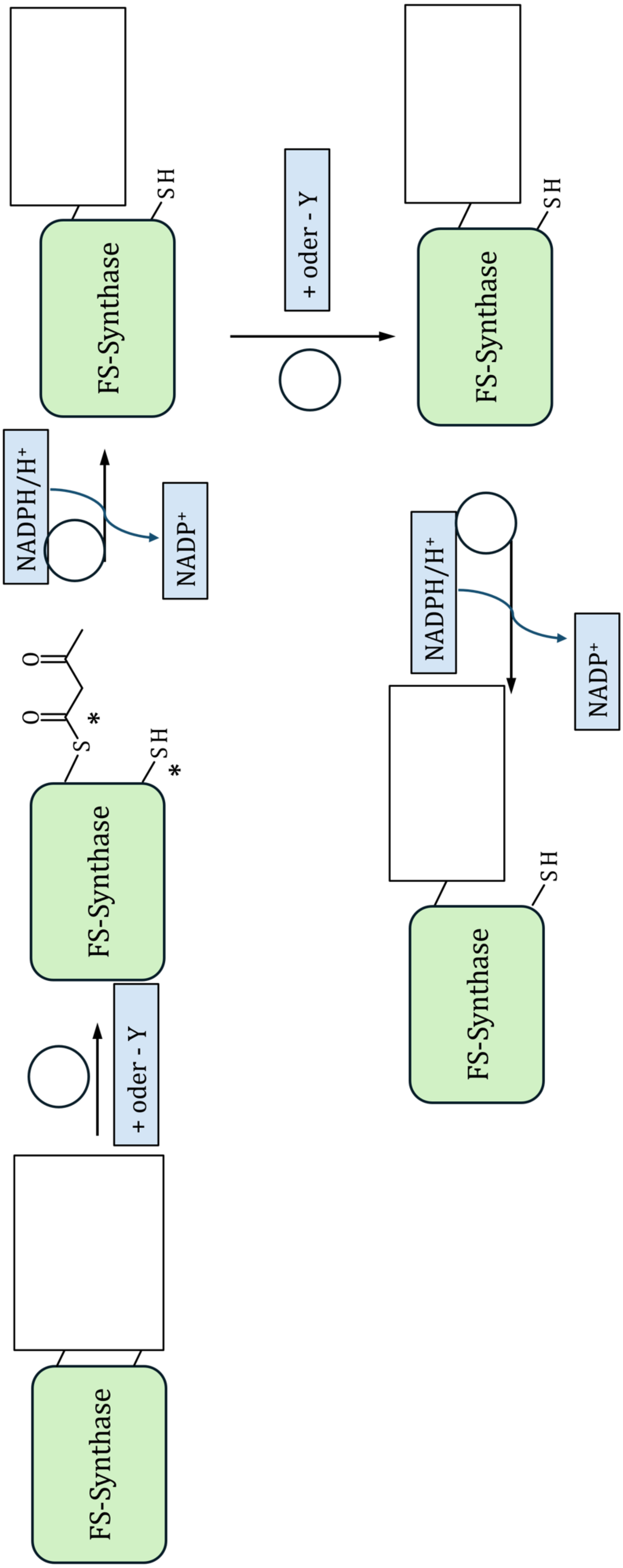
Glg. 2: $\textbf{Biotin-Enzym} + \textbf{A} \longrightarrow \textbf{C} + \textbf{D} + \textbf{Acetyl-CoA} \longrightarrow \textbf{Malonyl-CoA} + \textbf{E}$

*5.1 Draw structures **A-D** and **malonyl-CoA** or write adequate abbreviations for complex structures if possible from Eqs. 1 and 2.*

5.2 Zeichnen bzw. schreiben Sie in die vorgesehenen Kästchen der FS-Synthese (nächste Seite) die Strukturformeln der Zwischenprodukte und die Abkü./Summenformeln der Nebenprodukte. Schreiben Sie in die Kreise bei den Reaktionspfeilen die Abkürzungen für die notwendigen Enzyme

*5.3 Benennen Sie die beiden funktionellen Gruppen, welche im FS-Schema mit einem * gekennzeichnet sind.*

5.4 Zeichnen Sie die Strukturformel von Palmitinsäure (Hexadecansäure) auf und geben Sie an, wie oft der Cyclus der vorgestellten FS-Biosynthese zu ihrer Herstellung durchlaufen werden muss.


FS-Synthase
+ oder - Y
FS-Synthase
S
O
O
SH
*
*
NADPH/H⁺
NADP⁺
FS-Synthase
SH
+ oder - Y
FS-Synthase
SH
NADPH/H⁺
NADP⁺
FS-Synthase
SH

Problem 6 (I. Stadler-Ulitsch) **4 Points**

Kinetics ABC

The following reaction proceeds via an unknown mechanism:

$$A + 2\,B \rightarrow AB_2. \qquad (\mathbf{R1})$$

Let us first assume that the reaction is second order with respect to B.

