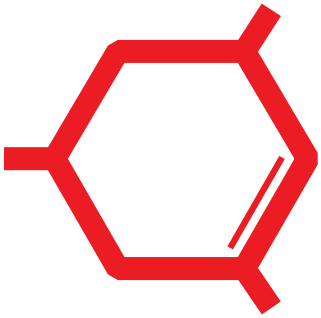


44th Austrian Chemistry Olympiad
National Competition

Theoretical Part
May 31st, 2018

Solutions

Problem 1 **8 Points**

Determining the Concentration of Lead(II) in 1950

1.1 Calculate the volume of hydrochloric acid necessary to reach pH=9.5. Neglect any possible influence of potassium cyanide and lead(II) ions for your calculation.

$9{,}50 = 9{,}25 - lgx \qquad x = \frac{n_{NH_4^+}}{n_{NH_3}} = 0{,}5623$

$n_{NH_4^+} + n_{NH_3} = \frac{35 \cdot 0{,}35 \cdot 0{,}88}{17{,}04} \cdot \frac{75}{100} = 0{,}4745 \text{ mol}$

$\frac{n_{NH_4^+}}{0{,}4745 - n_{NH_4^+}} = 0{,}5623$

$n_{NH_4^+} = \frac{0{,}4745 \cdot 0{,}5623}{1+0{,}5623} = 0{,}171 \text{ mol}$

$n_{HCl} = n_{NH_4^+} = 0{,}171 \text{ mol}$

$V_{HCl} = \frac{n_{HCl}}{c_{HCl}} = \frac{0{,}171\ mol}{6\ \frac{mol}{L}} = 0{,}02846 \text{ L}$ **3 bp**

1.2 Give the pH value for which you expect substantial formation of hydrocyanic acid (i.e. at which the concentration of hydrocyanic acid exceeds that of cyanide ions) and under which the solution should not fall below.

9,40 **1 bp**

1.3 Calculate the maximum concentration of lead in a sample (in mol/L) that can be analyzed with this method.

$m_{Dithizon} = 0{,}00005 \cdot 7{,}5\ mL \cdot 1{,}594 \frac{g}{mL} = 5{,}98 \cdot 10^{-4}\ g$

$n_{Dithizon} = \frac{m_{Dithizon}}{M_{Dithizon}} = \frac{5{,}98 \cdot 10^{-4} g}{256{,}36 \frac{g}{mol}} = 2{,}33 \cdot 10^{-6}\ mol$

$n_{Pb^{2+}}^{\max} = \frac{n_{Dithizon}}{2} = 1{,}17 \cdot 10^{-6} \text{ mol}$

$c_{Pb^{2+}}^{\max} = \frac{n_{Pb^{2+}}^{\max}}{0{,}01L} = 1{,}17 \cdot 10^{-4} \text{ mol/L}$ **3 bp**

1.4 Calculate the lead concentration of a sample for an absorbance of A=0.328 measured in a cuvette of 1cm path length. Assume complete complexation and extraction.

$c_{Pb(HDz)_2} = \frac{A}{\varepsilon \cdot d} = \frac{0{,}328}{66450 \cdot 1} = 4{,}936 \cdot 10^{-6} \text{ mol/L}$

$n_{Pb(HDz)_2} = c_{Pb(HDz)_2} \cdot V_{Tetra} = 4{,}936 \cdot 10^{-6} \frac{\text{mol}}{\text{L}} \cdot 0{,}025\ L = 1{,}234 \cdot 10^{-7} \text{mol}$

$c_{Pb^{2+}} = \frac{n_{Pb(HDz)_2}}{0{,}01\ L} = 1{,}234 \cdot 10^{-5} \text{ mol/L}$ **3 bp**

1.5 Calculate the percentual amounts of the different lead-containing species at pH=9.5.

$[Pb^{2+}] = b$ $[PbOH^+] = b_1$ $[Pb(OH)_2] = b_2$ $[HPbO_2^-] = b_3$

(I) $b + b_1 + b_2 + b_3 = c(Pb^{2+})_{ges}$

(II) $\frac{b_1 \cdot 10^{-9,5}}{b} = 3 \cdot 10^{-7}$ ⇒ $b_1 = b \cdot 949$

(III) $\frac{b_2 \cdot (10^{-9,5})^2}{b} = 3 \cdot 10^{-18}$ ⇒ $b_2 = b \cdot 30,0$

(IV) $\frac{b_3 \cdot (10^{-9,5})^3}{b} = 7 \cdot 10^{-29}$ ⇒ $b_3 = b \cdot 2,21$

(Ia) $b + b \cdot 949 + b \cdot 30,0 + b \cdot 2,21 = c(Pb^{2+})_{ges}$

$b \cdot 982,21 = c(Pb^{2+})_{ges}$

Pb^{2+}: $\frac{1}{982,21} \cdot 100 = 0,10\%$

$PbOH^+$: $\frac{949}{982,21} \cdot 100 = 96,62\%$

$Pb(OH)_2$: $\frac{30}{982,21} \cdot 100 = 3,05\%$

$HPbO_2^-$: $\frac{2,21}{982,21} \cdot 100 = 0,23\%$ **6 bp**

1.6 Calculate the total concentration of all lead species in the aqueous phase after extracting with the abovementioned amount of dithizone in tetrachloromethane. Base your calculation on a sample that initially contained c=1.00·10⁻⁶ mol/L Pb(II).

$[Pb^{2+}] = b$ $[PbOH^+] = b_1$ $[H_2DZ]_{org} = d$ $[Pb(HDz)_2]_{org} = k_1$

$c(H_2Dz)_{ges} = \frac{n_{Dithizon}}{V_{Tetrachlormethan}} = \frac{2,33 \cdot 10^{-6}\, mol}{0,025\, L} = 9,33 \cdot 10^{-5}\, mol/L$

$c(Pb^{2+})_{ges} = 1 \cdot 10^{-6} \cdot \frac{10}{113,46} = 8,81 \cdot 10^{-8}$ mol/L

$c(H_2Dz)_{ges} \gg c(Pb^{2+})_{ges} \Rightarrow d \gg k_1$

(I) $d + 2k_1 = 9,33 \cdot 10^{-5}$ ⇒ $d \approx 9,33 \cdot 10^{-5}$

(II) $b + b_1 + k_1 \cdot \frac{0,025}{0,11346} = 8,81 \cdot 10^{-8}$

(III) $\frac{b_1 \cdot 10^{-9,5}}{b} = 3 \cdot 10^{-7}$ ⇒ $b_1 = b \cdot 949$

(IV) $\frac{k_1 \cdot (10^{-9,5})^2}{d^2 \cdot b} = 5,60$ ⇒ $k_1 = b \cdot \frac{5,60 \cdot (9,33 \cdot 10^{-5})^2}{(10^{-9,5})^2} = b \cdot 4,87 \cdot 10^{11}$

(IIa) $b + b \cdot 949 + b \cdot 4,87 \cdot 10^{11} \cdot \frac{0,025}{0,11346} = 8,81 \cdot 10^{-8}$

$b = 8,21 \cdot 10^{-19}$ mol/L

$b_1 = b \cdot 949 = 7,79 \cdot 10^{-16}$ mol/L

$b + b_1 = 7,80 \cdot 10^{-16}$ mol/L

$k_1 = 8,21 \cdot 10^{-19} \cdot 4,87 \cdot 10^{11} = 4,00 \cdot 10^{-7}$

$d = 9,33 \cdot 10^{-5} - 2k_1 = 9,247 \cdot 10^{-5} \approx 9,33 \cdot 10^{-5}$

⇒ assumption correct! **9 bp**

Problem 2 **8 Points**

Chromium and its Compounds: Electrochemistry & Kinetics

2.1 Give balanced equations for <u>all</u> electrode processes.

Cathode:

$2\ H_3O^+ + 2\ e^- \rightarrow 2\ H_2O + H_2$ **0,5 bp**

$CrO_4^{2-} + 8\ H^+ + 6\ e^- \rightarrow Cr + 4\ H_2O$ **1 bp**

Anode:

$6\ H_2O \rightarrow 4\ H_3O^+ + 4\ e^- + O_2$ **0,5 bp**

2.2 Calculate the current yield for the deposition of chromium on the cathode.

$$n(H_2) = \frac{p \cdot V}{R \cdot T} = \frac{1 \cdot 10^5 Pa \cdot 4{,}15\ m^3}{8{,}314\ Jmol^{-1}K^{-1} \cdot 298\ K} \approx 167{,}5\ mol$$

$$\eta = \frac{n \cdot z \cdot F}{I \cdot t} = \frac{167{,}5\ mol \cdot 2 \cdot 96485 Asmol^{-1}}{1500\ A \cdot 7h \cdot 3600 sh^{-1}} \approx 0{,}855 \Rightarrow 85{,}5\%\ H_2$$

1,5 bp

Current yield for chromium: $\eta = 0{,}145 => 14{,}5\%$ **0,5 bp**

2.3 Calculate the mass of chromium deposited.

$$n(Cr) = \frac{I \cdot t \cdot \eta}{z \cdot F} = \frac{1500\ A \cdot 7h \cdot 3600 sh^{-1} \cdot 0{,}145}{6 \cdot 96485 Asmol^{-1}} \approx 9{,}5\ mol$$

1,5 bp

Mass of chromium: $m = n \cdot M = 9{,}5\ mol \cdot 52 gmol^{-1} = 492\ g$ **0,5 bp**

2.4 Calculate the volume of the gas having developed on the anode at standard conditions (25°C, 1.00 bar).

$$n(O_2) = \frac{I \cdot t \cdot \eta}{z \cdot F} = \frac{1500\ A \cdot 7h \cdot 3600 sh^{-1} \cdot 1}{4 \cdot 96485 Asmol^{-1}} \approx 97{,}9\ mol$$ **0,5 bp**

$$V(O_2) = \frac{n \cdot R \cdot T}{p} = \frac{97{,}9\ mol \cdot 8{,}314\ Jmol^{-1}K^{-1} \cdot 298\ K}{1 \cdot 10^5 Pa} \approx 2{,}43\ m^3$$ **0,5 bp**

2.5 Calculate the missing potentials x and y.

$$x = \frac{6 \cdot 0{,}295 - 3 \cdot (-0{,}741) - 0{,}55 - 1{,}34}{1} = 2{,}10\ V$$

$$y = \frac{3 \cdot (-0{,}741) - (-0{,}424)}{2} = -0{,}90\ V$$ **2,5 bp**

2.6 Demonstrate that Cr(IV) can disproportionate to Cr(III) and Cr(VI) via suitable calculation.

Cr(IV) disproportionates,
because $E^O(Cr(IV)|Cr(III)) = 2{,}10 > E^O(Cr(VI)|Cr(IV)) = 0{,}945$ **1 bp**

$$E^O(Cr(VI)|Cr(IV)) = \frac{0{,}55 + 1{,}34}{2} = 0{,}945$$

2.7 Calculate the equilibrium constant for this disproportioning reaction at 25°C.

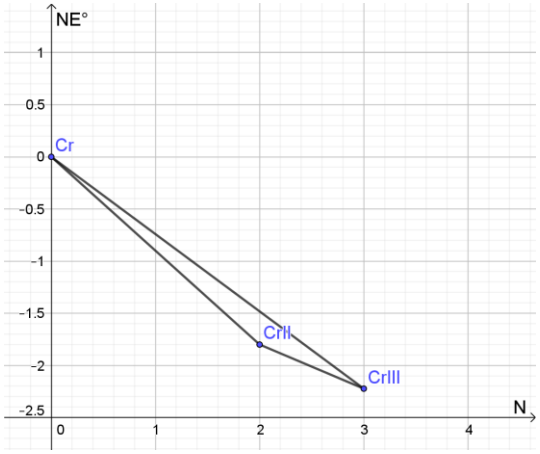
$\Delta E^O = 2{,}10 - 0{,}945 = 1{,}155$ V **0,5 bp**

$\Delta G^O = -z \cdot F \cdot \Delta E^O = -R \cdot T \cdot lnK$

$\Rightarrow lnK = \frac{2 \cdot 96485 \cdot 1{,}155}{8{,}314 \cdot 298} = 89{,}96 \Rightarrow K = 1{,}2 \cdot 10^{39}$ **1 bp**

2.8 Does Cr(II) tend to disproportionate to Cr(III) and Cr(0)? Tick the correct box and give a reason for your choice based on the Frost diagram of the relevant species.

O yes, tends to disproportionate X no, does not tend to disproportionate



Cr 0 V

Cr^{2+} $-0{,}90 \cdot 2 = -1{,}80$ V

Cr^{3+} $-0{,}741 \cdot 3 = -2{,}223$ V

2 bp

2.9 Name two species showing pH-independent redox reaction in the diagram, at least within a certain pH-range.

all with horizontal separating line i.e.: $Cr^{2+}|Cr^{3+}$ **0,5 bp**

2.10 Name two species showing protolysis that does not depend on pontential.

all with horizontal separating line i.e.: $Cr_2O_7^{2-}|CrO_4^{2-}$ **0,5 bp**

2.11 In which pH range does $Cr_2O_7^{2-}$ react to Cr^{3+}?

0 to 4 **0,5 bp**

2.12 Formulate the half equation for the redox pair $Cr_2O_7^{2-}$/ Cr^{3+}.

$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$ **0,5 bp**

2.13 Derive an equation E = f(pH) for the line between the two species $Cr_2O_7^{2-}$ and Cr^{3+} at 298 K. (Assumption: the activities of the chromium species do not change).

Voltage change per pH-step:

$$E = E° + \frac{RT}{6F} ln \frac{[Cr_2O_7^{2-}][H_3O^+]^{14}}{[Cr^{3+}]^2}$$

$$E = E° + \frac{RT}{6F} ln \frac{[Cr_2O_7^{2-}]}{[Cr^{3+}]^2} - \frac{RT}{6F}(-ln[H_3O^+]^{14})$$

and $\ln[H_3O^+]^{14} = \frac{14log[H_3O^+]}{loge} = 14 \cdot 2{,}3026 \cdot \log[H_3O^+]$

$$E = E° - \frac{RT \cdot 14 \cdot 2{,}3026}{6F}(-\log[H_3O^+])$$

$$E = E° - \frac{RT \cdot 14 \cdot 2{,}3026}{6F} pH$$

$$-\frac{RT \cdot 14 \cdot 2{,}3026}{6F} = -\frac{8{,}314 \cdot 298 \cdot 14 \cdot 2{,}3026}{6 \cdot 96485} = -0{,}138\ V$$

$$E = E° - 0{,}138pH$$ **3,5 bp**

2.14 Use this derived linear function to calculate E at pH=2.

$E_2 = 1{,}33 - 0{,}1380 \cdot 2 = 1{,}05\ V$ **0,5 bp**

2.15 Formulate a balanced equation for the reaction of $HCrO_4^-$ with ethanol to Cr^{3+} und ethanoic acid.

$HCrO_4^- + 7\ H^+ + 3\ e^- \rightarrow Cr^{3+} + 4\ H_2O$ |·4

$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4\ H^+ + 4\ e^-$ |·3

$4\ HCrO_4^- + 3\ CH_3CH_2OH + 16\ H^+ \rightarrow 4\ Cr^{3+} + 3\ CH_3COOH + 13\ H_2O$

