bi ndekgasse
43. ÖChO

43rd Austrian Chemistry Olympiad
National Competition

Theoretical Tasks

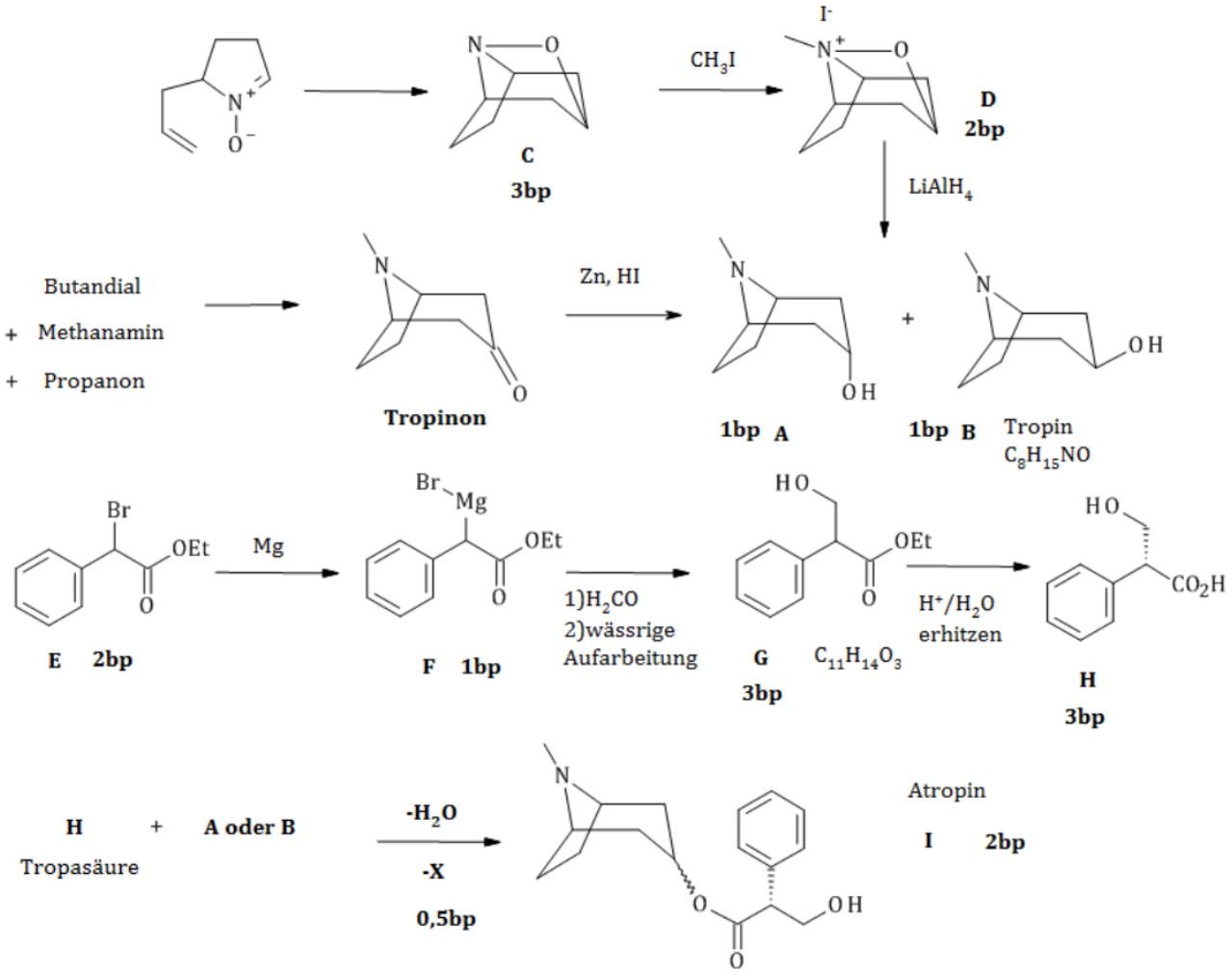
2017-05-25

Solutions

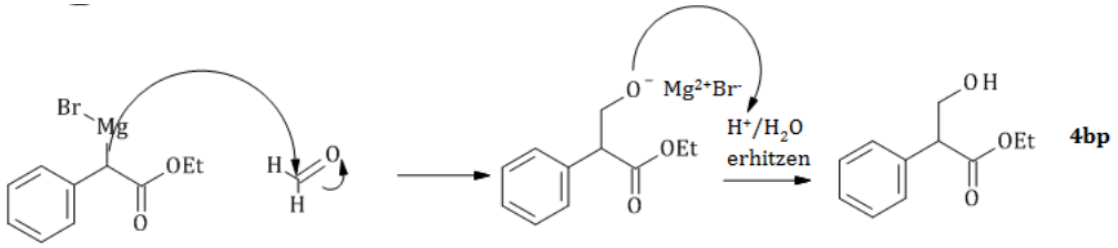
Task 1 **60 bp ≙16 rp**

Bicyclic Nitrogen Compounds and their Syntheses

*1.1 Draw the configuration formulae of the compounds **A**, **B** and **H** and the constitutional formulae of the compounds **C**, **D**, **F**, **G**, **I** and chemical formula of **X**.*