6.1 Select by checking the boxes those of the following mechanisms that would be consistent with this assumption.

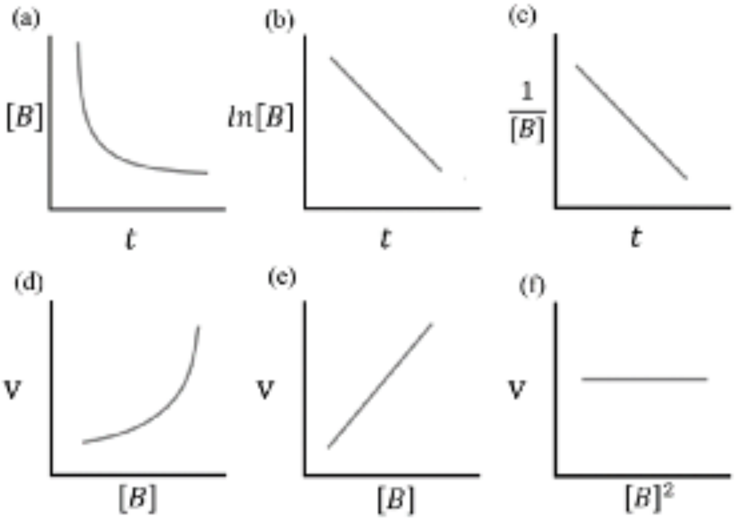
☐ $A + B \rightarrow AB$ slow
$AB + B \rightarrow AB_2$ fast

☐ $A + A \rightarrow A_2$ slow
$B + B \rightarrow B_2$ slow
$A_2 + B_2 \rightarrow AB_2 + A$ slow

☐ $B + B \rightarrow B_2$ slow
$A + B_2 \rightarrow AB_2$ fast

☐ $A + B \rightarrow AB$ fast
$AB + B \rightarrow AB_2$ slow

Diagrams are shown that can represent the relationship between [B] and time *t* as well as the reaction rate *v* and [B].



6.2 Write down the letters (a) to (f) of the diagrams that match the assumption made above. Assume a constant concentration for [A].

In reality, reaction **R1** proceeds via the following mechanism:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB \qquad (1)$$

$$AB + B \xrightarrow{k_2} AB_2 \qquad (2)$$

6.3	*For each of the conditions listed below, state the rate-determining step. Assume that [A] and [B] are much greater than [AB] and [AB$_2$].*		
$k_1 \gg k_{-1}; k_2 \gg k_1$	☐ Step1	☐ Step2	☐ neither of them
$k_1 \gg k_{-1}; k_2 \ll k_1$	☐ Step1	☐ Step2	☐ neither of them
$k_1 \gg k_{-1}; k_2 \cong k_1$	☐ Step1	☐ Step2	☐ neither of them
$k_1 \cong k_{-1}; k_2 \ll k_1$	☐ Step1	☐ Step2	☐ neither of them

Unknown amounts of reagents A and B were placed together in a container under conditions that favor reaction 1. At time $t = t_1$, the concentration of the intermediate AB had become constant, $[AB] = [AB]_{const}$, and the concentration of reagent A had reached a specific value, $[A] = [A]_1$.

6.4 At time t_1, express the ratio k_1/k_2 in terms of $[A]_1$ and $[AB]_{const}$. Assume that $k_1, k_2 \gg k_{-1}$..

Problem 7 (J. Novacek) **9 Points**

Complexes of Copper(II) with Amino Acids

Copper(II) ions form complexes with amino acids (HAS) with the molecular formula $[Cu(AS)_2(H_2O)]$. These complexes usually crystallize as a monohydrate and are present as distorted octahedral complexes. For the sake of simplicity, they will be considered as square planar complexes for the following calculations and water will be ignored as a ligand (unless otherwise stated).

A. Analysis of copper(II)-bisglycinate

The reaction of copper(II) acetate with glycine produces two different products (**complex *cis*-I** and ***trans*-I**). These cannot be analyzed by NMR due to the copper(II) ions, which is why the standard analysis method for these complexes is IR. The resulting spectra **A** and **B** are shown on the page 23.

To assign the individual peaks to different vibrations, the compound is "labeled" with different isotopes (e.g. ^{13}C, ^{15}N, ^{18}O,...). It is then analyzed which peaks have shifted as a result (note: the force constant does not change significantly). This was done for the assignment of the signals of spectrum B.

To determine how well the labeling worked, an elemental analysis was carried out on both the unlabeled and the ^{18}O-labeled **complex I** (copper(II) bisglycinate monohydrate, $CuC_4H_{10}N_2O_5$). The unlabeled complex had a carbon content of 20.9%, while the ^{18}O-labeled complex had a carbon content of 20.2%.

