50. Austrian Chemistry Olympiad
National competition

Theoretical exam
27. Mai 2024

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Name

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Problem 1 (I. Stadler-Ulitsch)

10 bp = 4 Points

Neptunium decay series

In this example, we are looking for three nuclides **A**, **B** and **C**, which are all part of the neptunium decay series. This series is considered prehistoric, as all ^{237}Np, which was formed during the formation of the earth, has since decayed.

Nuclide **A** decays when its nucleus emits an electron. This produces the nuclide ^{225}Ac.

Nuclide **A** is the decay product of nuclide **B**, from which a ^{4}He nucleus is emitted.

1.1 Name the two types of decay.
for nuclide **A** β^--decay   for nuclide **B** α-decay **1 bp**
*1.2 Tick the correct statement: ^{225}Ac is … to nuclide **A**.*
☐ isotopic   ☐ isobar (richtig)   ☐ isotonic **0,5 bp**
*1.3 Write down the complete equation for the decay of nuclide **A**.*
$^{225}_{88}\text{Ra} \rightarrow\ ^{225}_{89}\text{Ac} +\ ^{0}_{-1}\text{e} + \bar{\nu}_e$ **1,5 bp**
*1.4 Write down nuclide **B**.*
$^{229}_{90}\text{Th}$ **1 bp**

When nuclide **C** is formed, the mass defect per nucleon is 7.745 MeV/c², in total it is 1.8042 u. The nuclide has a mass of 212.9944 u.

*1.5   Calculate A and Z and write down nuclide **C**.*
Mass defect per nucleon $7{,}745 \cdot 10^6 \cdot \text{eV/c}^2$ $$\frac{7{,}819 \cdot 10^6 \text{eV} \cdot 1{,}6022 \cdot 10^{-19} \text{JeV}^{-1}}{(2{,}9979 \cdot 10^8)^2 \text{m}^2\text{s}^{-2} \cdot 1{,}6605 \cdot 10^{-27} \text{kg u}^{-1}} = 0{,}008394\ u$$ $$A = \frac{1{,}7880\ u}{0{,}008394\ u} \approx 213$$ $\Delta m = Z \cdot m_\text{p} + (A - Z)m_\text{n} + Z\,m_\text{e} - m$ $\quad\quad\quad = Z \cdot 1{,}0073 + 213 \cdot 1{,}0087 - Z \cdot 1{,}0087 + Z \cdot 5{,}4858 \cdot 10^{-4}$ $\quad\quad\quad - 212{,}9944 = 1{,}7880$ $Z = (1{,}788 - 213\ \cdot 1{,}0087 + 212{,}9944)/(1{,}0073 - 1{,}0087 + 5{,}4858 \cdot 10^{-4}) \approx 83$ $Z = 83$ $^{213}_{83}Bi$ **6 bp**

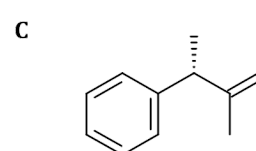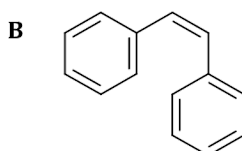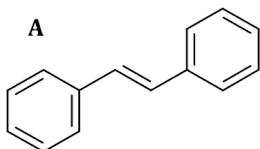**Problem 2 (M. Scherl)**   **69,5 bp = 13 Points**

Natural active substances against neurodegenerative diseases and stress in plants.
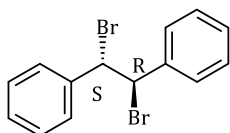
A. Warming up

The following three alkenes are reacted with bromine.

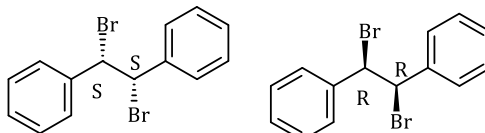**2.1** *Write down the structural formulae of all possible reaction products of **A**, **B** and **C** including stereochemistry. Write down the stereochemical relationship for each product (for **A**, **B** and **C**).*
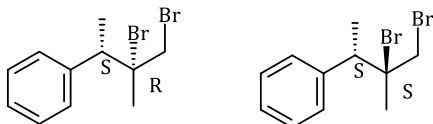
7,5 bp

2.2 *Name the mechanism of the present bromination.*

Elektrophilic Addition   **0,5 bp**

Let us now look at two other reactions:

2.3 *Write the structural formulas of the reaction products in the boxes and name the reaction mechanism in each case.*
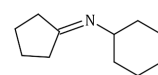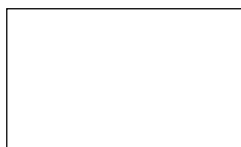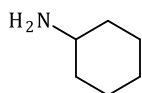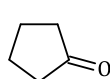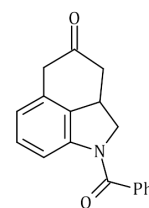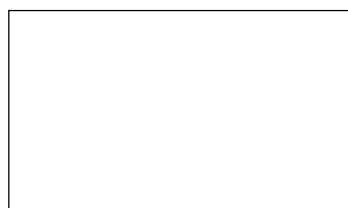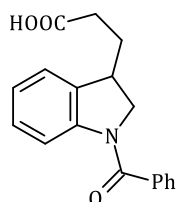
B. Merrilacton – against neurodegenerative diseases
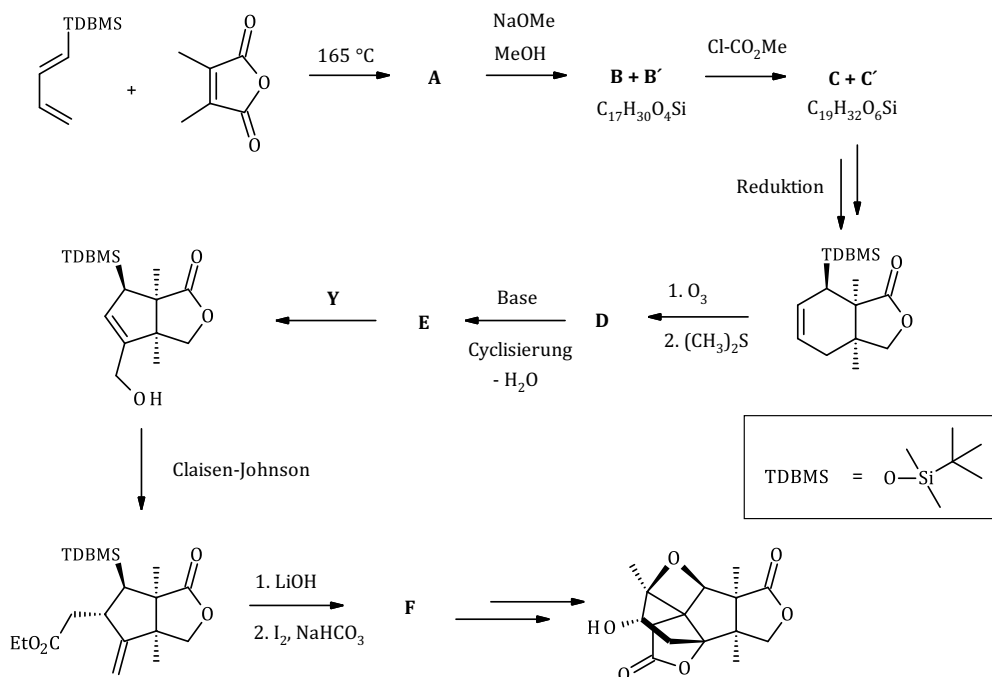
2.4	Write down the structural formulae of **A**-**F** (including stereochemistry) and the molecular formula for reagent **Y**.
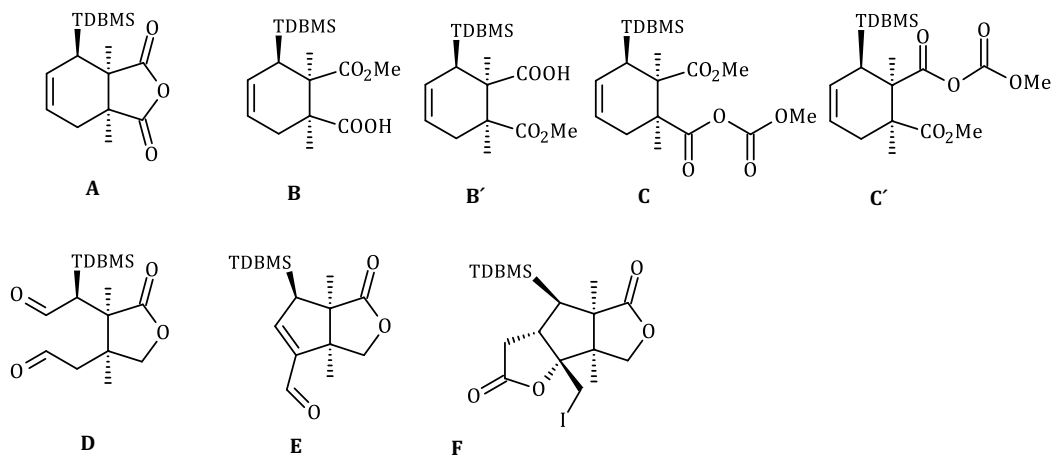
A: 2 bp, B`+B: 2,5 bp, C+C´: 2,5 bp, D: 2bp, E: 2,5 bp, F: 3bp

Y= NaBH$_4$.

1 bp

$\sum \mathbf{15,5\ bp}$

2.5	Name the type of isomerism present in **B** and **B'** or **C** and **C'**.

Constitutional isomers **1 bp**

C. Vitamin E - against neurodegenerative diseases

Vitamin E
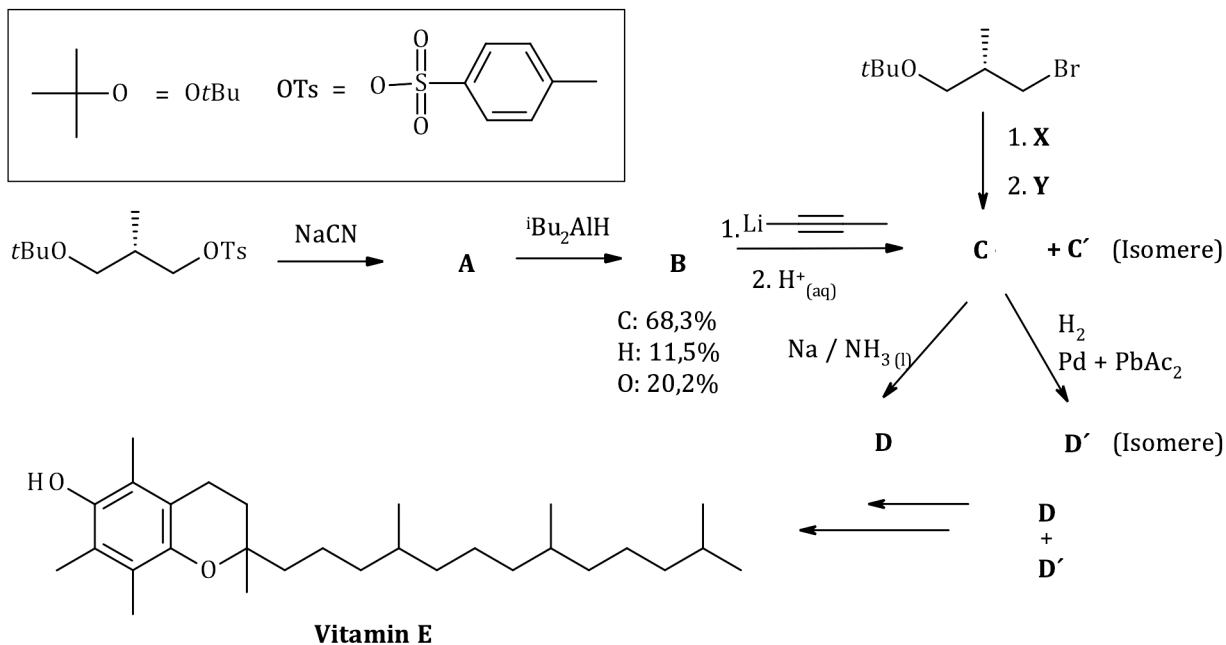
2.6	Give the molecular formula of **B**.
	C₉H₁₈O₂　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　**1,5 bp**