1,5 bp

2.16 As an example, calculate the concentration $[HCrO_4^-]_t$ for a titration volume $V(S_2O_3^{2-}) = 10.3$ mL.

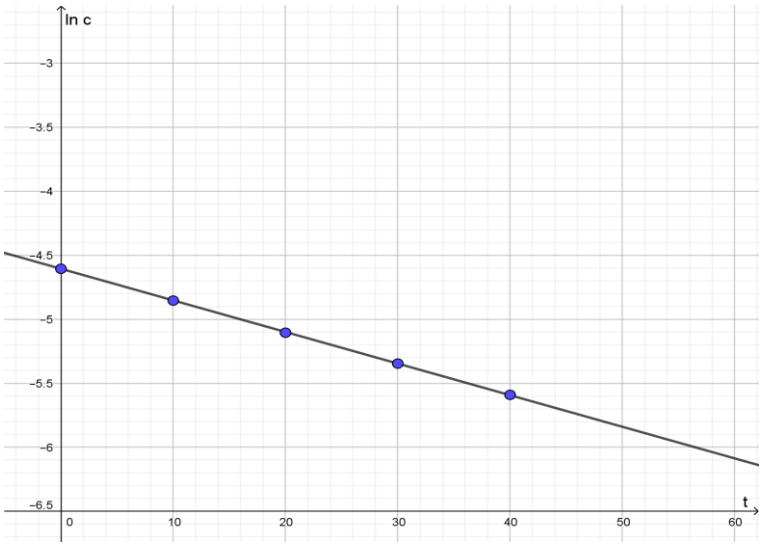
$n(S_2O_3^{2-}) = V(S_2O_3^{2-}) \cdot c(S_2O_3^{2-}) = 10{,}3\ \text{mL} \cdot 0{,}02\ \text{mol L}^{-1} = 0{,}206\ \text{mmol}$

$n(I_2) = \frac{1}{2}\ n(S_2O_3^{2-})$ und $n(HCrO_4^-) = \frac{2}{3}\ n(I_2) = \frac{1}{3} n(S_2O_3^{2-}) = 0{,}0687\ \text{mmol}$

$$c(HCrO_4^-) = \frac{n(HCrO_4^-)}{V(HCrO_4^-)} = \frac{0{,}0687}{10} = 0{,}00687\ \text{mol L}^{-1}$$

2 bp

2.17 Determine the reaction order x, by plotting concentration vs time in a suitable graph. Choose reasonable dimensions on each axis.



2 bp

A linear graph corresponds to first order kinetics. **0,5 bp**

2.18 Calculate the rate constant k and give the result with correct units.

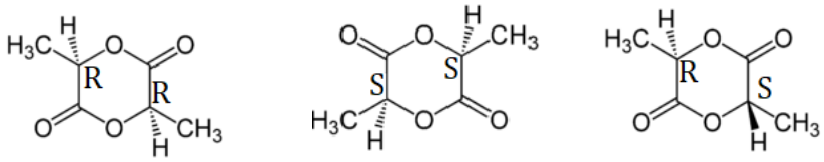
$\ln[HCrO_4^-]_t = \ln[HCrO_4^-]_0 - k\,t$

$k = \frac{ln\frac{[HCrO_4^-]_0}{[HCrO_4^-]_t}}{t} = \frac{ln\frac{0,01}{0,0078}}{10} = 0,025\ \text{min}^{-1}$ **1,5 bp**

Problem 3 **17 Points**

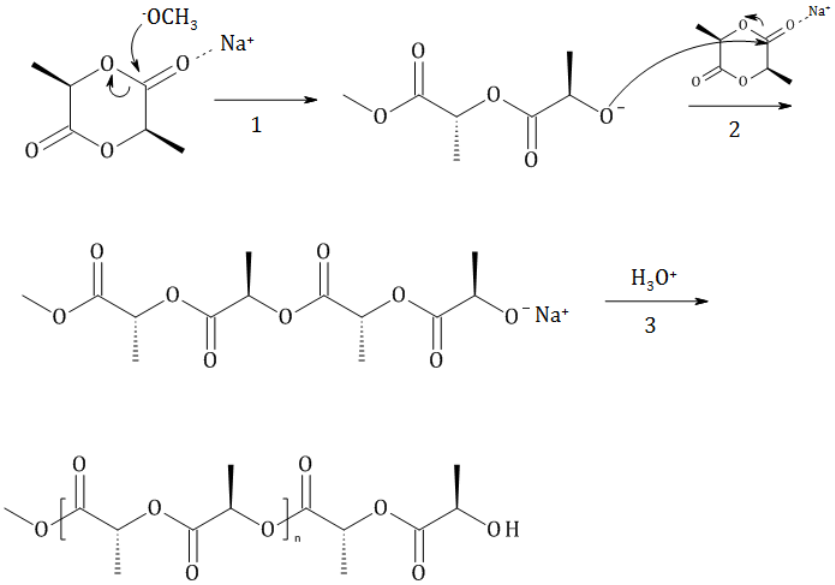
Organic Syntheses

3.1 Draw the configuration formulae of all possible stereo-isomers of lactide and determine the absolute configuration of each stereogenic center.



3 bp

*3.2 Formulate mechanisms (including arrows for attacking species) for initiation (1), propagation (2, with n(LA) = 1) and termination (3) of the ring-opening polymerization of lactide (LA). Keep **stereochemistry** in mind!*
Mark the repetitive unit in the product (after step 3) in the usual way.



5 bp

3.3 Tick the correct answer

Polymerization leads to ....

	a polyamide.
X	a polyester.
	a polyanhydride.
	a polycarbonic acid.

1 bp

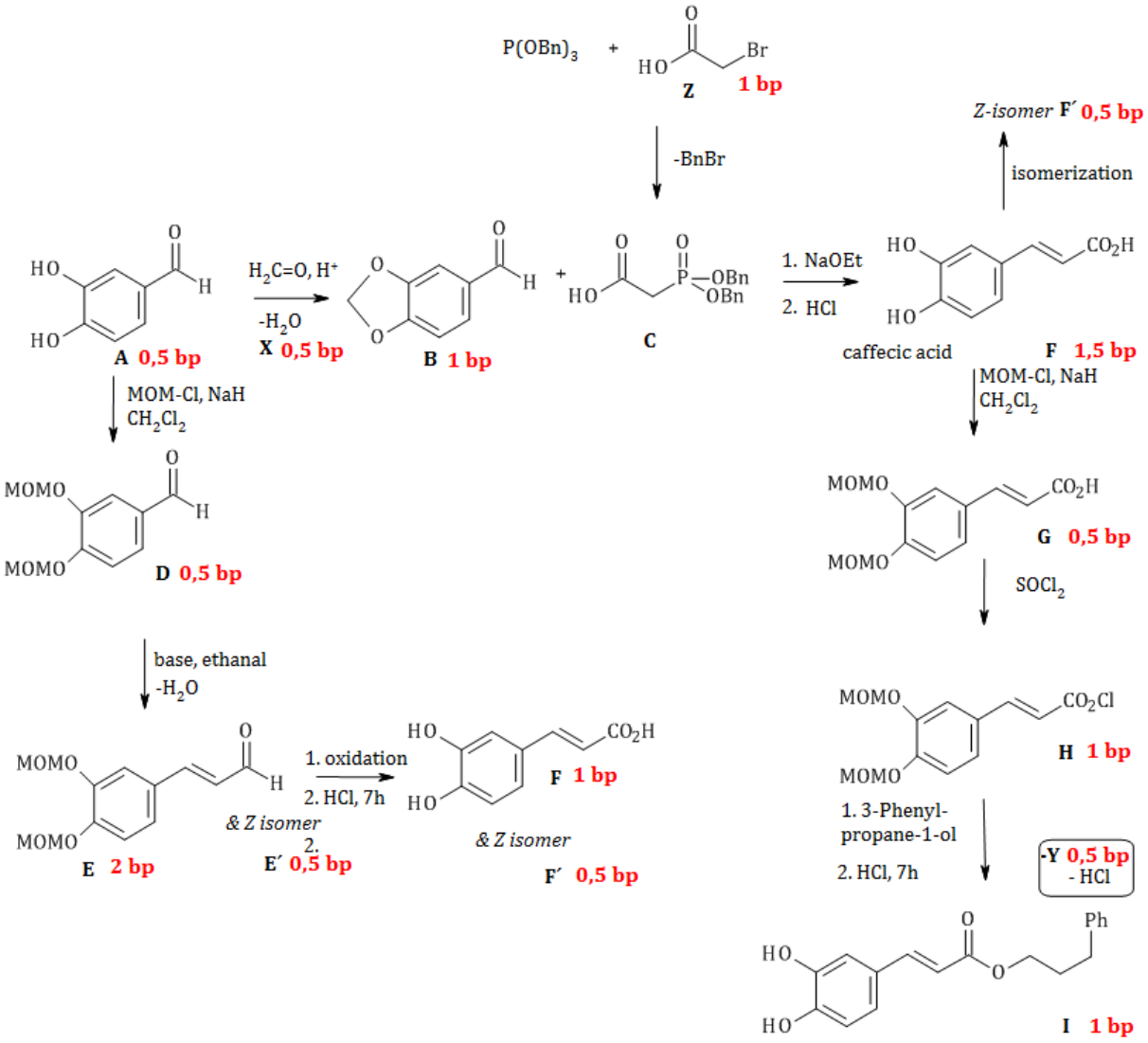
3.4 Give the IUPAC-name/s of the product/s of acidic hydrolysis of lactide. Include stereodescriptors, if necessary.