*1.2 Write the mechanism of the reaction **F→G**. Name the corresponding reaction type.*



Type of reaction: nucleophilic addition **1 bp**

*1.3 Name the type of stereoisomerism that occurs in **A** and **B**.*

Diastereomers (exo-endo isomers) **1 bp**

*1.4 Draw arrows in the structural formula in the starting material leading to compound **C**, which clarify the formation of **C**. Name the occurring reaction type.*

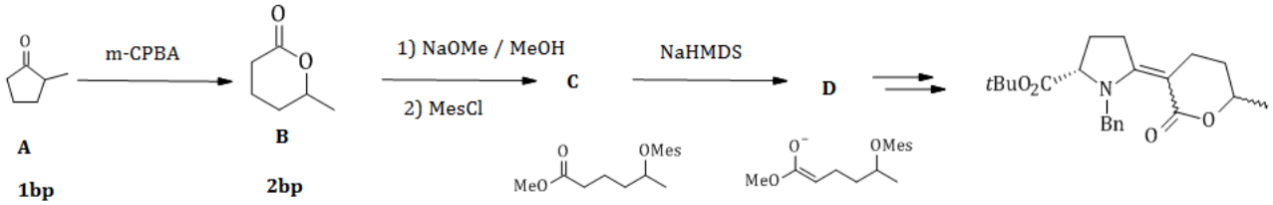
type of reaction:

pericyclic [4+2] cycloaddition (dipolarophile and dipolar (=diene)) **2 bp**

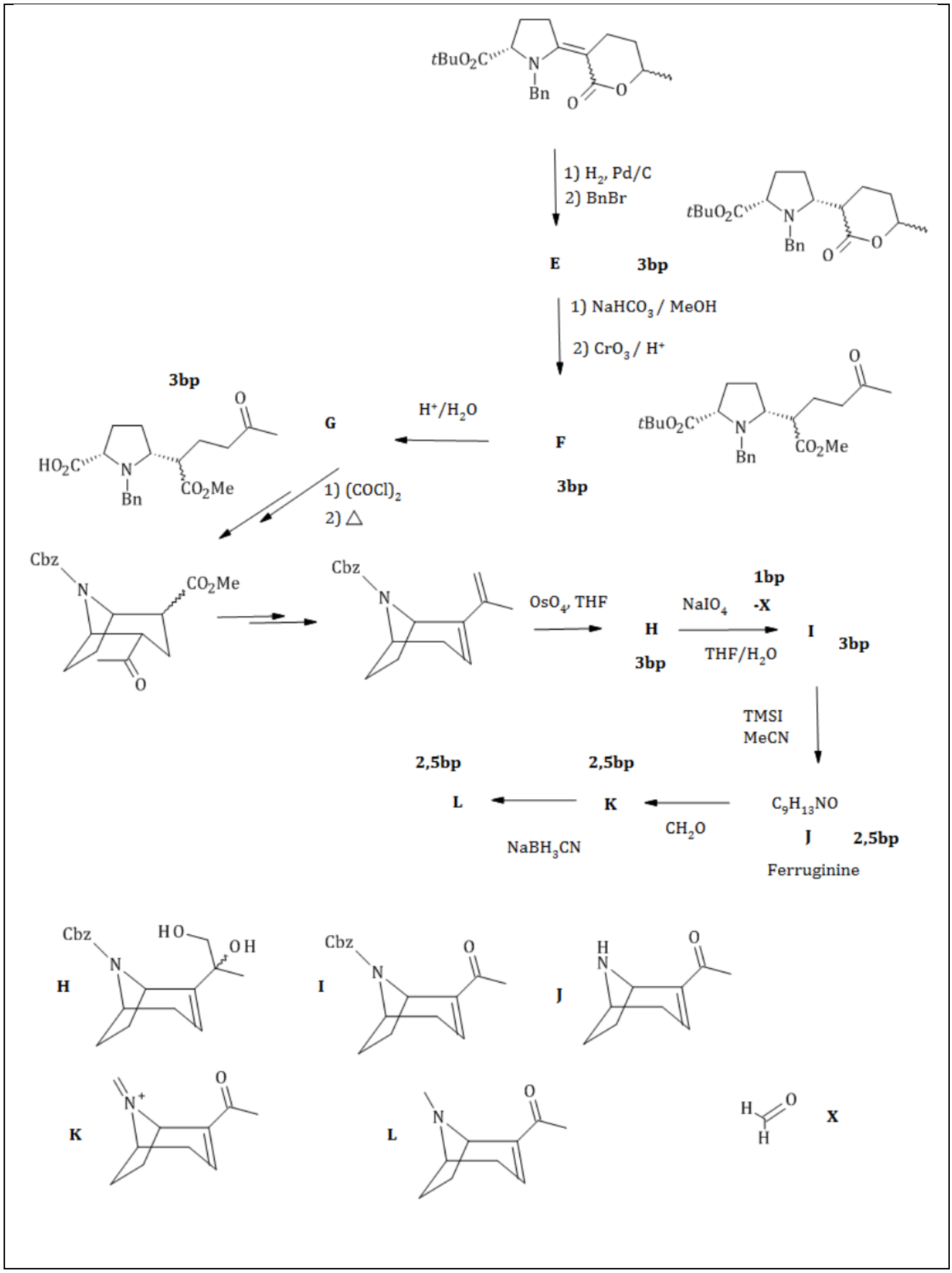
C **2bp**

B. Synthesis of ferruginine

*1.5 Draw the configurational formulae of **A**, **B** und **H** and the constitutional formulae of the compounds **C**, **D**, **E**, **F**, **G**, **I**, **J**, **K**, **L** and **X**.*



A **1bp** **B** **2bp** **C** **3bp** **D** **2bp**

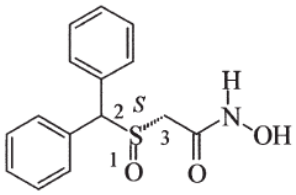

1) H_2, Pd/C
2) BnBr
E
3bp
1) $NaHCO_3$ / MeOH
2) CrO_3 / H^+
F
3bp
H^+/H_2O
G
3bp
1) $(COCl)_2$
2) △
OsO_4, THF
H
3bp
$NaIO_4$
-X
THF/H_2O
1bp
I
3bp
TMSI
MeCN
$C_9H_{13}NO$
J
2,5bp
Ferruginine
CH_2O
K
2,5bp
$NaBH_3CN$
L
2,5bp
H
I
J
K
L
X

Task 2 **27.5 bp ≙ 8 rp**

Pharmaceuticals, Stereochemistry and Spectroscopy

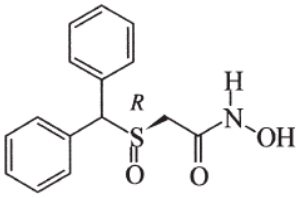
2.1. Draw the configuration formulae into the boxes as appropriate.