2.7　*Write down the structural formulae of **A-D'** and **Y** (including stereochemistry) and the molecular formula for reagent **X**.*
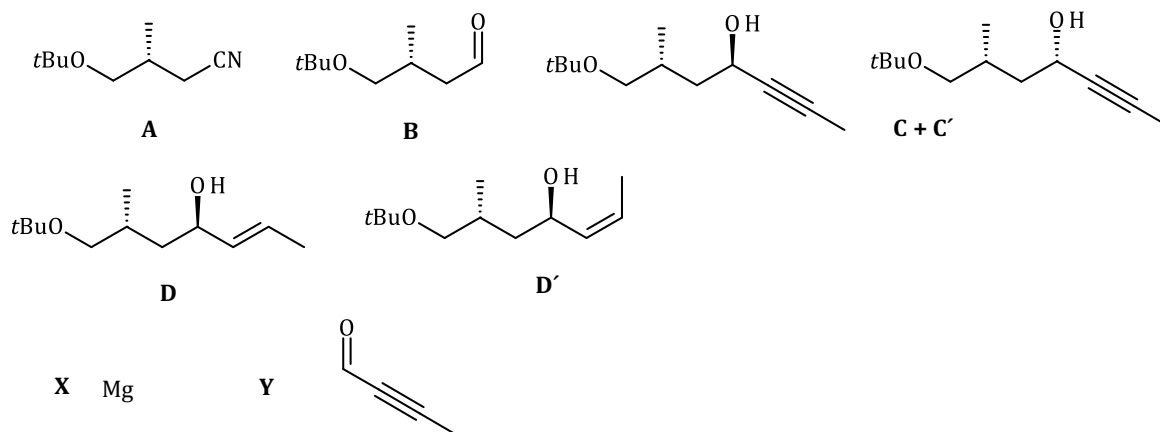
A: 2 bp, B: 2 bp, C+C´: 2,5 bp, D+D´: 3 bp, X: 0,5 bp, Y: 2 bp　　　　　　　**11 bp**

2.8	In the reactant, the alcohol group is esterified as a tosylate. Write "c" for correct or "i" for incorrect for the statements.	
	TsO⁻ ist ein schwächeres Nukleophil als OH⁻ :	
	OH⁻ ist im Vergleich zu TsO⁻ weniger reaktiv:	
	OH⁻ ist die bessere Abgangsgruppe:	
	Die neg. Ladung ist im TsO⁻ mesomeriestabilisiert:	**2 bp**

2.9	Write down the number of possible stereoisomers of vitamin E. Draw all stereocenters in the formula as R-configured by overwriting the bonds with ◀ or ⋯ıllı.	
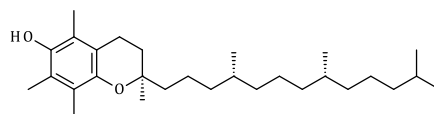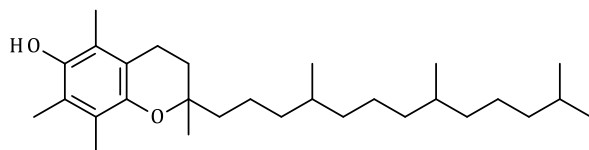
	2³ stereoisomers	**2 bp**

2.10	Indicate whether vitamin E belongs to the lipophilic or hydrophilic vitamins.	
	lipophilic	**0,5 bp**

D. Synthesis of a dipeptide

Researchers have succeeded in describing the role of the dipeptide (Tyr-Asp) in improving the resistance of plants to oxidative and salt stress. The dipeptide induces a modulation of the plant glucose metabolism towards the production of NADPH.
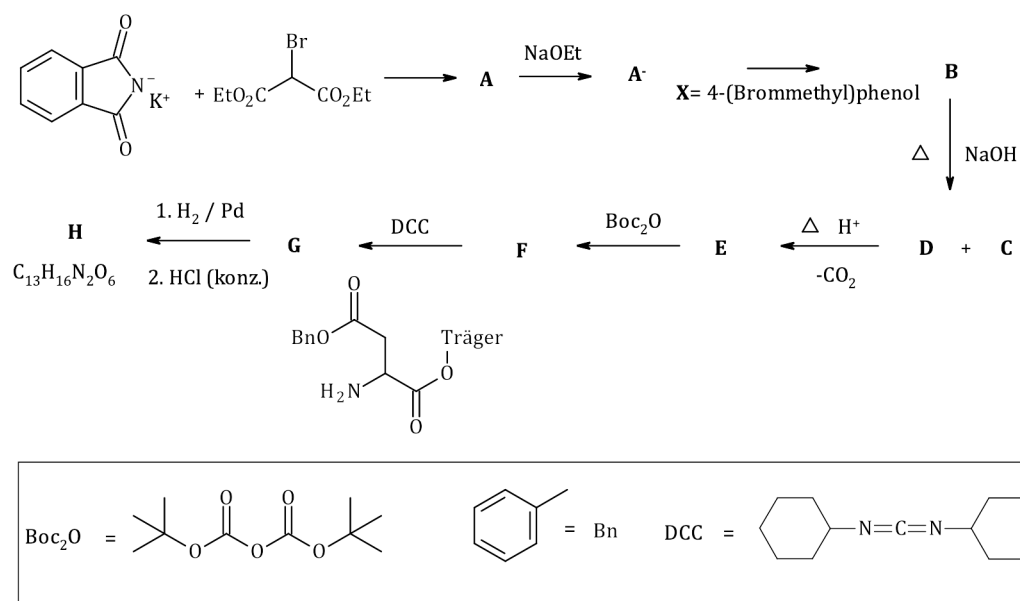
Note: $M(\mathbf{C})$ and $M(\mathbf{D})$ are greater than 50 g/mol, $\mathbf{C}$ is a by-product that does not react further.

2.11	What is the function of DCC? Write "c" for correct and "i" for incorrect for the terms.	
	Base:	
	Acid:	
	Catalyst:	
	Coupling reagent:	
	Solvent:	
	Activation of carboxylic groups:	**3 bp**
2.12	Name the functional group present in peptide bonds.	
	Amide	**0,5 bp**
2.13	Name the mechanism of the reaction from **B** to **C**.	
	nucleophilic addition	**0,5 bp**

2.14 Write down the structural formulae of **A-H** and **X**.
Draw **F** in its L-form in Fischer projection.
Draw **H** in the wedge-shaped form with both stereocenters S-configured.
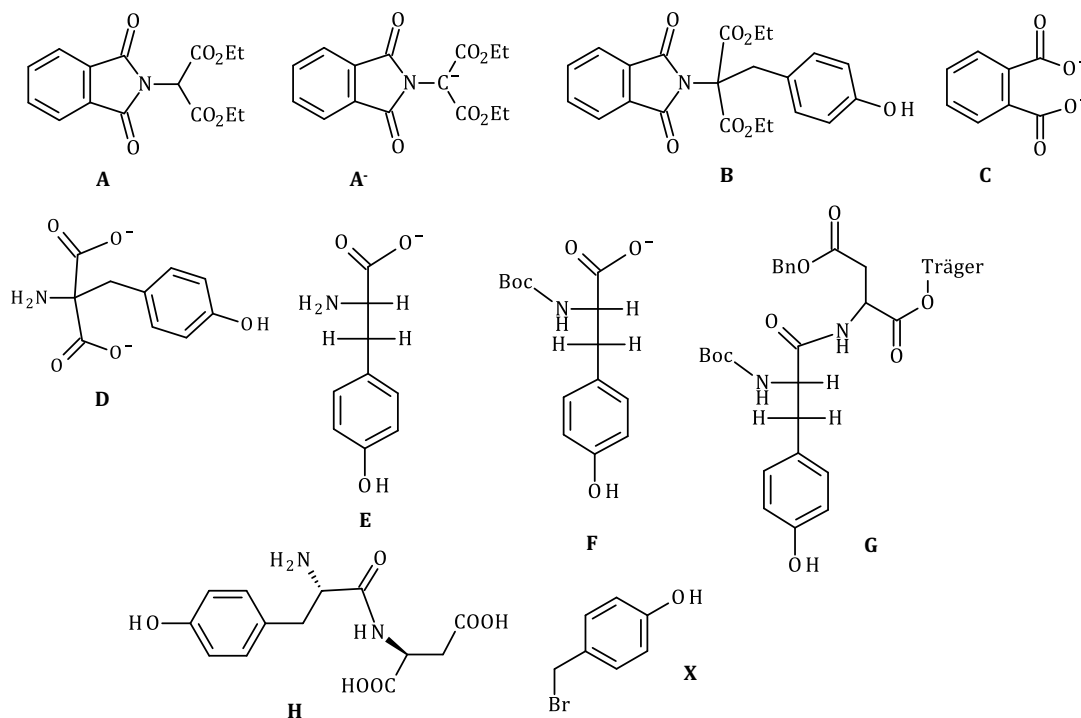
A: 2 bp, B: 2 bp, C: 2 bp, D: 2 bp, E: 2 bp, F: 2 bp, G: 2 bp, H: 3bp, X: 2 bp   **19 bp**

Problem 3 (W. Faber)   40 bp = 7 Points

Chemical equilibria – 3 acidic problems

A. The first acidic problem

We are looking for the structural formula of a monoprotic weak organic acid. Two experiments were carried out with the solid, anhydrous sodium salt of this acid.

1st experiment: 10.00 g of the salt were dissolved in 1.000 L of water. Then 10.00 mL of hydrochloric acid with a concentration of 3.000 mol/L was added. The resulting solution had a pH value of pH = 4.7903.

2nd experiment: 10.00 g of the salt were dissolved in 1.000 L of water. Then 15.00 mL of hydrochloric acid with a concentration of 3.000 mol/L was added. The resulting solution had a pH value of pH = 4.4246.