7.1	*Calculate the relative amount of labeled oxygen atoms in the copper(II) bisglycinate monohydrate.*

7.2	*Which type of bond is responsible for each of the following signals in spectrum B?*

3255 cm^{-1}:

2955 cm^{-1}:

1574 cm^{-1}:

7.3 Labeling the oxygen atoms with ^{18}O causes some signals to shift significantly in the IR spectrum. Mark the correct statements with a cross:

The signal at 3255 cm^{-1} is shifted
- ☐ to higher wave numbers.
- ☐ not significantly.
- ☐ to lower wave numbers.

The signal at 2955 cm^{-1} is shifted
- ☐ to higher wave numbers.
- ☐ not significantly.
- ☐ to lower wave numbers.

The signal at 1574 cm^{-1} is shifted
- ☐ to higher wave numbers.
- ☐ not significantly.
- ☐ to lower wave numbers.

The signal in spectra **B** at 475 cm^{-1} corresponds to a Cu-N-vibration (those vibrations can be found between 450-500 cm^{-1}), which is treated as harmonic oscillator.

7.4 Calculate the force constant k of the Cu-N vibration.

*7.5 Assign the IR spectra **A** and **B** to the corresponding complexes and give reasons for your assignment:*

cis-copper(II)-bisglycinate:

trans-copper(II)-bisglycinate:

Reason:

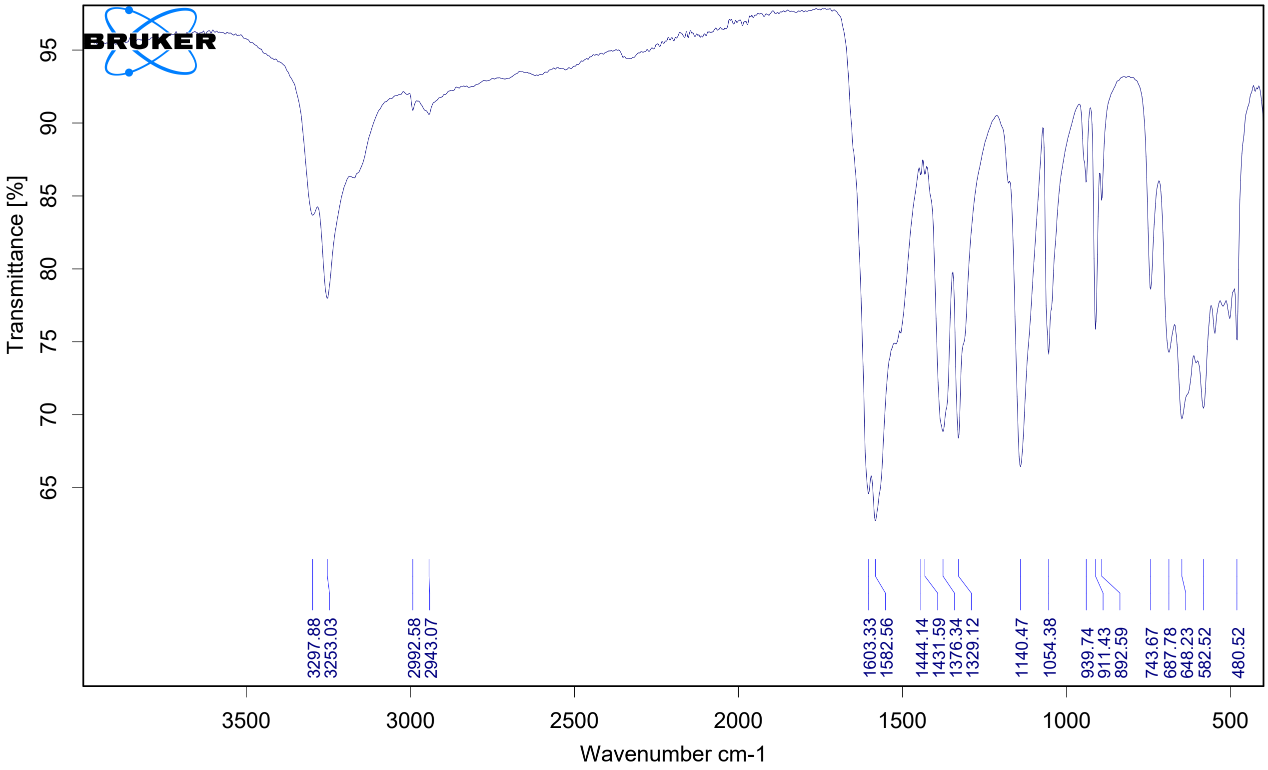


Fig. 1: ***Spectrum A***

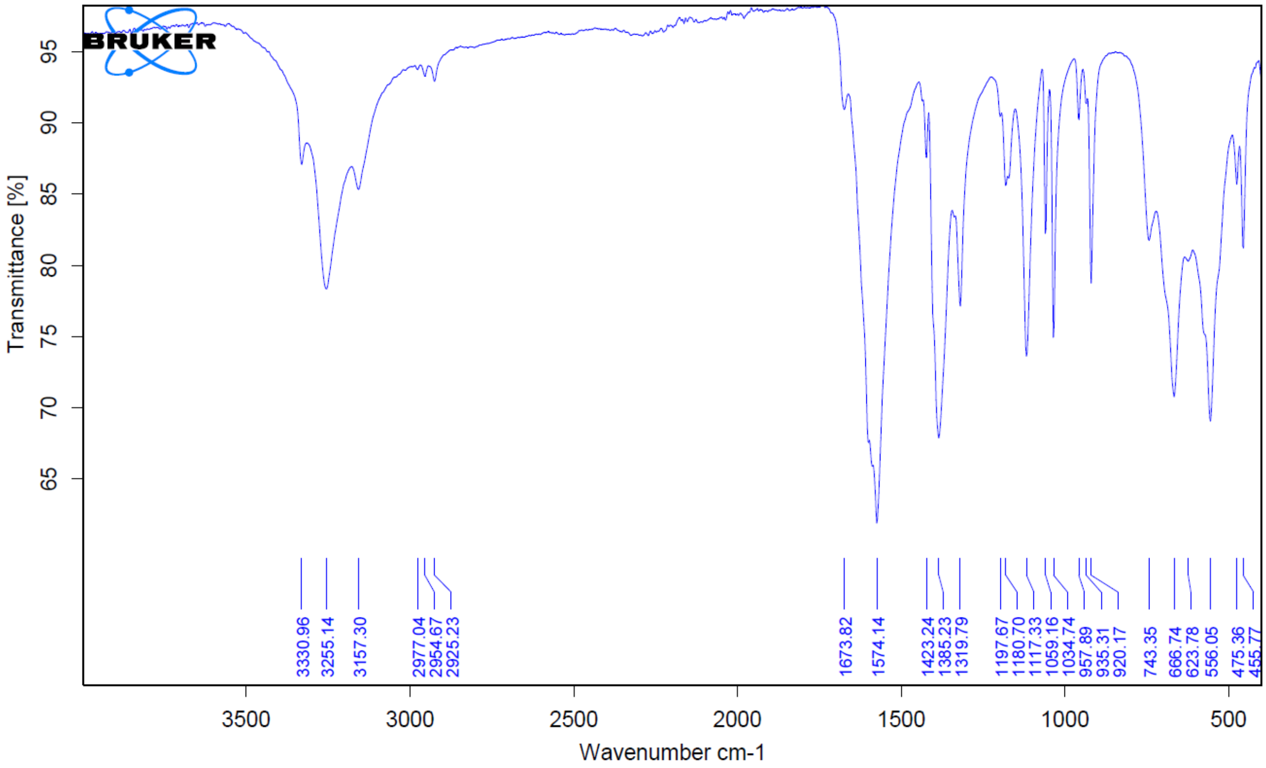


Fig 2: ***Spectrum B***

B. Chiral complexes of copper(II) with amino acids

The use of amino acids as ligands is not only advantageous due to the formation of chelate complexes, but also because chiral complexes are easily accessible - for example using alanine ((*R*)-2-aminopropanoic acid), proline ($C_5H_9NO_2$), leucine ($C_6H_{13}NO_2$), isoleucine ($C_6H_{13}NO_2$) and phenylalanine ($C_9H_{11}NO_2$).

One of these chiral complexes (**complex II**) shows the following isotope pattern in MS:

	M	**M+1**	**M+2**	**M+3**
Intensity	100	12	45	5

Natural abundance of isotopes:

Cu	has 2 natural isotopes, main isotop: $A = 63$ u	**N**	^{14}N: 99.6%, ^{15}N: 0.4%
C	^{12}C: 98.9%, ^{13}C: 1.1%	**O, H**	can be considered as pure isotopes for this task

7.6	*Write down the nominal mass of the second copper isotope and calculate the frequency of each isotope in % from the isotope pattern above:*

7.7	*Determine which amino acid was used for the synthesis of **complex II**. Show your calculation/reasoning:*

☐ Glycine ☐ Alanine ☐ Proline ☐ Leucine
☐ Isoleucine ☐ Phenylalanine ☐ none of the mentioned

7.8 *Draw (R)-2-aminopropanoic acid (alanine) as a skeletal formula (including stereochemistry) and in the Fischer projection and determine the stereodescriptor D/L:*

C. Asymmetric synthesis with chiral copper(II)-complexes

While the synthesis of chiral complexes may be interesting and challenging in its own, the question of application often arises. Fortunately, copper salts and complexes have proven to be extremely helpful (and inexpensive) catalysts for a wide variety of reactions.