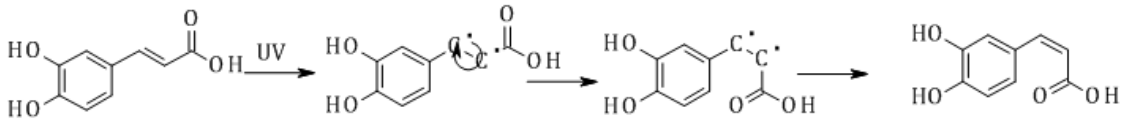
(R)-2-Hydroxypropanoic acid **2 bp**

*3.5 Write down the formulae of **F** and **F´**.*

$C_9H_8O_4$ **1 bp**

*3.6 Insert the structural formulae of **A, B, D, E, E´, F, F´, G, H, I,** and **Z** including correct stereochemistry into the boxes shown in the reaction scheme. In the same way add the empirical formulae of **X** and **Y**. Abbreviate possible benzyl-, phenyl- or MOM-residues as Bn, Ph or MOM.*	*3.6 Zei von Käs Gru*



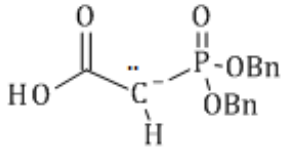
*3.7 Name the reaction mechanism for the reaction $P(OBn)_3$ + **Z** → **C** (1st step).*
S_N2 **0,5 bp**
*3.8 Write down the stereochemical relation of **E** and **E´** as well as **F** and **F´**.*
diastereomeric / geometric isomers **1 bp**
*3.9 Formulate the reaction mechanism of the isomerization from **F** to **F'** and suggest appropriate reaction conditions.*
 **2,5 bp**

*3.10 What is the role of NaOEt in the first step when producing **F** from **B** and **C**? Draw the constitution formula of the reactive intermediate formed during this reaction. Name the reaction mechanism between this intermediate and the other reactand. How is this name reaction called?*

base **0,5 bp**

A_N **0,5 bp**

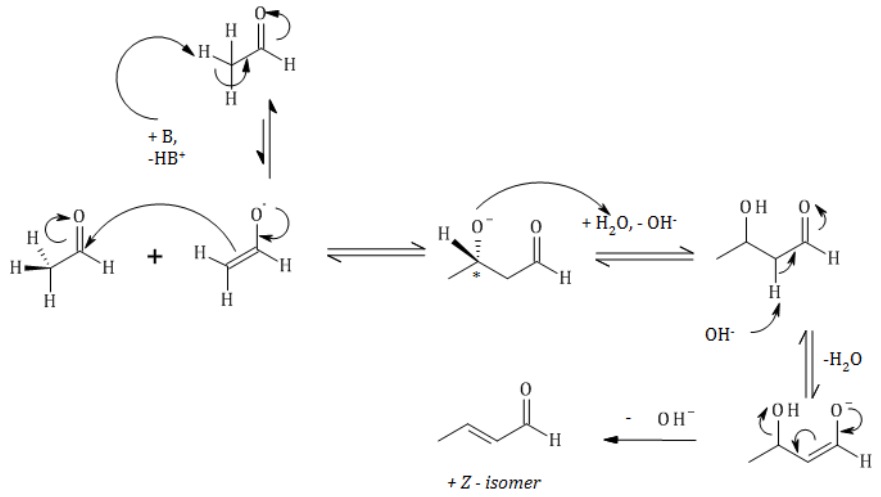
HWE-Wittig **0,5 bp**



1 bp

*3.11 Formulate a detailed reaction mechanism (use "R" for residues) for the formation of **E** and **E´** from **D** and ethanal. Use arrows for attacking species. Name the reaction mechanism.*

A_N



5 bp

*3.12 Which is the underlying name reaction for the formation of **D** from **A**? Name the corresponding reaction mechanism.*
Explain why this step is necessary within the reaction scheme.

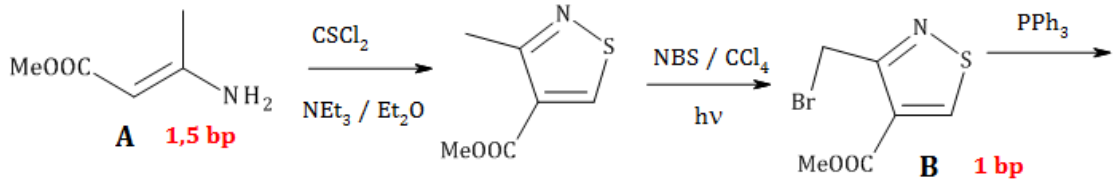
Williamson ether synthesis **0,5 bp**

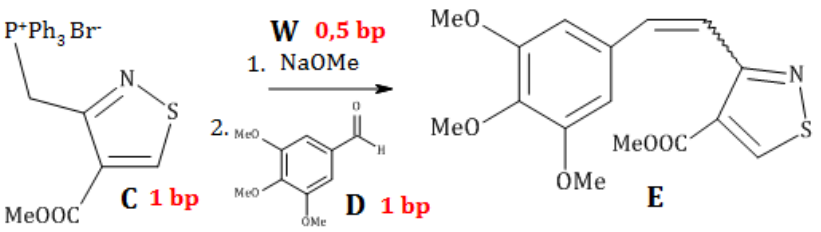
S_N2 **0,5 bp**

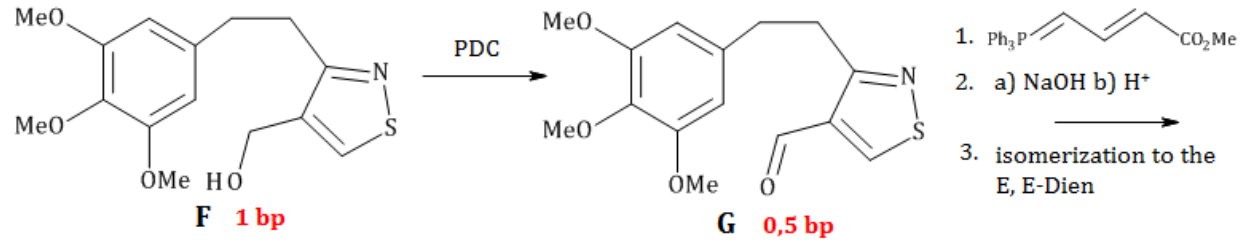
protecting group; prevents oxidation of phenols **1 bp**