S – enantiomer:



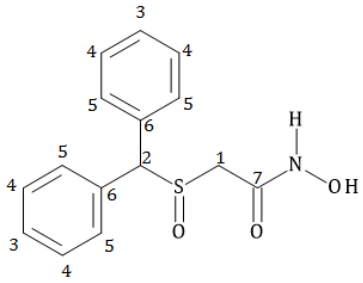
1 bp

R – enantiomer:



1 bp

2.2 Assign all signals of the ^{13}C-NMR spectrum to the corresponding C atoms of Adrafinil. For that purpose, assign each carbon atom of the configuration formula below the corresponding number (1 to 7).

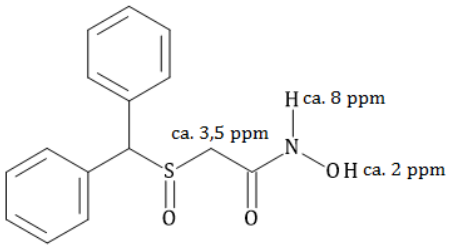


0.25 bp each → **1.75 bp**

2.3 Write the number of the ^{1}H-NMR spectrum of Adrafinil into the box below. Assign chemical shifts in ppm to at least two different protons in the constitutional formula below to clearly justify your selection of spectrum.

Spectrum No.: 1

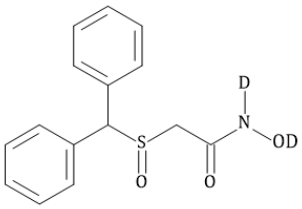
Assignment:



3 bp

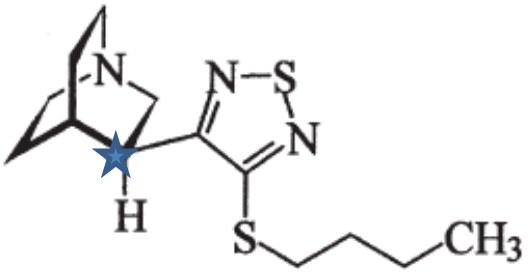
2.4 Assume that the solvent is replaced by CD_3OD. Does the spectrum still contain all signals in this case? If „no“: Draw the resulting – changed – constitutional formula.

O yes X no (tick the correct answer) **0,5 bp**



2 bp

2.5 Mark the chiral center(s) with an asterisk. Furthermore, state the absolute configuration(s) of Vedaclidine by assigning the correct stereo descriptor tot he respective center(s).