The ^{1}H-NMR of this acid is also available:

HSP-49-390
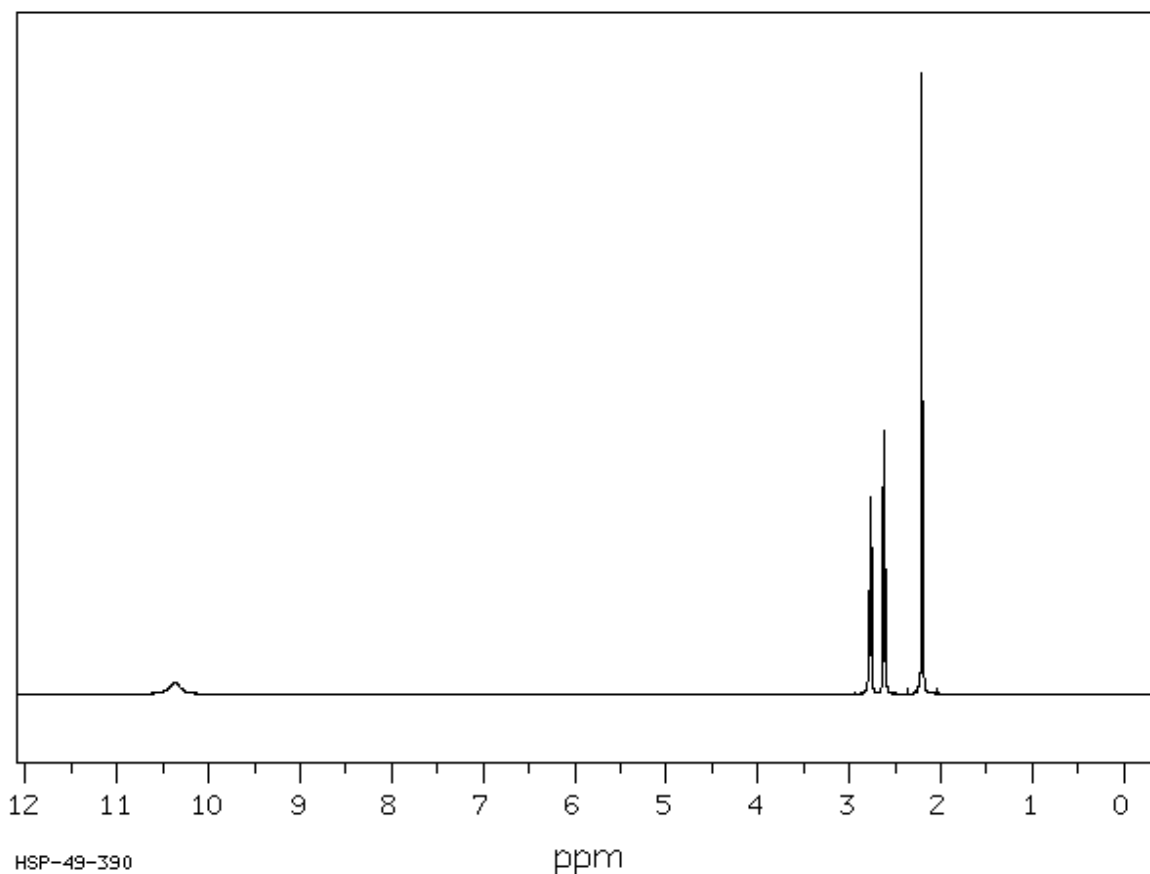
The peak at 2.2 ppm is a singlet, the two peaks at 2.6 and 2.8 ppm are triplets.

3.1 Calculate the pK_A value of this acid and its molar mass.

(I) $4{,}7903 = pK_A - \log\left(\dfrac{0{,}03}{\frac{10}{M}-0{,}03}\right)$

(II) $4{,}4246 = pK_A - \log\left(\dfrac{0{,}045}{\frac{10}{M}-0{,}045}\right)$

(I)-(II): $0{,}3657 = \log\left(\dfrac{0{,}045}{\frac{10}{M}-0{,}045}\right) - \log\left(\dfrac{0{,}03}{\frac{10}{M}-0{,}03}\right)$

$0{,}3657 = \log\left(\dfrac{\left(\frac{0{,}045}{\frac{10}{M}-0{,}045}\right)}{\left(\frac{0{,}03}{\frac{10}{M}-0{,}03}\right)}\right)$

$2{,}3211 = \dfrac{\left(\frac{0{,}045}{\frac{10}{M}-0{,}045}\right)}{\left(\frac{0{,}03}{\frac{10}{M}-0{,}03}\right)} = \left(\dfrac{0{,}045}{\frac{10}{M}-0{,}045}\right)\cdot\left(\dfrac{\frac{10}{M}-0{,}03}{0{,}03}\right)$

$1{,}5474 \cdot \left(\dfrac{10}{M}-0{,}045\right) = \dfrac{10}{M}-0{,}03$

$1{,}5474 \cdot \dfrac{10}{M}-\dfrac{10}{M} = 1{,}5474 \cdot 0{,}045 - 0{,}03$

$\dfrac{10}{M} = \dfrac{0{,}03963}{0{,}5474} = 0{,}0724$

$M = 138{,}12\ \text{g}\cdot\text{mol}^{-1}$

In (I): $4{,}785 = pK_A - \log\left(\dfrac{0{,}03}{\frac{10}{139{,}23}-0{,}03}\right)$

$pK_A = 4{,}64$ **12 bp**

3.2 Give the sum formula and structural formula of this acid. Justify your statements by calculation and NMR.

$M(\text{HA}) = M(\text{NaA}) - M(\text{Na}) + M(\text{H}) = 138{,}12-22{,}99+1{,}01 = 116{,}14\ \text{g/mol}$

$M(\text{HA}) - M(\text{COOH}) = 71{,}12\ \text{g/mol}$

First possibility: C_5H_{11}, doesn't fit NMR

Second possibility: C_4H_7O – 4-Oxopentanic acid, fits NMR data (CH3-X, X-CH2-CH2-X)

Other isomers don't fit NMR data (spin systems, number of signals…)
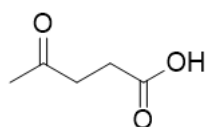
4-oxopentanoic acid
Molecular Weight: 116,12

Solution: **4 bp**

B. The second acidic problem

Maleic acid ((Z)-but-2-enedioic acid) is a solid, diprotic acid at room temperature. We are looking for the two pK_A values of this acid.

First, 20.00 g of this acid were dissolved in 1.000 liters of water. This solution had a pH value of pH = 1.408. Assume that in this experimental set-up only the first protolysis stage of maleic acid plays a role in the pH value.

3.3	Calculate pK_{A1}.

Maleic acid $C_4H_4O_4$

$M = 116,08$ g/mol

pH = 1,408

$[H_3O^+] = 10^{-1,408} = 0,03908$ mol $\cdot$ L^{-1} = [HMal$^-$]

$n = \dfrac{20g}{116,08g \cdot mol^{-1}} = 0,1723$ mol

$c = 0,1723$ mol $\cdot$ L^{-1}

$[H_2Mal] = c - [HMal^-] = 0,1723 - 0,03908 = 1,3321$ mol $\cdot$ L^{-1}

$K_{A_1} = \dfrac{[H_3O^+] \cdot [HMal^-]}{[H_2Mal]} = \dfrac{0,03908 \cdot 0,03908}{1,3321} = 1,1467 \cdot 10^{-2}$

$pK_{A_1} = -\log(1,1467 \cdot 10^{-2}) = 1,94$

6 bp

In a second experiment, 10.00 g of solid sodium hydroxide was added to the prepared maleic acid solution. This solution had a pH value of 6.135.

3.4	*Berechnen Sie* pK_{A_2}.

$n_{NaOH}^{Start} = \frac{10}{40} = 0,25$ mol

Step 1:

complete reaction: $H_2Mal + NaOH \rightleftharpoons HMal- + Na^+ + H_2O$

$n(H_2Mal) \approx 0$

$n(HMal^-) = 0,1723$

$n(Mal^{2-}) \approx 0$

$n_{NaOH}^{after\ step\ 1} = 0,25 - 0,1723 = 0,0777$ mol

Step 2:

partial reaction, until all NaOH has reacted: $HMal- + NaOH \rightleftharpoons Mal^{2-} + H_2O$

$n(H_2Mal) \approx 0$

$n(HMal^-) = 0,1723 - 0,0777 = 0,0946$ mol

$n[Mal^{2-}] = 0,0777$ mol

$n_{NaOH}^{after\ step\ 2} \approx 0$

$pH = pK_{A_2} - \log\left(\frac{[HMal^-]}{[Mal^{2-}]}\right)$

$6,135 = pK_{A_2} - \log\left(\frac{0,0946}{0,0777}\right)$

$pK_{A_2} = 6,22$

8 bp

C. The third acidic problem

A diluted sulphuric acid solution of unknown concentration has a pH value of pH = 1.000. We are looking for the molar concentrations of all sulphuric acid species in this solution. For the sake of simplicity, assume that the first protolysis of the sulphuric acid is complete. For sulphuric acid the acid constants are pK_{A1} = -3.00 and pK_{A2} = 1.92.

3.5	*Calculate the concentrations of hydrogen sulphate and sulphate assuming that the first protolysis of the sulphuric acid is complete.*

c...total concentration of all sulphuric acid species
$s = [H_2SO_4]$
$h = [HSO_4^-]$
$a = [SO_4^{2-}]$
$[H_3O^+] = 0{,}100 \ mol \cdot L^{-1}$
Assumption: s≈0
(I) $0{,}1 = h + 2 \cdot a$
(II) $10^{-1{,}92} = \frac{a \cdot 0{,}1}{h} \Rightarrow h = a \cdot 10^{0{,}92}$
(II) in (I): $0{,}1 = a \cdot 10^{0{,}92} + 2a = 10{,}318 \cdot a$
$a = [SO_4^{2-}] = 0{,}00969 \ mol \cdot L^{-1}$
in (II): $h = [HSO_4^-] = 0{,}0806 \ mol \cdot L^{-1}$

6 bp

3.6	*Check whether the assumption of complete protolysis was justified or not and calculate the sum of the concentrations of all sulphur-containing species in this solution.*

$10^3 = \frac{h \cdot 0{,}1}{s}$
$s = \frac{0{,}0806 \cdot 0{,}1}{10^3} = 8{,}06 \cdot 10^{-6}$
The concentration of the remaining sulphuric acid is three orders of magnitude lower than that of the other two species, so the assumption s≈0 is justified.
$c = a + h + s = 0{,}00969 + 0{,}0806 + 8{,}06 \cdot 10^{-6} = 0{,}0903 \ mol \cdot L^{-1}$

4 bp

Problem 4 (J. Novacek) | 31 bp = **7 Points**
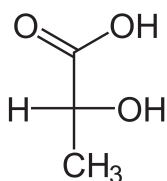
Stereocomplex branched multi-block polylactic acid and other polymers

A. Stereocomplex branched multi-block polylactic acid (a.k.a. sb-PCLDA)

Around 250000 tonnes of lactic acid (2-hydroxypropanoic acid) are produced worldwide every year, which is mainly used in the food industry and for the production of polymers (polylactides, PLA). As a biocompatible and biodegradable plastic, PLA has numerous applications - from packaging materials to horticulture and medical technology. PLA is also one of the most commonly used materials in 3D printing.

However, PLA also has disadvantages such as low thermal stability, mainly due to its poor crystallization ability. In order to improve the properties of PLA, stereocomplex polylactic acids are therefore produced. Stereocomplex lactic acid (sc-PLA) is produced by mixing the two enantiomers of PLA and has a higher crystallization rate and a melting point approx. 50°C higher than PLA. However, as sc-PLA is not yet the perfect solution, attempts are being made to cross-link the individual PLA polymer strands to produce branched multi-block polymers.