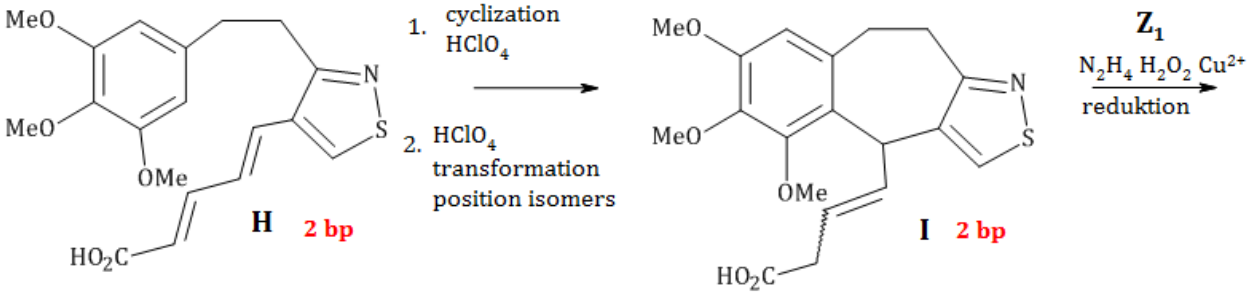
*3.13 Insert the structural formulae of **A, B, C, D, F, G, H, I, L, M, N, O, P,** and **R** into the boxes shown in the reaction scheme. In the same way add the empirical formulae of **W, X,** and **Y. Several boxes already contain substructures of the respective compound, which you only need to complete.***