The simple ketone **K** is converted into enolates using the reactions below. Depending on the reagents and reaction conditions used, different products are formed (whereby a main isomer and a secondary isomer are formed in a ratio of ~4:1 in each case). *Cy = cyclohexyl*

$$\textbf{Enolat } \mathbf{E_1} \xleftarrow[Et_3N]{Cy_2BCl} \textbf{Keton K} \xrightarrow[DMF]{Me_3SiCl,\ NaBr} \textbf{Enolat } \mathbf{E_2}$$

A ^{1}H-NMR and a MS(EI) of keton **K** have been recorded:

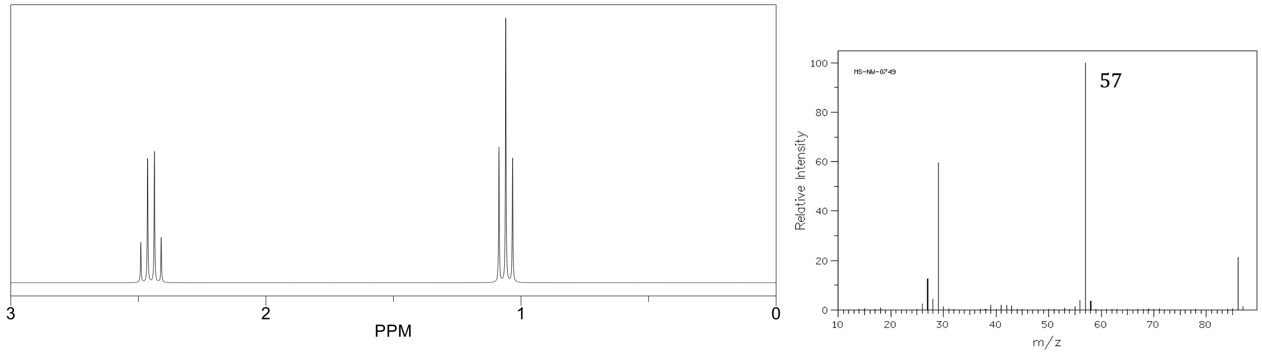
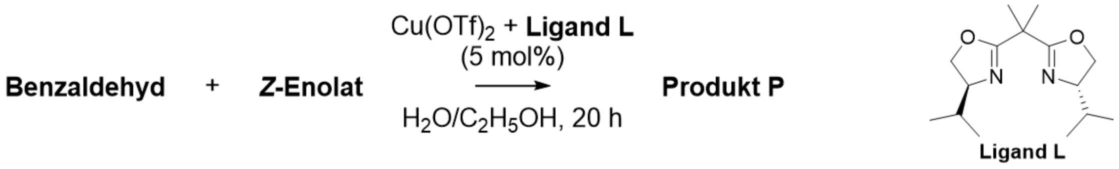


*Abbildung 3: NMR- and MS-spectra of ketone **K** (no other signals present).*

7.9 *Draw the structural formulae of ketone **K**, enolate **E₁** (main isomer) and enolate **E₂** (main isomer).*		
K	**E$_1$**	**E$_2$**

*7.10 Suggest a fragmentation pathway for ketone **K** that leads to the fragment of the base peak.*

Benzaldehyde is now reacted with the *Z*-enolate in the presence of a chiral copper complex. The ligand L used here is also synthesized from a proteinogenic amino acid.



While these reactions are usually carried out in anhydrous aprotic solvents at very low temperatures (–78°C), Kobayashi showed that by choosing a suitable catalyst, the reaction can even be carried out in aqueous solvents (water/ethanol 1/9) at relatively high temperatures (-15°C to 0°C) (admittedly with selectivities that can still be improved).

7.11 What task(s) does the chiral copper complex have in this reaction?

☐ Oxidant
☐ Reductant
☐ Base
☐ Lewis-acid-catalyst
☐ Brønsted-acid-catalyst
☐ phase transfer catalyst
☐ nucleophile
☐ electrophile
☐ none of the above

*7.12 Draw the main product **P** of this reaction with the correct stereochemistry. The substituent at the β-position has (S)-configuration.*
*Sketch the transition state that leads to the formation of the main product **P** in the above reaction.*