4.1 Draw the D-lactic acid in Fischer projection.
1 bp
4.2 Tick the correct box(es):
O *D*-lactic acid is identical to *S*-lactic acid. O *D*-lactic acid is an enatiomer of *S*-lactic acid. O *D*-lactic acid is a diastereoisomer of *S*-lacitc acid. O from the structure given one can deduce that it is (+)-lactic acid. O from the structure given one can deduce that it is (−)-lactic acid. Enantiomer von S-Milchsäure. **1 bp**

Lactic acid can react to form a cyclic diester (lactide).
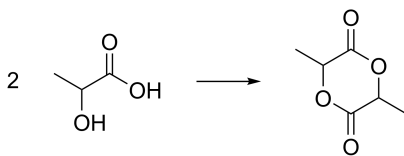
4.3	Write down the number of stereoisomers of the lactide drawn above.	
	3 - (R,R), (S,S), meso.	**1 bp**

4.4	Determine the number of NMR signals for (S,S)-lactide and state the expected integrals, multiplicities and shifts for the ^{1}H-NMR spectrum.	

Signals in ^{1}H-NMR
(inkl. integrals, multiplicities and approximate chemical shifts):
   Signal 1: 1 (2) H, q, 5 ppm (3,5-6 ppm okay)
   Signal 2: 3 (6) H, d, 1,5 ppm (1-2 ppm okay)

Number of signals in ^{13}C-NMR: ___ 3

Number of signals in ^{16}O-NMR: ___ 0 (^{16}O not NMR-active)

4 bp

Polycaprolactone (PCL) is also a biodegradable plastic - but based on crude oil. The monomer for this is ε-caprolactone. The polymer synthesis of PCL diol is started by adding compound A.

ε-Caprolacton   **A**
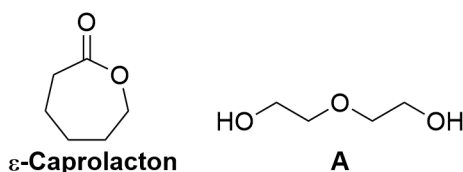
4.5	Draw the structural formula of PCL-Diol.	
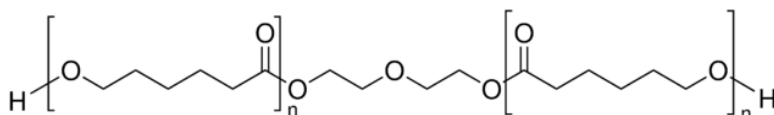
2 bp

The synthesis of stereocomplexed branched multi-block polylactic acid (sb-PCLDA) is shown here:

L-Lactide   D-Lactide
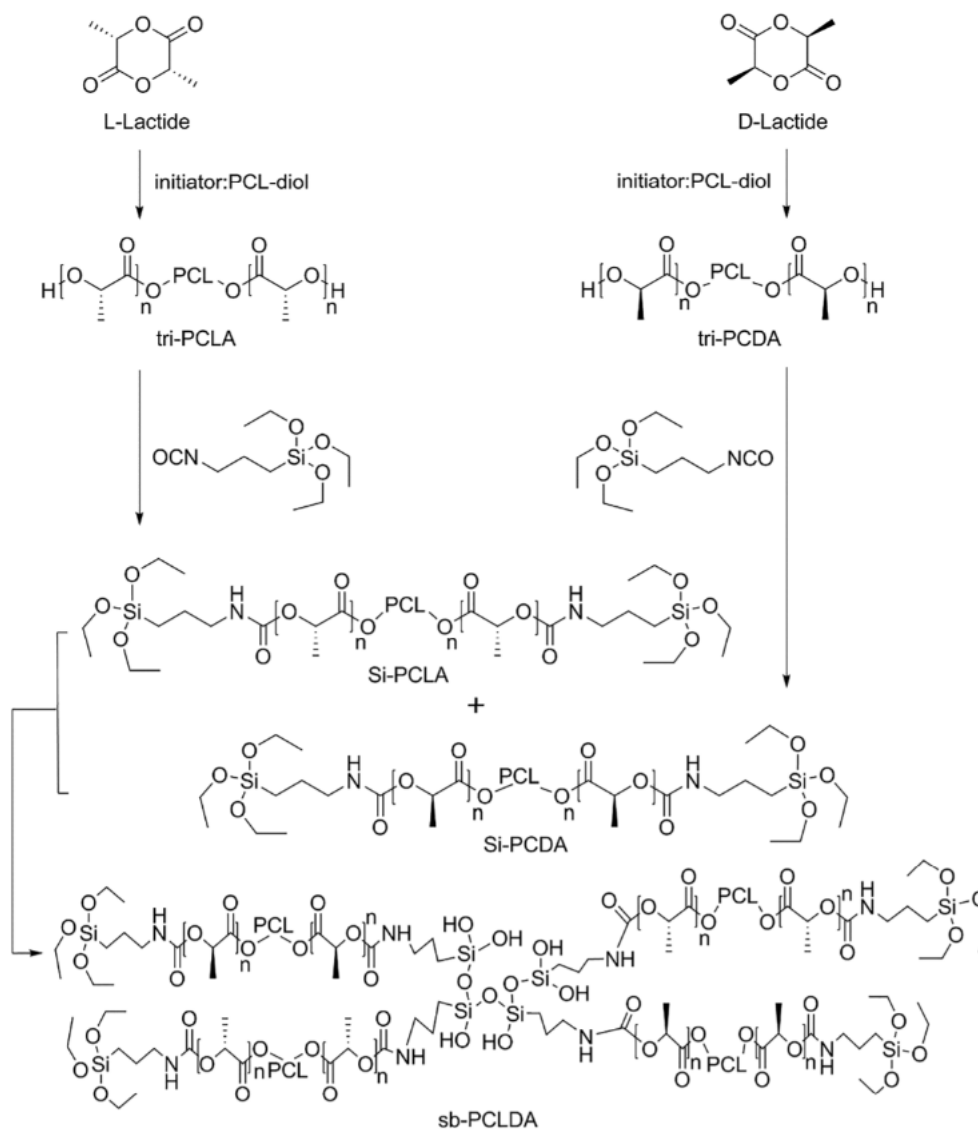
The PCL diol (with M_n = 2780 g/mol) is used as an initiator for the synthesis of tri-PCLA and tri-PDLA. These two polymers are synthesized separately but under identical conditions and differ only in their stereochemistry.

The free OH end groups of tri-PCDA (or tri-PCLA) are reacted with an isocyanate to form Si-PCDA (or Si-PCDA). These polymers are cross-linked in the final step to form the desired stereocomplex branched multi-block polylactic acid (sb-PCLDA).

The following formulas play a role in the characterization of polymers and may be helpful.

$$P_n = \frac{M_n}{M_{Monomer}} \qquad M_n = \frac{\sum n_i M_i}{\sum n_i} \qquad M_w = \frac{\sum m_i M_i}{\sum m_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} \qquad PDI = \frac{M_w}{M_n}$$

GPC was performed to analyze sb-PCLDA, tri-PCDA and another polymer **B**. The result is shown on the right.

tri-PCDA:
M_w = 20.40 kg/mol, PDI = 1.36

sb-PCLDA:
M_w = 157.31 kg/mol, PDI = 1.93
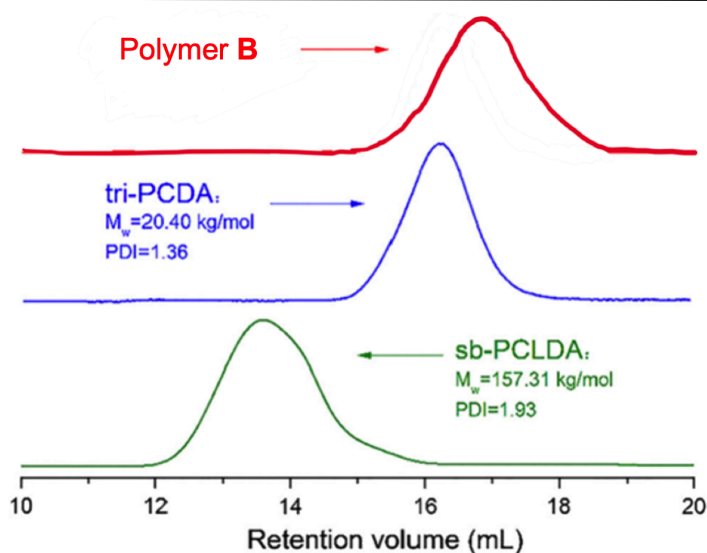
4.6	Calculate n in tri-PCDA.
	M_n(tri-PCDA) = M_w/PDI = 20400 g/mol / 1,36 = 15000 g/mol M_n (PCL) = 2780 g/mol ΔM_n = M_n(tri-PCDA) - M_n(PCL) = 12220 g/mol M(single polymer unit) = 72 g/mol $2n$ = ΔM_n / M(single polymer unit) = 170 n = 85 **4 bp**
4.7	Calculate M_n in sb-PCDLA and the average number of tri-PCDA/tri-PCLA chains (total number only!) in sb-PCLDA (rounded to one decimal place).
	M_n(sb-PCDLA) = M_w/PDI = 157310 g/mol / 1,93 = 81508 g/mol M_n(sb-PCDLA) / M_n(tri-PCDA) = 81508 g/mol / 15000 g/mol = 5,4 **2 bp**
4.8	Look at polymer **B** and tick the correct box(es): Polymer **B** has a … than tri-PCDA.
	O higher average molar mass　　　　O larger molar mass distribution O similar average molar mass　　　　O similar molar mass distribution O lower average molar mass　　　　O smaller molar mass distribution lower average molar mass & larger molar mass distribution　　　　**1 bp**

C. Chaos of polymers

The following four polymerizations from the monomers **C** to **H** are carried out in a polymer chemistry laboratory.

Polymerisation I

AIBN

C

Polymerisation II

D + **E**
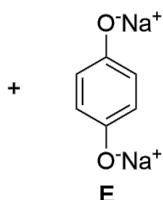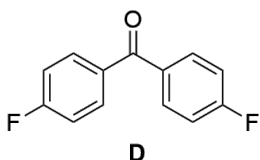
Polymerisation III

F + **G**
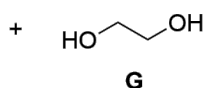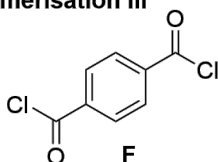
Polymerisation IV

L = CH$_3$(CF$_3$)$_2$CO$^-$

H
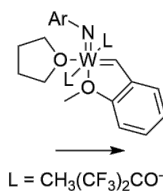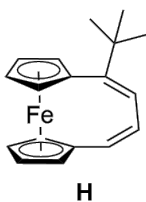
4.9	Draw the repetitive unit (constitutional repeating unit) for each of the polymerization products into the boxes above.
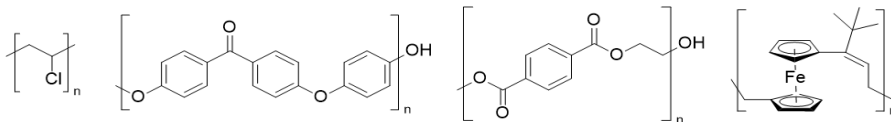
.   **4 bp**

4.10 In the table below, tick all the boxes that apply to the respective polymerization.

Polymerisation	chain-growht polymerisation	step-growth polymerisation	living polymerisation	Radikalische Polymerisation	polycondensation	polyaddition	ROMP
I	x			x		x	
II		x			x		
III		x			x		
IV			x			x	x

                                                       2 bp

Before the polymerizations are started, the monomers are analysed using various methods. The last Bachelor student was very motivated and had already carried out several analyses. Unfortunately, he was at least as chaotic. He did not label the analysis results and generally documented them very poorly. A Master's student wants to bring some order to the chaos and assign the spectra (if available) to the corresponding monomers C to H.