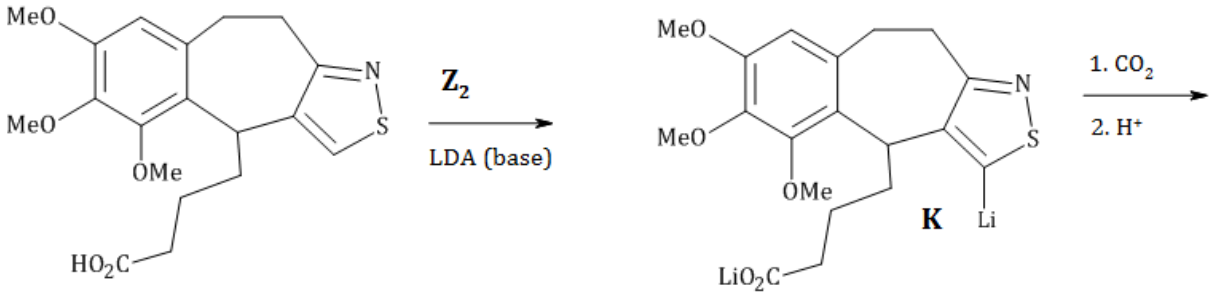
3.13 Zei Sur Sub

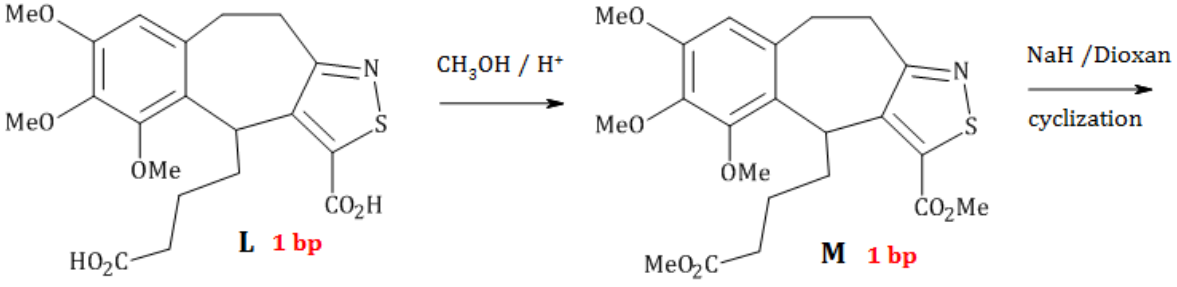


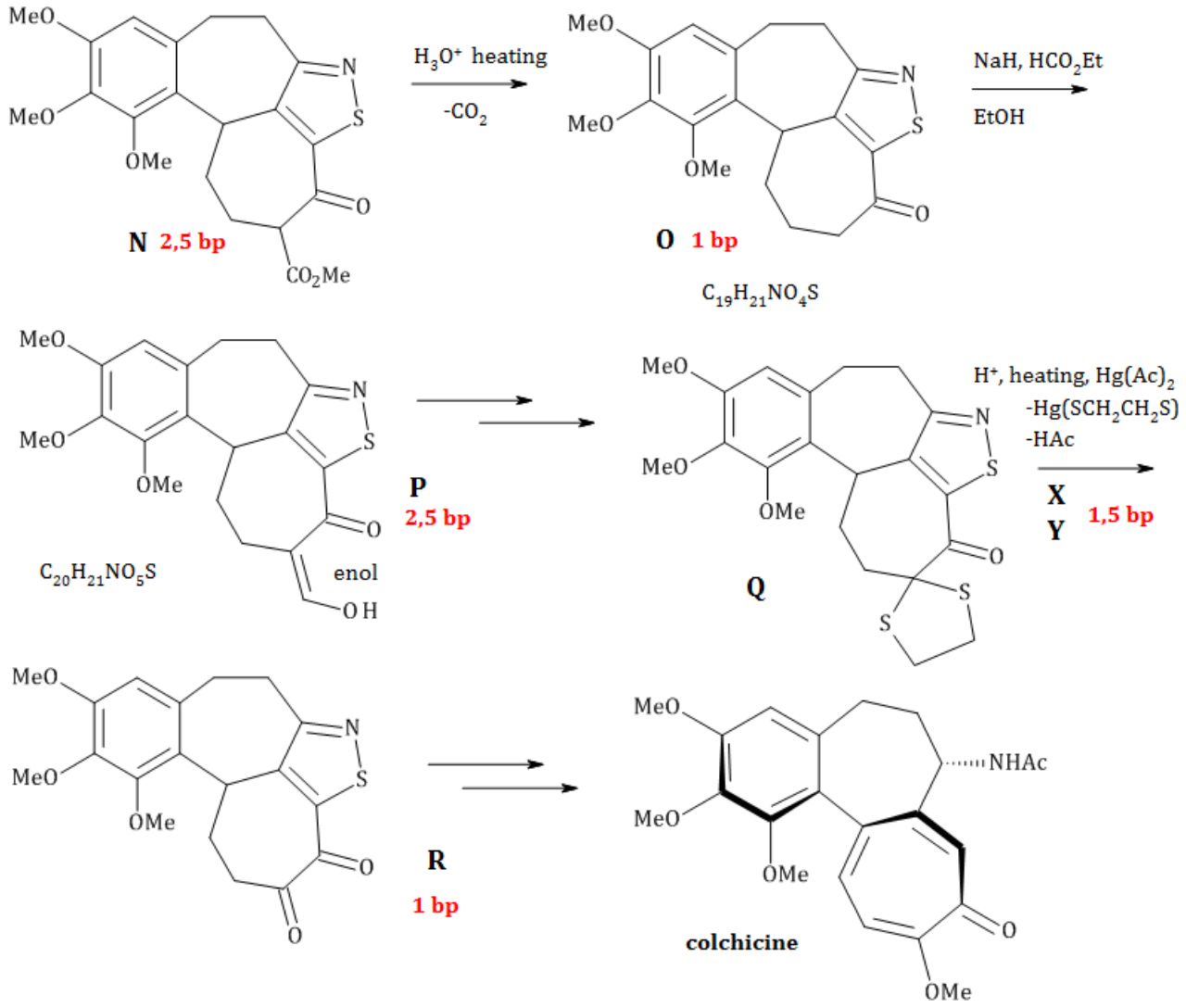










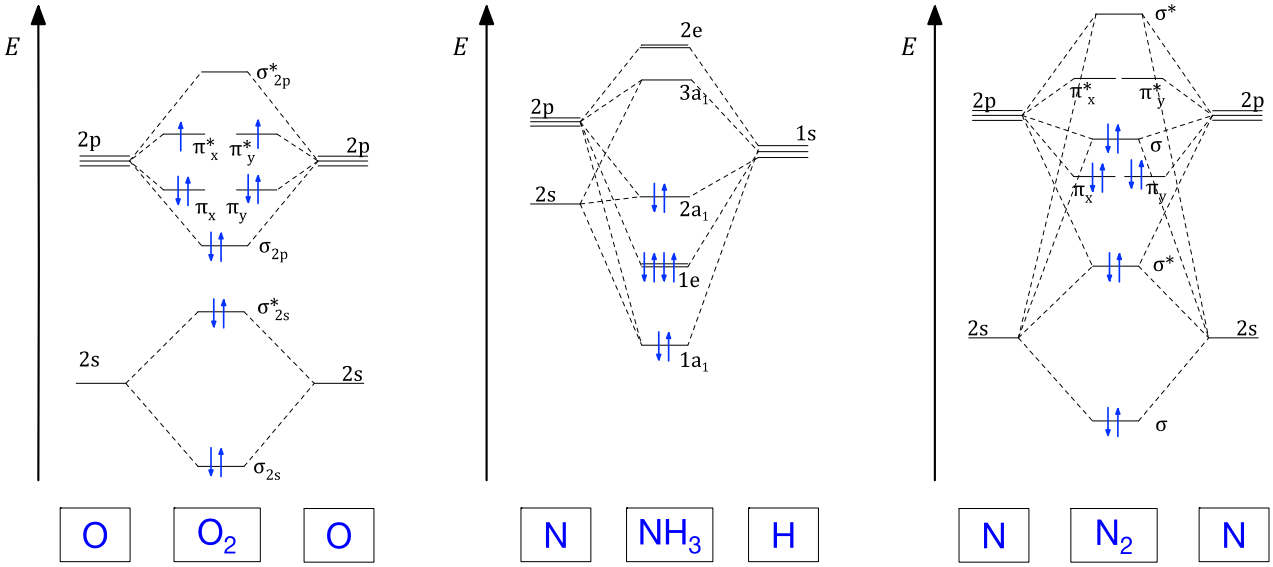


*3.14 Suggest reagents **Z1** and **Z2** for transforming **I** to **K**.*
$Z_1 = N_2H_4$, H_2O_2, Cu^{2+} Z_2 = LDA **1,5 bp**
*3.15 Which name reaction is the basis of the step from **H** to **I** (cyclization)? Name the corresponding reaction mechanism.*
Friedel–Crafts alkylation **1 bp** S_E **0,5 bp**
3.16 Which type(s) of chirality are present in colchicine? Also state their number.
axial chirality and a stereogenic centre **1 bp**
3.17 Give the stereodescriptor(s) of colchicine.
(aR)-, S- **2 bp**

Problem 4 **17 Points**

Nitrogen and its Compounds

4.1 Label the schemes by writing the correct element symbols and molecular formulae into the respective boxes. Populate the schemes with electrons (arrows).



correct labelling 0,5 bp each; correct e-count 0,5 bp each, correct configuration 0,5 bp each

total max.: **4,5 bp**

4.2 State magnetic behavior and bond order:

Nitrogen N_2

Bond order: __ 3 __ **0,5 bp**

X diamagnetic **0,5 bp**

☐ paramagnetic

Sauerstoff O_2

bond order: __ 2 __ **0,5 bp**

☐ diamagnetic

X paramagnetic **0,5 bp**

4.3 Calculate the overall quantity of heat Q_1 released during worldwide production of ammonia at isobaric conditions at 298 K in Joule.

$M(NH_3) = 17{,}04$ g/mol

180 mio tons $= 1{,}80 \cdot 10^{14}$ g correspond to $1{,}056 \cdot 10^{13}$ mol **1 bp**

$Q_1 = 45{,}9 \cdot 1{,}056 \cdot 10^{13} = \underline{4{,}85 \cdot 10^{17}\ \text{J}}$ **0,5 bp**

4.4 Calculate the overall quantity of heat Q_2 released for one batch of ammonia in the bomb calorimeter at 298 K.

for ½ N2 + 3/2 H2 → NH_3 is $\Delta U = \Delta H - \Delta nRT$ therefore $\Delta n = -1$

$\Delta U = -45{,}9 \cdot 10^3 + 8{,}314 \cdot 298 = -43{,}42$ kJmol^{-1}

for $1{,}056 \cdot 10^{13}$ mol are released $Q_2 = \underline{4{,}59 \cdot 10^{17}\ \text{J}}$ **2 bp**

4.5 Calculate the sum mass of educts the death star needs to hold for one load of ammonia.

Retain of mass hence 180 million tons **1 bp**

4.6 Calculate Kp for the formation of ammonia following equation R 4.1 at 298 K.

$\Delta_R S = -198{,}1\ \text{Jmol}^{-1}\text{K}^{-1}$ und $\Delta_R H = -91{,}8\ \text{kJmol}^{-1}$

$\Delta_R G = -91800 + 198{,}1 \cdot 298 = -32766{,}2\ \text{Jmol}^{-1}$

$K_p = \exp(32766{,}2/(8{,}314 \cdot 298) = 5{,}54 \cdot 10^5$ **3 bp**

4.7 Calculate Kp for ammonia formation at 400°C assuming that $\Delta_R H$ and $\Delta_R S$ have the same values as at 298 K.

$$ln\ K_{673} = ln\ K_{298} - \frac{\Delta H}{R}\left(\frac{1}{673} - \frac{1}{298}\right) = ln\ (554000) + \frac{91800}{8{,}314}\left(\frac{1}{673} - \frac{1}{298}\right) = -7{,}42$$

$K_{673} = 5{,}99 \cdot 10^{-4}$ **2 bp**

4.8 Based on these values calculate $\Delta_R H_{650}$ as accurately as possible.

use K_{600} and K_{700}

$$\Delta H = \frac{ln\ K_{600} - ln\ K_{700}}{1/600 - 1/700} \cdot R = -102{,}5\ \text{kJ mol}^{-1}$$ **2 bp**

4.9 Calculate Cp of NH_3. Assume that the Cp values of H_2, N_2, and NH_3 are independent of temperature.

$$\Delta_R H^{\ominus}_{650} = \Delta_R H^{\ominus}_{298} + \Delta_R C_p^{\ominus}\,(650 - 298)$$

$$\Delta_R C_p^{\ominus} = \frac{\Delta_R H^{\ominus}_{650} - \Delta_R H^{\ominus}_{298}}{352} = -30{,}4\ \text{J mol}^{-1}\ \text{K}^{-1}$$ **1 bp**

$$C_{p\text{NH}_3} = \frac{1}{2}(\Delta_R C_p^{\ominus} + C_{p\text{N}_2} + 3C_{p\text{H}_2})$$
$$= \frac{1}{2}(-30{,}4 + 29{,}1 + 3 \cdot 28{,}8)$$
$$= 42{,}6\ \text{J mol}^{-1}\ \text{K}^{-1}$$ **1,5 bp**

4.10 Caclulate E_A based on a suitable thermodynamic cycle.

thermodynamic cycle **2 bp**

½ N2 + 3/2 H2 → N + 3 H	E_A
N + 3 H → NH + 2 H	$\Delta_R H$ = -314 kJ/mol
NH + 2 H → NH_2 + H	$\Delta_R H$ = -389 kJ/mol
NH_2 + H → NH_3	$\Delta_R H$ = -460 kJ/mol
NH_3 → ½ N_2 + 3/2 H_2	$\Delta_R H$ = - $\Delta_f H$ = 45,9 kJ/mol
total: 0 → 0	0

$E_A = 314 + 389 + 460 - 45{,}9 = \underline{1117\ \text{kJ/mol}}$ **1,5 bp**

4.11 Give the frequency of occurrence for the following molecules in %.

^{14}N-^{14}N: 99,634 % · 0,99634 = <u>99,269 %</u> **0,5 bp**

^{14}N-^{15}N: 2 · 99,634 % · 0,00366 = <u>0,7294 %</u> **0,5 bp**

^{15}N-^{15}N: 0,366 % · 0,00366 = <u>0,00134 %</u> **0,5 bp**

4.12 Calculate the reduced masses μ for each molecule below in amu and kg using five significant figures. Demonstrate the calculation in detail for one of them.