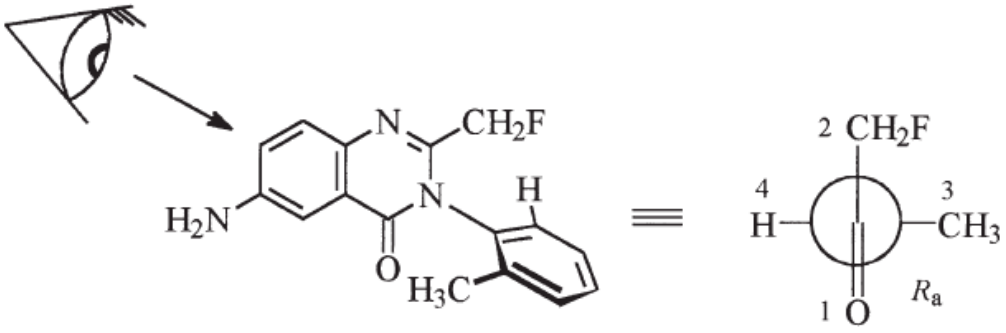


S - configuration **2 bp**

2.6 State the reason, why afloqualone is chiral.

chiral axis **1 bp**

2.7 Draw the configuration formula of afloqualone and state the corresponding stereo descriptor(s).

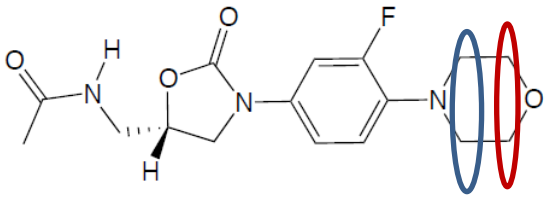


3 bp

2.8 Explicitly mark those C atoms in the formula of linezolid that lead to the same signal in ^{13}C-NMR and state how many signals in the spectrum are caused by more than one C atom.

Number of signals from more than one C atom: **2** **0.5 bp**

Linezolide:



2 bp

2.9 Calculate the molecular formula of the unknown compound:

$$n(H_2O) = \frac{m}{M} = 0.01797mol$$

$$m(H) = 2 \cdot n(H_2O) \cdot M(H) = 0.0363g$$

$$p(H) = \frac{0.03630}{0.5000} = 7.26\%$$

$$n(CO_2) = n(C) = \frac{pV}{RT} = \frac{1.0135bar \cdot 0.6839l}{0.08314 \cdot 298} = 0.02798mol$$

m(C)=0.3360g p(C)=67.20%

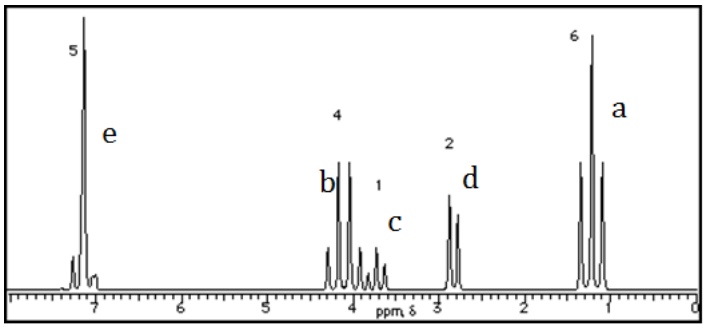
assumed mass 100g:

$$n(C) = \frac{67.20}{12.01} = 5.595mol$$

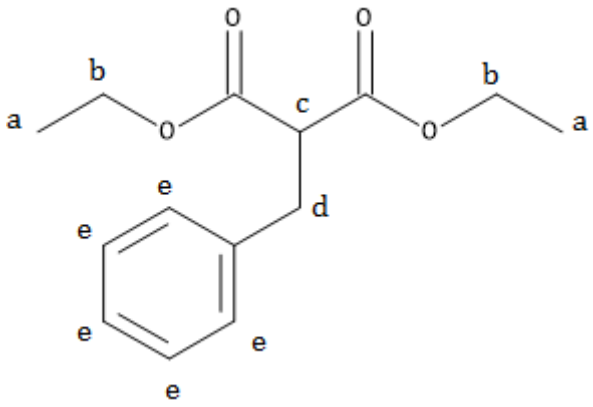
$$n(H) = \frac{7.26}{1.01} = 7.188mol$$

$$n(O) = \frac{25.54}{16.00} = 1.596mol \longrightarrow C_{3.5}H_{4.5}O_1 \longrightarrow C_7H_9O_2$$

***sum formula**: $C_{14}H_{18}O_4$* **4 bp**



2.10 Draw the constitutional formula of the unknown compound. Clearly assign each signal of the ^1H NMR spectrum to a proton in the molecule by assigning lower-case letters a, b, c, etc. both to the peaks in the spectrum and the corresponding protons of the constitutional formula.