In the five MS analyses carried out, only the intensities of the molecular peaks (in %, distance between two peaks always 1 g/mol) but not the molar masses were given.

Spectrum 1

Spectrum 2

Spectrum 3

Spectrum 4
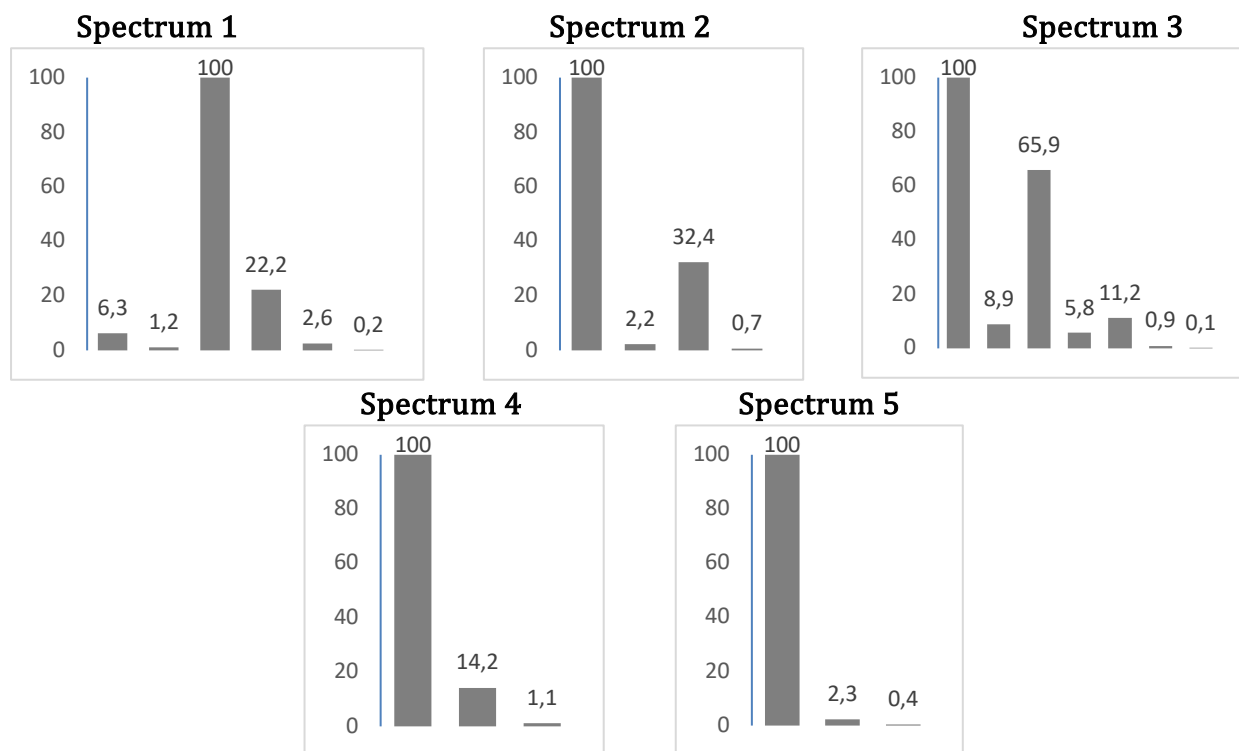
Spectrum 5

In addition, an IR spectrum, a ^{13}C-NMR spectrum and the data from two ^{1}H-NMR spectra were also found.

Spectrum 6:

Spectrum 7:

Peaks labeled: 193.8422 | 167.0944, 163.7244 | 133.7196, 133.6788, 132.5815, 132.4598 | 115.7253, 115.4351 | 77.4641, 77.0406, 76.6171

Lösungsmittel

f1 (ppm) axis: 210, 200, 190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0

Intensity axis: 15000, 14000, 13000, 12000, 11000, 10000, 9000, 8000, 7000, 6000, 5000, 4000, 3000, 2000, 1000, 0, -1000
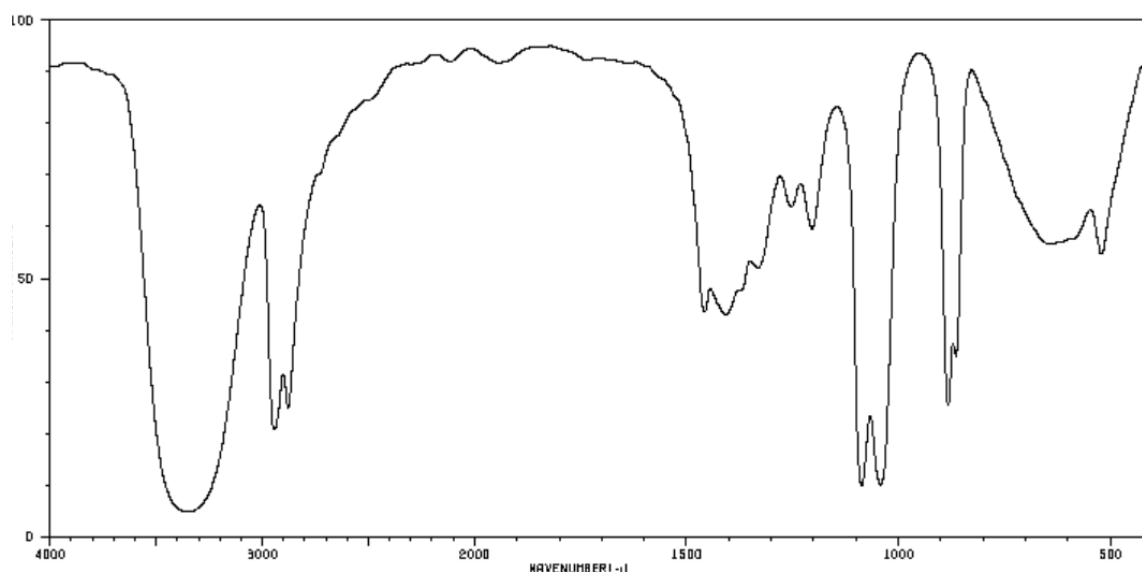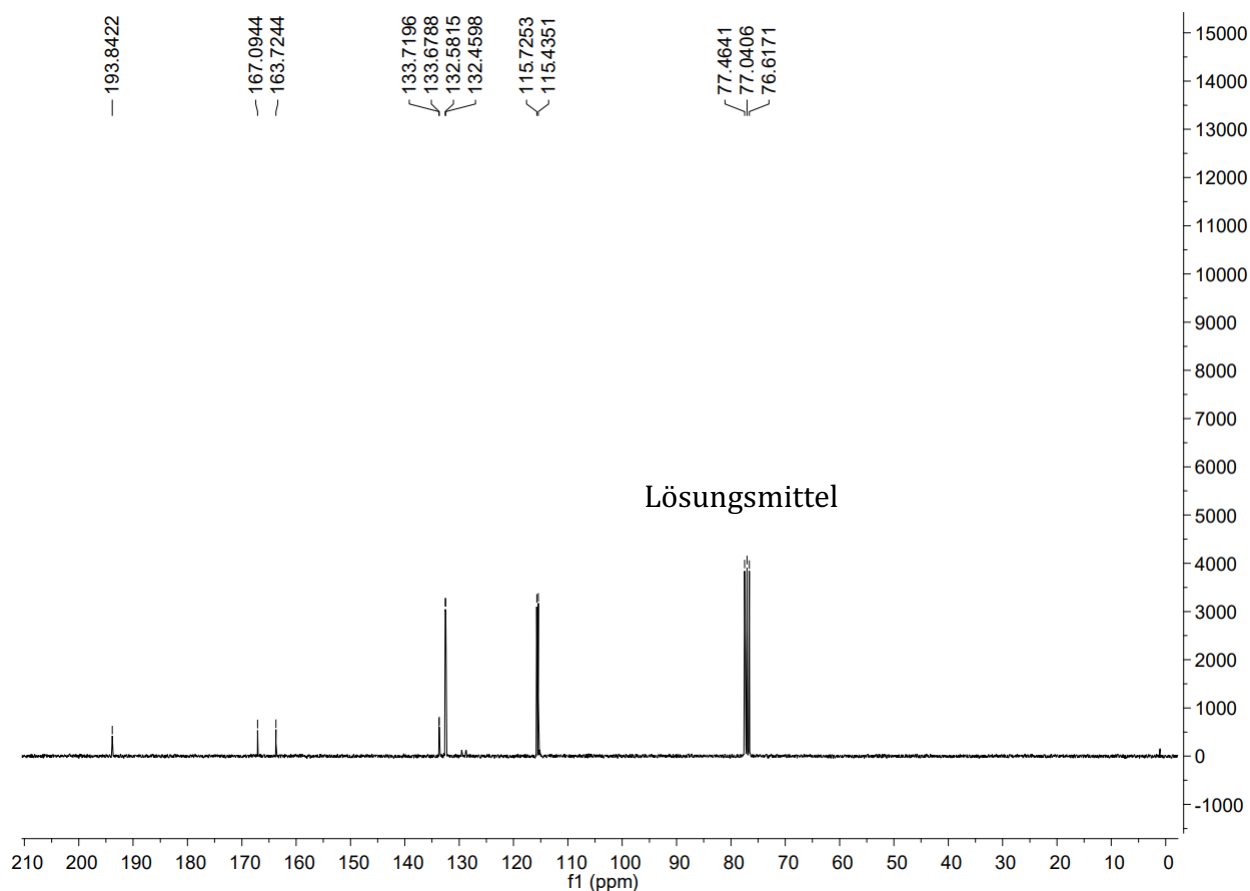
Spectrum 8: ^{1}H-NMR: δ 5.25 (1H, dd, $J = 8.0, 2.1$ Hz), 5.36 (1H, dd, $J = 14.9, 2.1$ Hz), 6.74 (1H, dd, $J = 14.9, 8.0$ Hz).

Spectrum 9: ^{1}H-NMR: δ 3.17(1H, s), 3.72 (2H, s).

4.11 Assign one of the monomers **C-H** to each of the given spectra.
(Some monomers occur several times. Only the M$^+$ peaks can be seen in the MS).