$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{14{,}0031 \cdot 15{,}0001}{14{,}0031 + 15{,}0001} = 7{,}2422$ **0,5 bp**

μ(^{14}N-^{14}N) = 7,0016 amu = $1{,}1630 \cdot 10^{-26}$ kg **1 bp**

μ(^{14}N-^{15}N) = 7,2422 amu = $1{,}2026 \cdot 10^{-26}$ kg **1 bp**

4.13 Calculate the force constant k of the N-N bond in gaseous nitrogen.

$$\omega = \sqrt{\frac{k}{\mu}}$$

$$\Rightarrow k = \omega^2\mu = 4\pi^2\nu^2\mu = 4\pi^2c^2\tilde{\nu}^2\mu$$

$$= 4\pi^2(2{,}998 \cdot 10^8\ \mathrm{m\,s^{-1}})^2 \cdot (245\,600\ \mathrm{m^{-1}})^2 \cdot 1{,}1630 \cdot 10^{-26}\ \mathrm{kg}$$

$$= 2489\ \mathrm{kg\,s^{-2}}$$

2 bp

4.14 Calculate the zero point energies E_0 of ^{14}N-^{14}N and ^{14}N-^{15}N in J.

^{14}N-^{14}N

$$E_0 = \frac{1}{2}h\nu = \frac{1}{2}hc\tilde{\nu} = \underline{2{,}439 \cdot 10^{-20}\ \mathrm{J}}$$ **1 bp**

^{14}N-^{15}N

$$E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar\sqrt{k/\mu} = 0{,}5 \cdot 1{,}055 \cdot 10^{-34} \cdot \sqrt{(2489/1{,}2026 \cdot 10^{-26})}$$

$$\underline{= 2{,}400 \cdot 10^{-20}\ \mathrm{J}}$$ **1,5 bp**

4.15 Calculate the ratio of rate constants k_{1414}/k_{1415} for bond breaking in ^{14}N-^{14}N and ^{14}N-^{15}N, respectively.

Calculation of energies in J /mol **1,5 bp**

Arrhenius-equation: $\ln k = \ln A - E_A/RT$ with $E_A = E^{\ddagger} - E_0$ **2 bp**

$$\ln \frac{k_{1414}}{k_{1415}} = \frac{1}{RT}(E_{0(1414)} - E_{0(1415)}) \cdot N_A$$

$$= \frac{1}{8{,}314 \cdot 298}(2{,}439 - 2{,}400) \cdot 10^{-20} \cdot 6{,}022 \cdot 10^{23}$$

$$= 0{,}094836$$

$\frac{k_{1414}}{k_{1415}} = 1{,}099$ **0,5 bp**

4.16 The oscillation at … cm^{-1} corresponds to situation (tick the correct one):

1500 cm^{-1}	☐ gas	X α	☐ β	☐ γ	**1 bp**
2100 cm^{-1}	☐ gas	☐ α	☐ β	X γ	**1 bp**

4.17 What is the activation energy of the catalyzed reaction?

4 kJ/mol	**1 bp**
4.18 What is the enthalpy of formation of $NH_{3(ad)}$?	
– 95,9 kJ/mol	**1 bp**

4.19 State the rate law for the change in concentration of NH_3.

$-\frac{d[NH_3]}{dt} = k_1[NH_3] - k_{-1}[NH_4^+][OH^-]$ **1 bp**

4.20 State a term for $\frac{dx}{dt}$, assuming that x denotes the momentary deviation from equilibrium concentration.

$[NH_3] = [NH_3]_{eq} - x, [NH_4^+] = [NH_4^+]_{eq} + x\,, [OH^-] = [OH^-]_{eq} + x$

$$\frac{dx}{dt} = k_1\big([NH_3]_{eq} - x\big) - k_{-1}([NH_4^+]_{eq} + x)([OH^-]_{eq} + x)$$

$$\frac{dx}{dt} = -k_1x - k_{-1}[NH_4^+]_{eq}x - k_{-1}[OH^-]_{eq}x + k_1[NH_3]_{eq} - k_{-1}[NH_4^+]_{eq}[OH^-]_{eq} - k_{-1}x^2$$

$$\frac{dx}{dt} = -\{k_1 + k_{-1}([NH_4^+]_{eq} + [OH^-]_{eq})\}x + k_1[NH_3]_{eq} - k_{-1}[NH_4^+]_{eq}[OH^-]_{eq} - k_{-1}x^2$$

$k_{-1}x^2$ neglected and $k_1[NH_3]_{eq} = k_{-1}[NH_4^+]_{eq}[OH^-]_{eq}$

$$\frac{dx}{dt} \approx -\{k_1 + k_{-1}([NH_4^+]_{eq} + [OH^-]_{eq})\}x$$

3 bp

4.21 Calculate the rate constants k_1 and k_{-1}.

The rate constants are related with

$$K_B = \frac{k_1}{k_{-1}} = \frac{[NH_4^+]_{eq}[OH^-]_{eq}}{[NH_3]_{eq}} = 1{,}78 \cdot 10^{-5} moldm^{-3}$$

Because of $e^{-k\tau} = e^{-1}$, thus $k\tau = 1$ if k is the relaxation rate constant.

Hence:

$$\frac{1}{\tau} = k_1 + k_{-1}([NH_4^+]_{eq} + [OH^-]_{eq})$$

$k_1 = K_B \cdot k_{-1}$ und $[NH_4^+]_{eq} = [OH^-]_{eq} = (K_B[NH_3])^{1/2}$

$$\frac{1}{\tau} = K_B \cdot k_{-1} + 2 \cdot k_{-1}(K_B[NH_3])^{\frac{1}{2}} = k_{-1}\{K_B + 2(K_B[NH_3])^{\frac{1}{2}}\}$$

$$\boldsymbol{k_{-1}} = \frac{1}{\tau\left\{K_B + 2(K_B[NH_3])^{\frac{1}{2}}\right\}} =$$

$$= \frac{1}{7{,}61 \cdot 10^{-9}\, s\left\{1{,}78 \cdot 10^{-5} moldm^{-3} + 2(1{,}78 \cdot 10^{-5} \cdot 0{,}15)^{\frac{1}{2}} moldm^{-3}\right\}}$$

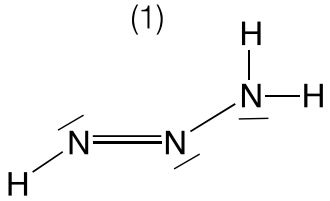
$$\boldsymbol{k_{-1} = 4{,}0 \cdot 10^{10} dm^3 mol^{-1} s^{-1}}$$

$$\boldsymbol{k_1} = K_B \cdot k_{-1} = 1{,}78 \cdot 10^{-5} moldm^{-3} \cdot 4{,}0 \cdot 10^{10} dm^3 mol^{-1} s^{-1} = \boldsymbol{7{,}1 \cdot 10^5 s^{-1}}$$

4 bp

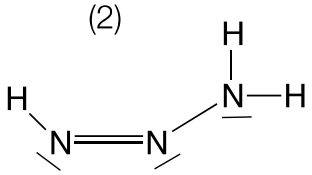
4.22 Add the missing H-atoms and complete the Lewis formulae. Assign formal charges, if necessary.

(1)



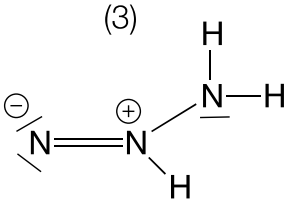
1,5 bp

(2)



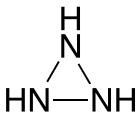
1,5 bp

(3)



2bp

4.23 There is also a triazane with the empirical formula N_3H_3. Draw its constitutional formula.

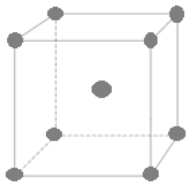


1,5 bp

Problem 5 **10 Points**

Chromium and its Compounds: Lattices, Nuclei and Complexes

5.1 Draw the chromium atoms as spheres into the unit cell of the body-centered cubic unit cell. Also state the number of atoms per unit cell.