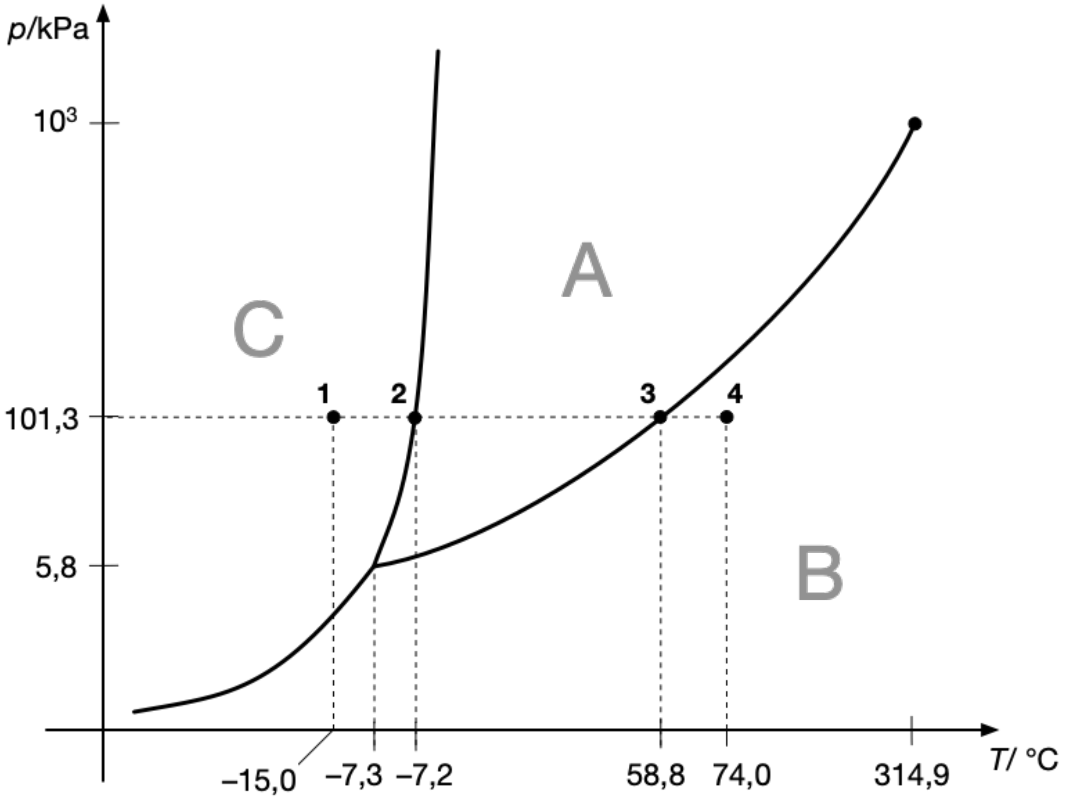
Main product P	Transition state

Problem 8 (G. Schellander) **12 Points**

Bromine from a Physicochemical Point of View

The Phases

Shown is a phase diagram of bromine (Br_2), the axes are labelled but not to scale, as you will easily recognise.



Then you can find some thermodynamical data for 298 K. All of them shall be independent on temperature:

	$\Delta_f H^\ominus$/kJmol^{-1}	C_p / JK^{-1}mol^{-1}
$Br_2(s)$		47,4
$Br_2(l)$	0,00	75,7
$Br_2(g)$	29,96	36,0

8.1 Correctly assign the letters s, l and g, which are normally used in phase diagrams, to fields A-C.

A: B: C:

8.2 Bromine is present in all three states of aggregation if... (tick the right box)

☐ $T < -7{,}3$ °C; $p > 5{,}8$ kPa

☐ $T = -7{,}3$ °C; $p = 57{,}2$ matm

☐ $T = -7{,}3$°C; $p = 5{,}8$ atm

☐ $T = -7{,}3$ °C; $p = 101{,}3$ kPa

☐ $T = 7{,}3$°C; $p = 58$ kPa

At 101325 Pa the boiling point of bromine is 58,8°C (332 K). At 328,8 K the vapour pressure is 10 % lower.

8.3	*Calculate the standard enthalpy of vaporisation $\Delta_{\text{vap}}H^\ominus$. Assume that it does not depend on pressure or temperature. If you do not obtain a result here, use $\Delta_{\text{vap}}H^\ominus = 23$ kJ/mol if necessary in further calculations.*

0,100 mol Br_2 are present at point **1** in the phase diagram and are now heated isobarically (isobar **1**-**2**-**3**-**4**).

8.4	*Sketch the course of the temperature T against q for this process. The q-axis has no units, so you do not need to take numerical values for the heat quantities into account. However, note the markings on the T-axis.*

For the 0,100 mol Br_2 on the path form **1** to **4** a total energy of 4644 J needs do be added.

8.5	*Calculate the standard enthalpy of $\Delta_{\text{fus}}H^\ominus$ of Br_2.*

The Bond Energies

The bromine molecule can be homolytically cleaved:

R1: $Br_{2(g)} \rightarrow 2\ Br_{(g)}$ $\Delta_{R1}H^{\ominus} = 223{,}8\ kJ\ mol^{-1}$

8.6 Report the standard enthylpy of formation for $Br_{(g)}$ in kJ/mol.

Let us take a few more reactions around bromine into consideration.