    Spectrum 1: ____   Spectrum 2: ____   Spectrum 3: ____

    Spectrum 4: ____   Spectrum 5: ____   Spectrum 6: ____

    Spectrum 7: ____   Spectrum 8: ____   Spectrum 9: ____

    1H, 2C, 3F, 4D, 5G, 6G, 7D, 8C, 9G.   **9 bp**

Problem 5 (G. Schellander) **38 bp = 10 Points**

Thermodynamics and orbitals – Carbides

Carbides are compounds that contain carbon as the most electronegative element. There are salt-like, covalent and metallic carbides. Within the salts the following distinction is made:

	(1)	(2)	(3)
Name	Methanides	Acetylides	Allenides
Anion	C^{4-}	C_2^{2-}	C_3^{4-}

5.1	Assign the correct name to the following compounds by writing (1), (2) or (3) below them.

Al_2C_6	Be_2C_3	BaC_2	Li_4C_3	
2	3	2	3	**2 bp**

5.2	Write down the complete electron configuration of the methanide anion.
$1s^2\,2s^2\,2p^6$	**0,5 bp**

On contact with water, hydrocarbons are formed from these carbides. For the following considerations aluminum methanide is reacted with aqueous sodium hydroxide solution:

5.3	Write down a balanced equation for this process in which only electrically neutral species occur.
$Al_4C_3 + 12\,H_2O + 4\,NaOH \rightarrow 4\,Na[Al(OH)_4] + 3\,CH_4$	**3 bp**

5.4	Complete the MO diagram for the acetylide C_2^{2-}. Populate with electrons and state the bonding order and magnetic behavior.
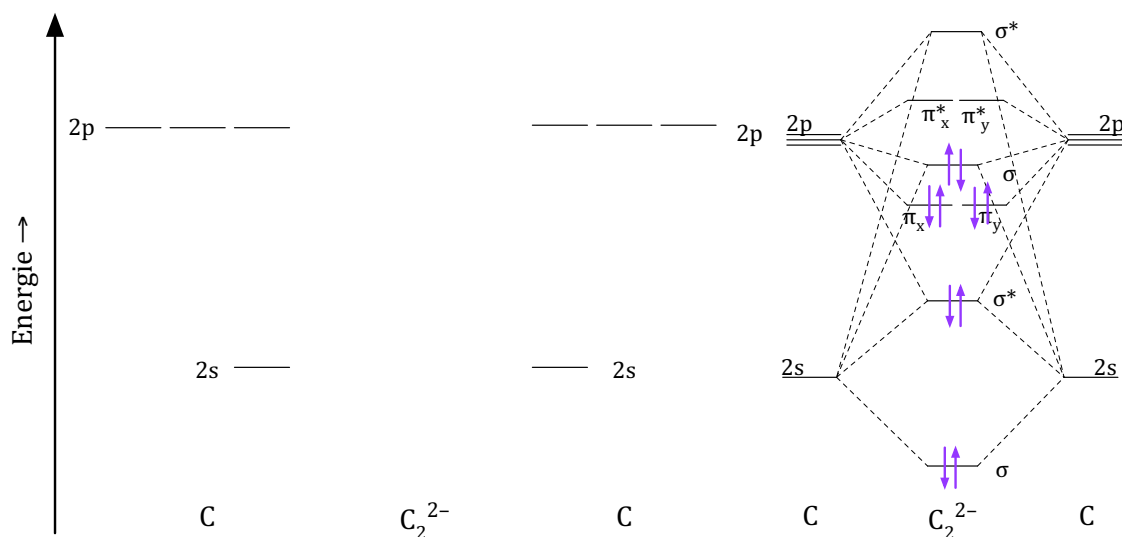
Bond order = 3   O paramagnetic   O diamagnetic X diamagnetic

5 bp

The allenide ion is remarkably symmetrical and so are its molecular orbitals, some of which you can see here.

| (1) | (2) | (3) | (4) |

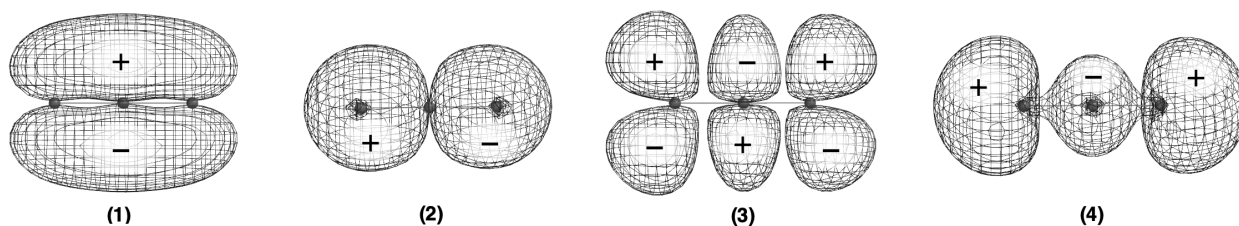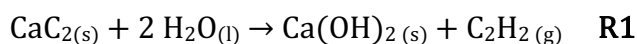| 5.5	Tick the correct box(es) in each case.				
	antibonding orbital	☐ (1)	☐ (2)	☐ (3)	☐ (4) **(3)**
	bonding orbital	☐ (1)	☐ (2)	☐ (3)	☐ (4) **(1,2,4)**
	σ - orbital	☐ (1)	☐ (2)	☐ (3)	☐ (4) **(2,4)**
	π- orbital	☐ (1)	☐ (2)	☐ (3)	☐ (4) **(1, 3)**
	δ - orbitale	☐ (1)	☐ (2)	☐ (3)	☐ (4) **(non)**
	p-orbitals are involved in:	☐ (1)	☐ (2)	☐ (3)	☐ (4) **(1,2,3,4)**
					6 bp

Calcium carbide is the best known carbide. It reacts with water according to the equation

$$CaC_{2(s)} + 2\,H_2O_{(l)} \rightarrow Ca(OH)_{2\,(s)} + C_2H_{2\,(g)} \quad \textbf{R1}$$

The gas pressure of the resulting ethine is used in the carbide method (CM) to determine the residual moisture of screed and wall samples. 50.0 g of the sample is placed in a steel bottle together with a glass ampoule containing calcium carbide and a few steel balls. This is sealed and the ampoule is destroyed by the steel balls when shaken. There is a pressure gauge on the lid which indicates the overpressure.

One ampoule contains 7.00 g CaC₂.
Let us assume that this contains 4.50 % (m/m) of unreactive impurities.

5.6	Calculate the maximum water content that the sample may have so that all the water can still be converted. Give your answer in mass percent.
	$M(CaC_2) = 64{,}01\,gmol^{-1}$
	6,685g CaC₂ correspond to 0,1043 mol
	→ 0,2086 mol H₂O are max. possible, corresponds to 3,76g
	3,76/50 = 0,0752 → 7,5 % water **2 bp**

A steel bottle has a volume of 700 cm³. The solid sample has a density of 2 gcm⁻³, the added steel balls have a total volume of 4.80 cm³ and the ampoule with carbide has a volume of 11 cm³. These volumes do not change during the reaction. The bottle is filled at atmospheric pressure and the pressure gauge only shows the overpressure created by the ethine as the pressure p (in bar). The temperature after the reaction is 20 °C.

5.7 Derive a relationship that shows the water content w_{H2O} of the sample (in mass percent) as a function of the observed pressure p (in bar).	
$V_{gas} = 700–50/2 – 4,8 – 11 = 659,2$ cm³	**1 bp**
$n_{ethine} = \dfrac{pV}{RT} = \dfrac{p \cdot 10^5 \text{Pa bar}^{-1} \cdot 659,2 \cdot 10^{-6} \text{m}^3}{8,3145 \text{ Pa m}^3\text{K}^{-1}\text{mol}^{-1} \cdot 293,15 \text{ K}} = p \cdot 0,02705 \text{ mol bar}^{-1}$	
$w_{H_2O} = \dfrac{m_{H_2O}}{50g} \cdot 100\% = \cdot \dfrac{n_{H_2O} \cdot 18,02 \text{ gmol}^{-1}}{50} 100\% = \dfrac{2 \cdot n_{C_2H_2} \cdot 18,02 \text{ mol}^{-1}}{50} 100\%$	
$w_{H2O} = p \cdot 1,95 \% \text{ bar}^{-1}$	**2 bp**

Michi, a promising young chemist from the Bucklige Welt, wants to measure a reaction energy himself. To do this, he improvises a calorimeter: He fills an insulating container with almost 3 liters of water and attaches a thermometer. To calibrate it, he hangs an electric heating wire in the water. He connects a 24.0 V battery and allows a current of 4.57 A to flow through the wire for 312 seconds. The temperature in the calorimeter rises by 2.74 K.

5.8 Calculate the converted electrical energy (= power times time).	
$W_{el} = UIt = 24 \text{ JC}^{-1} \cdot 4,57 \text{ Cs}^{-1} \cdot 312s = 34220 \text{ J}$	**1 bp**

5.9 Calculate the heat capacity C_K of the calorimeter.	
$W_{el} = Q = C\Delta T$ $\Rightarrow C = W_{el} / \Delta T = 34220 \text{ J}/2,74 \text{ K} = 12489 \text{ JK}^{-1}$	**1 bp**

Next, Michi takes the CM bottle and adds an ampoule of 7.0 g pure CaC_2 and a test ampoule with 1.0 g water together with the steel balls. Before starting the reaction, he leaves the whole bottle outside at 8.0°C for a long time. He then places the bottle in the calorimeter (which has a temperature of 24.4°C) and waits until the mixing temperature (23.6°C) has been reached.

5.10 Calculate the heat capacity C_F of the bottle including filling.

temperature compensation (F-bottle, K-calorimeter)

$C_F(23,6 - 8) = C_K(24,4 - 23,6) \Rightarrow C_F = 12489\text{JK}^{-1}\frac{0,8}{15,6} = 640,5\,JK^{-1}$

2 bp

Then Michi shakes the CM bottle, the reaction starts and he reads 24.0°C after a short time.

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*5.11 Calculate the reaction energy $\Delta_R U$ for **R1** resulting from Michi's measurement. If you have not previously obtained any values, use $C_K = 14000$ J/K, $C_F = 450$ J/K.*

reaction

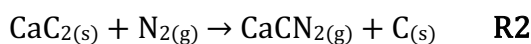$$q_R = (C_F + C_K)\cdot(24 - 23,6) = 5,25\,kJ$$

Substance amount $n(\text{H}_2\text{O}) = 0,0555$ mol;

$\Delta_R U = \frac{5,25\,kJ}{0,02775\,mol} = 189,21$ kJmol^{-1}

2 bp

Historically, calcium carbide was important in the Frank-Caro-process for nitrogen fixation. According to the equation

$$\text{CaC}_{2(s)} + \text{N}_{2(g)} \rightarrow \text{CaCN}_{2(g)} + \text{C}_{(s)} \qquad \textbf{R2}$$

calcium cyanamide was produced. The reaction was originally carried out at 1000°C (1273 K).

	$\Delta_f H^\ominus$ /kJmol^{-1}	$S^\ominus$ /JK^{-1}mol^{-1}	C_p /JK^{-1}mol^{-1}
C $_{(s)}$	0.0	5.7	8.5
CaCN$_{2\,(s)}$	−350.6	81.6	91.8
CaC$_{2\,(s)}$	−59.8	70.0	62.7
N$_{2\,(g)}$	0.0	191.6	29.1

Thermodynamic data at 298 K, **only C_p is considered to be dependent on temperature.**

---

*5.12 Calculate the standard reaction enthalpy of **R2** at 1273 K.*

$\Delta_R H_{298} = -350,6 + 59,8 = -290,8$ kJmol^{-1}　　　　　　　　**0,5 bp**

$\Delta_R C_p = 8,5 + 91,8 - 62,7 - 29,1 = 8,5\,JK^{-1}mol^{-1}$　　　　　**1 bp**

$\Delta_R H_{1273} = \Delta_R H_{298} + \Delta_R C_p(1273 - 298) = -290,8 + 0,0085\cdot 975$

$= -282,5$ kJ mol^{-1}　　　　　　　　　　　　　　　　　　**1 bp**

5.13	Calculate the standard reaction entropy of **R2** at 1273 K.
	$$\Delta_R S_{298} = 5{,}7 + 81{,}6 - 70 - 191{,}6 = -174{,}3 \text{ J K}^{-1}\text{mol}^{-1}$$ $$\Delta_R S_{1273} = \Delta_R S_{298} + \Delta_R C_p \ln\frac{1273}{298} = -174{,}3 + 8{,}5 \cdot \ln\frac{1273}{298} = -162{,}0 \text{ J K}^{-1}\text{mol}^{-1} \quad \textbf{2 bp}$$

The calcium cyanamide can itself be used as a nitrogen fertilizer, but can also be hydrolyzed to ammonia.