1 bp

Number of atoms per unit cell: 2 **0,5 bp**

5.2 Calculate the lattice parameter a in pm.

$$\rho = \frac{m_{EZ}}{V_{EZ}} = \frac{\text{atome/uc} \cdot M}{N_A \cdot a^3}$$

$$a = \sqrt[3]{\frac{\frac{Atome}{EZ} M}{\rho \cdot N_A}} \quad a = 2{,}8920 \cdot 10^{-8}\text{cm} = 289{,}20\ pm$$ **3 bp**

5.3 Give a balanced, complete disintegration equation for electron capture. Note both mass number and atomic number for every nuclide.

$^{51}_{24}Cr + e^- \longrightarrow {}^{51}_{23}V + \nu_e$ **1bp**

5.4 Calculate the half-life of ^{51}Cr in hours from the data given.

$$n = \frac{m}{M} = \frac{2}{50{,}945} = 0{,}039258 mol$$

$N(0) = 0{,}039258 \cdot N_A = 2{,}3641 \cdot 10^{22}$ **1 bp**

$\lambda = \frac{A(0)}{N(0)} = \frac{6{,}84701 \cdot 10^{15}}{2{,}3641 \cdot 10^{22}} = 2{,}8962 \cdot 10^{-7}$ **1 bp**

$t_{1/2} = \frac{ln2}{\lambda} = 2{,}39330 \cdot 10^6 s = 664{,}80 h$ **1,5 bp**

5.5 Formulate balanced ion equations for:
a) Oxidation of chromium(III) by hydrogen peroxide,
b) Reduction of chromate by iron(II), and
c) Oxidation of Iron(II) by permanganate.
Explicitly state every stoichiometric coefficient, including "1".

$10\ OH^- + 2\ Cr^{3+} + 3\ H_2O_2 \longrightarrow 2\ CrO_4^{2-} + 8\ H_2O$ **1 bp**

$8\ H^+ + 3\ Fe^{2+} + 1\ CrO_4^{2-} \longrightarrow 3\ Fe^{3+} + 1\ Cr^{3+} + 4\ H_2O$ **1 bp**

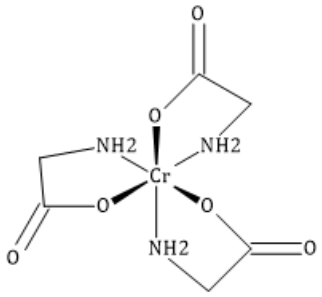
$8H^+ + 5\ Fe^{2+} + 1\ MnO_4^- \longrightarrow 5\ Fe^{3+} + 1\ Mn^{2+} + 4\ H_2O$ **1 bp**

5.6 Calculate the fraction of chromium in the alloy in %(w/w).

$17{,}20 \cdot 0{,}020 = 0{,}344\ mmol\ KMnO_4$	**0,5 bp**
$5 \cdot 0{,}344 = 1{,}72\ mmol Fe^{2+}$	**0,5 bp**
$25 \cdot 0{,}1 - 1{,}72 = 0{,}78 mmol Fe^{2+}$	**0,5 bp**
$\frac{0{,}78}{3} = 0{,}26 mmol\ Cr\ in\ 150 mg$	**0,5 bp**
$m(Cr) = 2{,}6 \cdot 52{,}0 = 135{,}2 mg\ in\ 1500 mg$	**0,5 bp**
$p(Cr) = 9{,}013\%$	**0,5 bp**

5.7 State the name of the coordination polyhedron formed by the complex. State the donor atoms explicitly and use only the skeletal structure of the ligands otherwise.

Coordination polyhedron: octahedron **1bp**



2 bp

*5.8 State the number of possible geometrical isomers (=**diastereomers**!) for the tris-glycinato-chromium(III) complex and all corresponding stereo descriptors. Consider that each ligand molecule contains two different donor atoms.*

2	**1 bp**
fac, mer	**0,5 bp each**

5.9 Tick the box below the absorption spectrum of ruby.

No. (4) **1,5 bp**

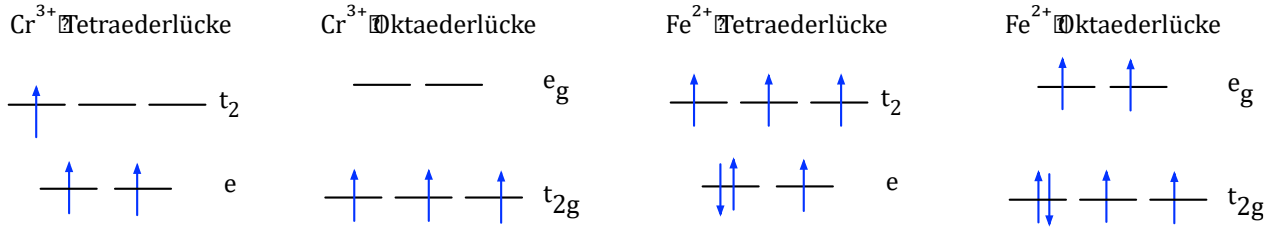
5.10 Write down the correct and complete formula of the complex. The structural drawing should make clear which ligands are located in which coordination sphere of chromium.

1 mol $CrCl_3H_{12}O_6$ ≙ 1 mol Cl^-

Gentle heating: 1 mol $CrCl_3H_{12}O_6$ ≙ 2mol H_2O

$[CrCl_2(OH_2)_4]Cl \cdot 2H_2O$ **4 bp**

5.11 Occupy the d-orbital schemes of tetrahedral and octahedral voids of Cr^{3+} and Fe^{2+}, respectively. Do this by inserting arrows in the usual way.



1bp each – max. **4 bp**

5.12 Determine whether $FeCr_2O_4$ is a normal or an inverse spinel. For that purpose, calculate the LSFE for both Fe^{2+} and Cr^{3+} in both types of voids in units of Δ_0. Then, calculate the LFSE for normal and inverted spinel and state your decision.

Fe^{2+} tetrahedral void:

$$3\frac{3}{5}\Delta_t - 3\frac{2}{5}\Delta_t = \frac{9}{5}\Delta_t - \frac{6}{5}\Delta_t = \frac{3}{5}\Delta_t$$

$$\Delta_t = \frac{4}{9}\Delta_0$$

$$\frac{3}{5}\Delta_t = 0{,}266\Delta_0$$ **1 bp**

Fe^{2+} octahedral void:

$$4\frac{2}{5}\Delta_0 - 2\frac{3}{5}\Delta_0 = \frac{8}{5}\Delta_0 - \frac{6}{5}\Delta_0 = \frac{2}{5}\Delta_0 = 0{,}4\Delta_0$$ **0,5 bp**

Cr^{3+} tetrahedral void:

$$2\frac{3}{5}\Delta_t - \frac{2}{5}\Delta_t = \frac{4}{5}\Delta_t = 0{,}356\Delta_0$$ **1 bp**

Cr^{3+} octahedral void:

$$3\frac{2}{5}\Delta_0 = \frac{6}{5}\Delta_0 = 1{,}2\Delta_0$$ **0,5 bp**

normal spinel ($Fe^{T}Cr^{O}Cr^{O}O_4$): LFSE = 0,266 Δ_0 +2·1,2 Δ_0 =2,666 Δ_0 **0,5 bp**

inverse spinel ($Fe^{O}Cr^{T}Cr^{O}O_4$): LFSE = 0,4Δ_0 + 0,356 Δ_0 +1,2 Δ_0 =1,956 Δ_0 **0,5 bp**

attains normal spinel configuration **0,5 bp**

total max. 4,5bp