R2: $Br_{2(g)} \rightarrow Br^{+}_{(g)} + Br^{-}_{(g)}$ $\Delta_{R2}H^{\ominus} = ??$
R3: $K_{(s)} + ½\ Br_{2(l)} \rightarrow KBr_{(s)}$ $\Delta_{R3}H^{\ominus} = -393{,}8\ kJ\ mol^{-1}$
R4: $K_{(s)} \rightarrow K_{(g)}$ $\Delta_{R4}H^{\ominus} = 89{,}0\ kJ\ mol^{-1}$
R5: $K_{(g)} \rightarrow K^{+}_{(g)} + e^{-}$ $\Delta_{R5}H^{\ominus} = 418{,}8\ kJ\ mol^{-1}$
R6: $KBr_{(s)} \rightarrow K^{+}_{(g)} + Br^{-}_{(g)}$ $\Delta_{R6}H^{\ominus} = 671\ kJ\ mol^{-1}$
R7: $Br_{(g)} + e^{-} \rightarrow Br^{-}_{(g)}$ $\Delta_{R7}H^{\ominus} = ??$
R8: $Br_{(g)} \rightarrow Br^{+}_{(g)} + e^{-}$ $\Delta_{R8}H^{\ominus} = 1{,}140 \cdot 10^{3}\ kJ\ mol^{-1}$

8.7 The energy conversions associated with some processes have special names. If one of the above processes matches one the following names, add the designation R2...R8; if none matches, add X.

Ionisation energy of potassium _______
Electron affinity of potassium _______
Enthalpy of formation of potassium bromide _______
Lattice enthalpy of potassium bromide _______
Enthalpy of vaporisation of potassium _______
Enthalpy of sublimation of bromine _______

8.8 Set up a suitable thermodynamic cycle and calculate $\Delta_{R7}H^{\ominus}$. Clearly state form wich reactions (R...) the cycle is established and which enthalpy values you use for your calculation. If you cannot calculate a value, use $\Delta_{R7}H^{\ominus} = -300$ kJ/mol for further calculations.

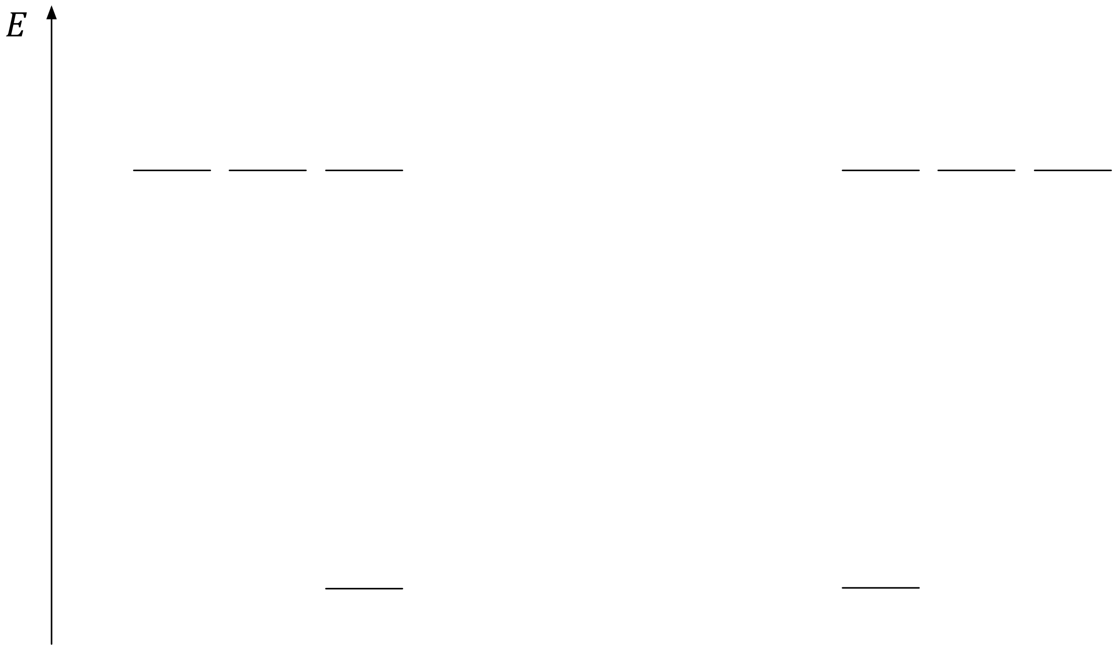
*8.9 Use all the information you have gathered so far to calculate $\Delta_{R2}H^{\ominus}$ of **R2**, i.e. the heterolytic bond cleavage of bromine in the gas phase. Again, clearly state which enthalpy values you are using.*

The Orbitals

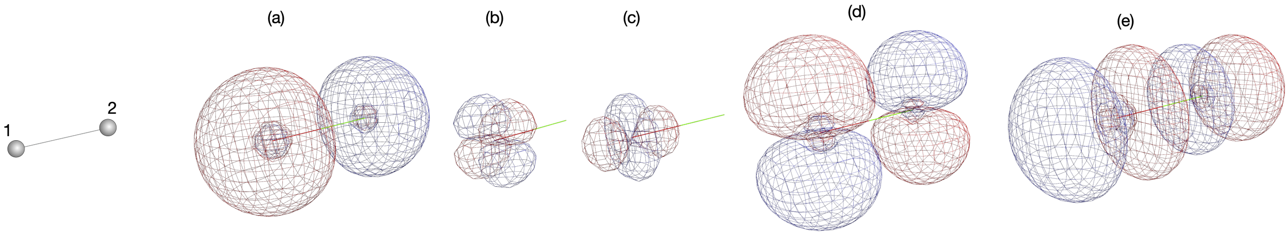
Halogens and interhalogen compounds are also interesting in terms of molecular orbitals.