5.14	Give a balanced chemical equation for the reaction in which ammonia and another substance (with $M \approx 100$ g/mol) are formed from $CaCN_2$ and water.
	$CaCN_2 + 3\,H_2O \rightarrow 2\,NH_3 + CaCO_3$ **1 bp**

5.15	Give a Lewis formula (including non-bonding electron pairs and formal charges) for the $CN_2{}^{2-}$-anion.
	1 bp

When reacted with water in the presence of CO_2, H_2NCN (cyanamide), the amide of cyanic acid, is formed.

5.16	Draw two tautomeric forms of cyanamide.
	2 bp

5.17	An anion of this amide plays a role in the conversion to cyanamide. Draw two mesomeric resonance structures of this anion, as well as curved arrows that explain the rearrangement.
	2 bp

Problem 6 (I. Stadler-Ulitsch) **19 bp = 7 Points**

Kinetics with halogen compounds

The following problem deals with various halogen compounds.

A. Sulfuryl chloride

Sulphuryl chloride is a colorless, high-density substance that corrodes in the presence of water and can serve as a starting material for aromatic sulphonic acid chlorides. At a certain temperature, SO_2Cl_2 decomposes according to 1st order kinetics with $k = 2.81 \cdot 10^{-3}$ min^{-1}.

6.1 Specify the half-life of the reaction.	
$\tau = \frac{\ln 2}{k} = 246{,}67$ min	**0,5 bp**

6.2 Specify the period of time after which the concentration of SO_2Cl_2 decreases to 10 % of the initial value.	
$0{,}1 = e^{-2{,}81 \cdot 10^{-3} \cdot t}$ $t = \frac{\ln 0{,}1}{-0{,}00281} = 819{,}42$ min	**1 bp**

B. Hydrogen chloride

The kinetics of the reaction

$$2\ ICl_{(g)} + H_{2(g)} \rightarrow I_{2(g)} + 2\ HCl_{(g)} \qquad R6.1$$
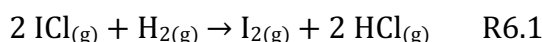
were investigated and the following data were obtained:

Experiment	[ICl]$_0$ /(mmol dm^{-3})	[H$_2$]$_0$ /(mmol dm^{-3})	v_0 /(mmol dm^{-3} s^{-1})
1	1.5	1.5	3.7 ·10^{-7}
2	3.0	1.5	7.4 ·10^{-7}
3	3.0	4.5	22 · 10^{-7}
4	4.7	2.7	?

6.3 Determine the reaction orders in relation to ICl and H_2 and write down the differential rate law for R6.1.	
$v = k \cdot [ICl] \cdot [H_2]$	**3 bp**

6.4 Enter the rate constant for R6.1 in the correct unit and calculate the initial rate for experiment 4.	
$k_1 = 1{,}64 \cdot 10^{-4}$ L·mol^{-1}·s^{-1} $k_2 = 1{,}64 \cdot 10^{-4}$ L·mol^{-1}·s^{-1} $k_3 = 1{,}63 \cdot 10^{-4}$ L·mol^{-1}·s^{-1} $k = 1{,}6395 \cdot 10^{-4}$ L·mol^{-1}·s^{-1} $v = 1{,}6395 \cdot 10^{-4} \cdot 4{,}7 \cdot 10^{-3} \cdot 2{,}7 \cdot 10^{-3} = 2{,}0805 \cdot 10^{-9}$ mol·L^{-1}·s^{-1}	**3 bp**

C. Benzendiazonium chloride

Benzendiazonium chloride is a strong, unstable electrophile. It can react with water, releasing N_2 to form phenol. The activation energy for this reaction is 99.1 kJ/mol.

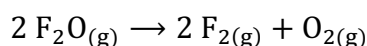| 6.5 Calculate the temperature at which the reaction rate is 10 % higher than at 25 °C. |
| --- |

$$\ln \frac{k(T_1)}{k(T_2)} = -\frac{E_A}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{k}{k \cdot 1,1} = -\frac{99100}{8,314} \cdot \left(\frac{1}{298,15} - \frac{1}{T_2} \right) \rightarrow T_2 = 298,86 \text{ K}$$
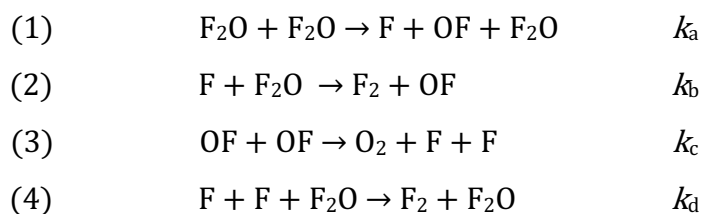
2,5 bp

D. Oxygen difluoride

Oxygen difluoride is a colorless gas and one of the strongest oxidizing agents. It even reacts with xenon. It is thermally decomposed to fluorine and oxygen:

$$2 \, F_2O_{(g)} \longrightarrow 2 \, F_{2(g)} + O_{2(g)}$$

The following rate law has been found experimentally:

$$-\frac{d[F_2O]}{dt} = k_R[F_2O]^2 + k_R'[F_2O]^{\frac{3}{2}}$$

J. Czarnowski and H. J. Schumacher proposed the following reaction mechanism:

(1)	$F_2O + F_2O \rightarrow F + OF + F_2O$	k_a
(2)	$F + F_2O \rightarrow F_2 + OF$	k_b
(3)	$OF + OF \rightarrow O_2 + F + F$	k_c
(4)	$F + F + F_2O \rightarrow F_2 + F_2O$	k_d

Note:

In (1), a molecule of a foreign gas X can also appear as a collision partner: $F_2O + X \rightarrow F + OF + X$.

Here, however, we consider a situation in which only F_2O occurs as a collision partner.

6.6   *Using the steady-state model, show that this mechanism is consistent with the experimentally found rate law.*

     Express the empirical constants k_R and k'_R by $k_{a...d}$.

$$\frac{d[OF]}{dt} = k_a \cdot [F_2O]^2 + k_b \cdot [F][F_2O] - 2 \cdot k_c \cdot [OF]^2 = 0$$

$$\frac{d[F]}{dt} = k_a \cdot [F_2O]^2 - k_b \cdot [F][F_2O] + 2 \cdot k_c \cdot [OF]^2 - 2 \cdot k_d \cdot [F]^2[F_2O] = 0$$

Combination of this terms lead to:

$$k_a \cdot [F_2O]^2 + k_a[F_2O]^2 - 2 \cdot k_d \cdot [F]^2[F_2O] = 0$$

This leads to:

$$[F] = \sqrt{\frac{k_a}{k_d}}[F_2O]$$

Inserting into

$$-\frac{d[F_2O]}{dt} = k_a[F_2O]^2 + k_b[F][F_2O]$$

gives

$$-\frac{d[F_2O]}{dt} = k_a[F_2O]^2 + k_b\sqrt{\frac{k_a}{k_d}}[F_2O] \cdot [F_2O]$$

and thus

$$-\frac{d[F_2O]}{dt} = k_a[F_2O]^2 + k_b \cdot k_a^{\frac{1}{2}} \cdot k_d^{-\frac{1}{2}} \cdot [F_2O]^{\frac{3}{2}}$$

$$k_R = k_a$$

$$k'_R = k_b \cdot \left(\frac{k_a}{k_d}\right)^{\frac{1}{2}}$$

9 bp

Problem 7 (N. Langer) **23 bp = 6 Points**

Electrochemistry - a beautiful reddish glow - or is it blue-green?

Copper is one of the most important utility metals. It is used in its pure form or as an alloy with other metals. Copper can form ions of the type Cu^+ und Cu^{2+}. Ions of the type Cu^{3+} und Cu^{4+} also occur in complex compounds.

These potentials can be represented in a Latimer diagram (pH = 0):
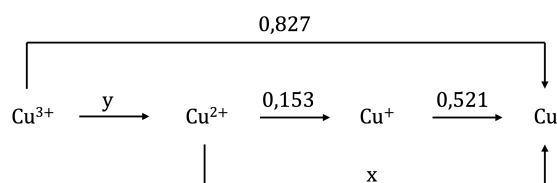
7.1	Use this diagram to specify x and y.

$$2x = 0.153 + 0.521$$
$$x = 0.337$$

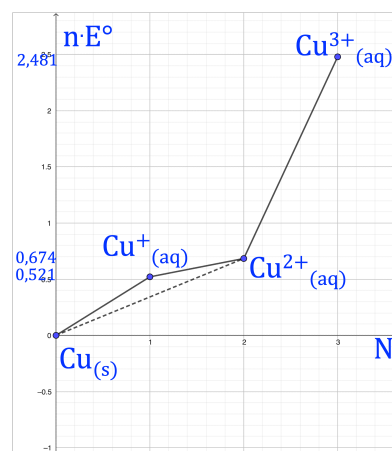$$3 \cdot 0.827 = y + 0.153 + 0.521$$
$$y = 1.807$$

2 bp

7.2	Draw a frost diagram of the 4 copper species. Label the axes and make it clear that Cu^+ tends to disproportionate.

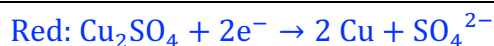Cu^+ lies above $Cu - Cu^{2+}$ line. **4 bp**

When solid copper(I) sulphate is mixed with the chelating ligand ethane-1,2-diamine ('en'), a complex formation reaction and a disproportionation reaction are observed simultaneously. The reaction products are the copper(II) chelate complex with coordination number 4 and elemental copper.

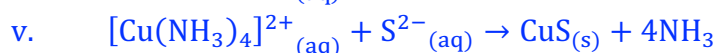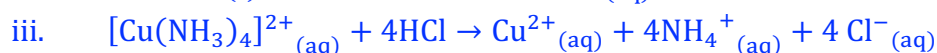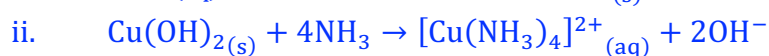| 7.3	*Formulate the two partial equations as well as the overall equation of the redox reaction including complex formation starting from solid copper(I) sulphate.*	
	Red: $Cu_2SO_4 + 2e^- \rightarrow 2\,Cu + SO_4{}^{2-}$ Ox: $Cu_2SO_4 + 4en \rightarrow 2[Cu(en)_2]^{2+} + 2e^- + SO_4{}^{2-}$ Redox: $Cu_2SO_4 + 2en \rightarrow Cu + [Cu(en)_2]^{2+} + SO_4{}^{2-}$	**2,5 bp**

Gaseous ammonia is added into an aqueous, slightly bluish solution containing $Cu^{2+}_{(aq)}$-ions.
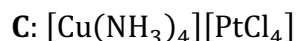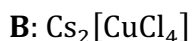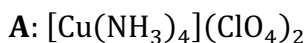
i. Initially, the formation of sparingly soluble copper(II) hydroxide is observed.
ii. If the introduction of ammonia is continued, the precipitate dissolves again to form the dark blue tetraammine copper(II) complex.
iii. If hydrochloric acid is gradually added to the solution of the tetraammine copper(II) complex, the dark blue colour of the complex disappears and the solution becomes slightly bluish again.
iv. If, on the other hand, a NaCN solution is added to the tetraammine copper(II) complex, a colourless solution is finally obtained.
v. If the tetraammine copper(II) complex is mixed with a sulphide-containing solution, a black precipitate is formed.

7.4	<u>*Give*</u> *the balanced chemical equation for the reactions i – v:*	
	i. $\quad Cu^{2+}{}_{(aq)} + 2H_2O + 2NH_3 \rightarrow Cu(OH)_{2\,(s)} + 2NH_4{}^+{}_{(aq)}$	
	ii. $\quad Cu(OH)_{2\,(s)} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}{}_{(aq)} + 2OH^-$	
	iii. $\quad [Cu(NH_3)_4]^{2+}{}_{(aq)} + 4HCl \rightarrow Cu^{2+}{}_{(aq)} + 4NH_4{}^+{}_{(aq)} + 4\,Cl^-{}_{(aq)}$	
	iv. $\quad [Cu(NH_3)_4]^{2+}{}_{(aq)} + 4CN^-{}_{(aq)} \rightarrow [Cu(CN)_4]^{2-}{}_{(aq)} + 4NH_3$	
	v. $\quad [Cu(NH_3)_4]^{2+}{}_{(aq)} + S^{2-}{}_{(aq)} \rightarrow CuS_{(s)} + 4NH_3$	
		5 bp

The following four complex compounds are now considered:

A: $[Cu(NH_3)_4](ClO_4)_2$ **B**: $Cs_2[CuCl_4]$ **C**: $[Cu(NH_3)_4][PtCl_4]$ **D**: $Cs[CuF_4]$

---

*7.5 Enter the names of compunds **A** and **B**.*

A: Tetraamminkupfer(II)-perchlorat

B: Caesiumtetrachloridocuprat(II)

1 bp

Dissolve 1 mmol copper(II) nitrate in 100 ml water or 100 ml NH3 solution (c=1.04 mol/L). These two solutions are combined to form a concentration cell using copper electrodes. The voltage measurement (at 25°C) gives 384 mV.

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*7.6 Berechnen Sie die Komplexbildungskonstante β für das Komplexkation von **A**.*

$$\Delta E = E^0 - \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{1}{[Cu^{2+}]_{H_2O}} - \left(E^0 - \frac{RT}{zF} \cdot \ln \frac{1}{[Cu^{2+}]_{NH_3}} \right)$$

$$= \frac{RT}{zF} \left(\ln \frac{1}{[Cu^{2+}]_{NH_3}} - \ln \frac{1}{[Cu^{2+}]_{H_2O}} \right) = 0,384\,V$$

$[Cu^{2+}]_{NH_3} = 1,04 \cdot 10^{-15} molL^{-1} \ll 0,01$ →most of the Cu^{2+} is in the complex→
$$[Cu - complex] \approx c_0(Cu^{2+}) = 0,01 M$$

$[NH_3] = c_0(NH_3) - 4\,c(\text{Cu-complex}) = 1\,M$

$$\beta = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}] \cdot [NH_3]^4} = \frac{0,01}{1,04 \cdot 10^{-15} \cdot 1^4} \approx 10^{13}$$

5 bp

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*7.7 Give the formula of a compound isomeric to **C**.*

$[Pt(NH_3)_4][CuCl_4]$
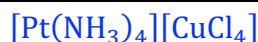
0,5 bp

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*7.8 Complex **D** has a ligand field splitting of 252 kJ/mol. Calculate the wavelength of the absorbed light and state the colour of the complex.*

$$\Delta_0 = 252 \frac{kJ}{mol} = 2,52 \cdot 10^5 \frac{J}{mol}$$

$$\lambda = \frac{N_A \cdot h \cdot c}{\Delta_0} = \frac{6.022 \cdot 10^{23} \cdot 6.626 \cdot 10^{-34} \cdot 3.00 \cdot 10^8}{2.52 \cdot 10^3} = 4.75 \cdot 10^{-7} = 475 nm$$

orange

3 bp

Problem 8 (H. Wachtler) 19 bp = 6 Points

Borium Metallhydridum

A. problem Metallhydride

Metal hydrides are suitable for the safe storage of large quantities of hydrogen (e.g. for the operation of fuel cells). An example of this is Mg_2NiH_4, which is obtained by strongly mixing magnesium hydride and elemental nickel. As a very simplified working hypothesis, assume that the nickel atoms in the elementary cell of Mg_2NiH_4 are face-centred cubic and that the Mg ions occupy tetrahedral vacancies. Four hydrogen atoms coordinate around one nickel atom.

|		
8.1	*Give the balanced chemical equation for the formation of Mg_2NiH_4. <u>Give</u> the conventional oxidation numbers of the elements in this reaction.*	
	$2\ MgH_2 + Ni \longrightarrow Mg_2NiH_4$ (Mg: +II; Ni: 0; H: -I)	**1,5 bp**
8.2	*Indicate the mass fraction of hydrogen in Mg_2NiH_4.*	
	$w(H)=3{,}621\%$	**0,5 bp**
8.3	*Draw two magnesium ions of your choice in the unit cell with all nickel atoms and indicate the corresponding tetrahedra in the drawing. How many tetrahedral gaps and how many octahedral gaps are there per unit cell?*	
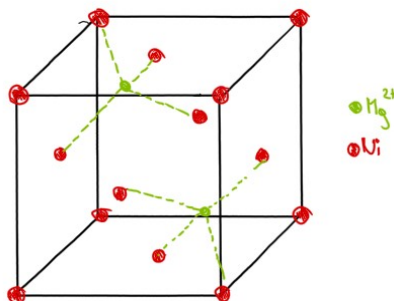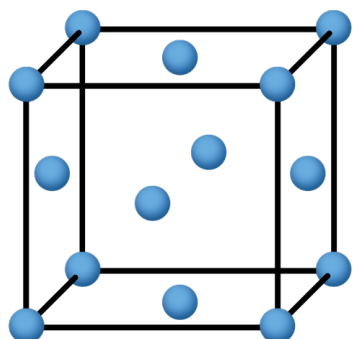
Tetrahedral gap: 8 — **0,5 bp**
Octahedron gap: ½ · 8 = 4 — **0,5 bp**
2bp

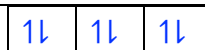|		
8.4	*How many formula units of Mg_2NiH_4 does one unit cell contain?*	
	Niatoms: $8 \cdot \frac{1}{8} + 6 \cdot \frac{1}{2} = 4$	
	Mg ions: 8	
	4 formula units	**1 bp**
8.5	*What is the geometric arrangement of the $[NiH_4]^{4-}$ polyhedron? Draw the electron distribution in this anion in Pauling notation.*	
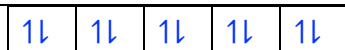
⇅	⇅	⇅	⇅	⇅		⇅		⇅	⇅	⇅		
3d						4s		4p			T_d	**3 bp**

The metal hydride was analysed using X-ray diffraction. First-order diffraction is performed using CuK_α radiation (λ = 1.542 Å) at an angle of 11.92°. The planes associated with this reflection are perpendicular to the spatial diagonal d_r of the unit cell and divide it into three sections of equal length.

8.6	*Berechnen Sie den Gitterparameter a der Elementarzelle (Kantenlänge des Würfels).*

$d = \frac{n \cdot \lambda}{2 \cdot \sin(\theta)} = \frac{1 \cdot 154.2\ pm}{2 \cdot sin(11.92°)} = 373.3\ pm$

Space diagonal d_r = 3·d

$a = \frac{d_r}{\sqrt{3}} = 646.5\ pm$ **2 bp**

8.7	*Calculate the density of the powder (in g/cm³).*

$m(4\ Mg_2NiH_4) = \frac{445.34}{N_A} = 7.395 \cdot 10^{-22} g$

$V(Elementarzelle) = (646.5 \cdot 10^{-10})^3 cm^3$

$\rho(Pulver) = \frac{m}{V} = \frac{7.395 \cdot 10^{-22} g}{(646.5 \cdot 10^{-10})^3 cm^3} = 2.737\ \frac{g}{cm^3}$

     3 bp

8.8	*Calculate the factor by which hydrogen can be stored more densely in Mg₂NiH₄ than in the form of liquid hydrogen (ρ_{H2} = 70.8 kg/m³ bei 20 K).*

w$(Wasserstoff\ in\ Mg_2NiH_4) = \frac{M(4H)}{M(Mg_2NiH_4)} = \frac{4.,04}{111.35} = 0.0362$

m$(Wasserstoff\ als\ Hydrid) = 2.737\ \frac{g}{cm^3} \cdot 0.0362 = 0.0991\ \frac{g}{cm^3}$

m$(Wasserstoff\ flüssig) = 0.0708\ \frac{g}{cm^3}$

$\frac{0.0991 \frac{g}{cm^3}}{0.0708 \frac{g}{cm^3}} = 1.40$

Around 1.4 times as much hydrogen can be stored in the hydride.   **2 bp**
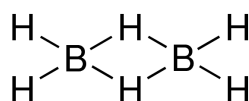
B. Problem Boron hydrides

A boron-hydrogen compound **A**, with a density of 1.16 kg/m3 at 1 bar and 15°C, occurs as a colourless gas and can be produced by reacting lithium hydride with a boron halide **B** (boiling point: -100°C). The by-product **C** is a salt consisting of the halogen and equimolar amounts of boron and lithium (w(Li) = 7.404%).

A is also formed by the reaction of **D** with the boron halide **E**. The anionic tetrahedral complex **G** is formed as a by-product. In contrast to B, E is liquid just above 0°C. Two other boron halides have a boiling point of 91°C and 209°C respectively

D is formed by the reaction of lithium hydride with aluminium chloride. This also produces the compound **F** with w(Li) = 16.37%.

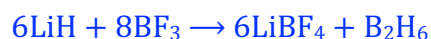| 8.9	*Draw the valence structural formula of A.*
	$M = \frac{\rho \cdot R \cdot T}{p} = \frac{1160 \cdot 8.314 \cdot 288}{100000} = 27.78 \frac{g}{mol} \approx M(B_2H_6)$ 1 bp

8.10	*Give the balanced chemical equation for the synthesis of A from lithium hydride and B. Show by calculation how you arrive at the formula for C.*
	$M(C) = \frac{6.94 \cdot n}{0.07404} = 93.73 \frac{g}{mol} \cdot n$ Annahme: n=1 $Li_1B_1X_4$ $M(4X) = 93.73 - M(Li) - M(B) = 75.98$ g/mol $= 4 \cdot M(F) =$ $6LiH + 8BF_3 \longrightarrow 6LiBF_4 + B_2H_6$ 1 bp

8.11	*Write down a balanced equation for each...*
	for the synthesis of **A** from **D** and **E** $3LiAlH_4 + 4BCl_3 \longrightarrow 2B_2H_6 + 3LiAlCl_4$ for the synthesis of **D** from aluminium chloride and lithium hydride $4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl$ 2 bp