8.10 Draw an MO diagram for Br_2. Consider only the s & p orbitals of the valence shell. Your diagram should contain: Labelling of the AO, MO (with labels σ, σ, π, π*, occupation of the MO ↑↓).*

Info: the order of σ- and π-MO is the same as for the N_2 molecule, not the same as for F2.



The MOs in the BrCl molecule include those shown below. The molecule is drawn in the same position in all figures, which is shown on the far left. Apart from the LUMO (e), all the MOs shown are occupied.



8.11 Answer the following questions by ticking the correct ☐.

Wich figures show σ* - orbitals?	☐ (a) ☐ (b) ☐ (c) ☐ (d) ☐ (e)
Which one is the chlorine atom?	☐ 1 ☐ 2
The LUMO is a	☐ σ ☐ π ☐ σ* ☐ π* MO
Two MO are practically only d atomic orbitals. From which of them can you see that the bond axis is the *z*-axis?	☐ (a) ☐ (b) ☐ (c) ☐ (d) ☐ (e)
Which other MO is also a d-AO?	☐ (a) ☐ (b) ☐ (c) ☐ (d) ☐ (e)

A student asked Chat-GPT about the ionisation energies for Br, Br_2 and IBr and was told that three ionisation energies had been found:

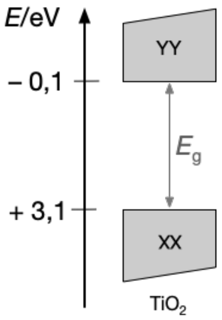
$$IE_1 = 9{,}85\ \text{eV}, \quad IE_2 = 11{,}8\ \text{eV}, \quad IE_3 = 10{,}5\ \text{eV}$$

To the deepest regret of the system, the assignment had fallen into oblivion due to numerous enquiries arriving at the same time on questions regarding the reliability of artificial intelligence and therefore no information could be given as to which ionisation energy referred to which species.

8.12 Assign the ionisation energies correctly by adding Br, Br_2 or IBr.

IE_1 ____________ , IE_2 ___________, IE_3 = ___________

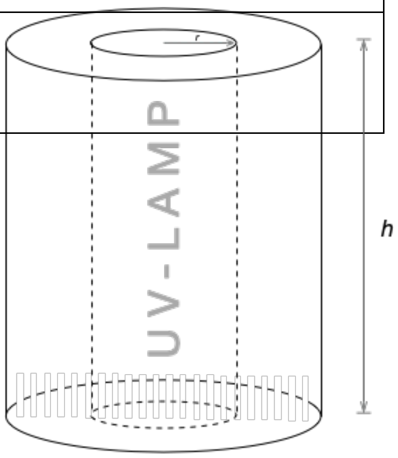
Interesting are attempts to produce bromine (Br_2) in a rather environmentally friendly way by photocatalytic oxidation from bromide in acidic solution. TiO_2 can be used as a catalyst. A section of its band structure is shown on the right.



8.13 Assign the abbreviations from the graphic to the volume designations (XX or YY)

Conduction band: ________ valence band: _________

8.14 Report the cutoff-wavelength λ_c for TiO_2 in nm.



In one experiment, 400 mL of a solution containing KBr (c(KBr) = $2.00\cdot10^{-3}$ molL^{-1}) and nitric acid (c(HNO_3) = $4.00\cdot10^{-3}$ molL^{-1}) were irradiated with light from a mercury vapour lamp (360 nm). The lamp was located inside a cylindrically shaped photoreactor. Light with an intensity of 7 mWcm^{-2} was emitted through the surface of the inner cylinder ($r = 2$ cm, $h = 10$ cm) into the solution, in which 10% of the photons were absorbed. After 5 hours of irradiation, 29% of the bromide ions had been converted to bromine.

The reaction mechanism is complicated; many partial reactions via radical intermediates are involved. Since oxygen is also blown in, the following gross reaction can be considered:

:

$$2Br^- + \tfrac{1}{2} O_2 + 2 H^+ \rightarrow Br_2 + H_2O$$

The quantum yield is given as $\Phi = (N_{\text{product molecules}})/(N_{\text{photons absorbed}})$

8.15 Calculate the quantum yield Φ.