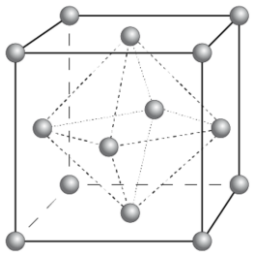
structure: **4.5 bp**

correct assignments 0.25 bp each → **1.25 bp** assignment

Task 3 **23.5 bp ≙ 7 rp**

Aluminum and Complexes

3.1 Draw spheres representing Al atoms into the unit cell below so that they reach cubic closest packing.



1 bp

3.2 Calculate the lattice parameter a in pm.

$$\rho = \frac{m_{UC}}{V_{UC}} = \frac{\text{atoms/UC} \cdot M}{N_A \cdot a^3}$$

$$a = \sqrt[3]{\frac{\frac{atoms}{UC} \cdot M}{\rho \cdot N_A}} \qquad a = 4.049 \cdot 10^{-8}\text{cm} = 405\ pm$$ **3 bp**

3.3 Assign the correct systematic names to the ions formed during both processes:

$[Al(H_2O)_6]^{3+}$	name: hexaaquaaluminium(III) - cation	**1 bp**
$[Al(OH)_4]^-$	name: tetrahydroxido aluminate(III)	**1 bp**

3.4 Give the reaction equations of both dissolution processes mentioned above:

$2\ Al + 6\ H^+ + 12\ H_2O \rightarrow 2\ [Al(H_2O)_6]^{3+} + 3\ H_2$ **1 bp**

$2\ Al + 2\ OH^- + 6\ H_2O \rightarrow 2\ [Al(OH)_4]^- + 3\ H_2$ **1 bp**

3.5 Complete the following reaction equations of the Bayer process by inserting correct stoichiometric coefficients and missing species, if necessary.

$Al_2O_3 + 2\ OH^- + 7\ H_2O \longrightarrow 2\ [Al(OH)_4(H_2O)_2]^-$ **1 bp**

$SiO_2 + 2\ OH^- \longrightarrow SiO_2(OH)_2^{2-}$ **1 bp**

$SiO_2(OH)_2^{2-} + Ca^{2+} \longrightarrow CaSiO_3 \downarrow + H_2O$ **1 bp**

$[Al(OH)_4(H_2O)_2]^- \longrightarrow Al(OH)_3 + OH^- + 2\ H_2O$ **1 bp**

$2\ Al(OH)_3 \longrightarrow Al_2O_3 + 3\ H_2O$ **1 bp**

3.6 Calculate the number of Cr^{3+} ions in this rod of ruby.

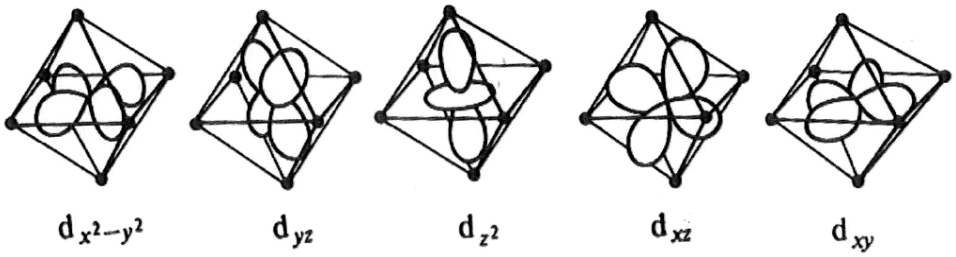
$$V = r^2\pi l = 0.575^2 \cdot \pi \cdot 15.2 = 15.788 cm^3$$

$$m(rod) = 15.788 \cdot 4.05 = 63.941\text{g}$$

$$m(Cr) = 63.941 \cdot \frac{0.05}{100} = 0.03197\ g$$

$$N(Cr) = 0.03197 \cdot \frac{10^{-3}}{52 \cdot 1.661 \cdot 10^{-27}} \approx 3.70 \cdot 10^{20}$$ **2 bp**

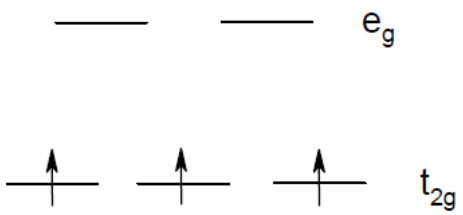
3.7 Write into each of the predefined box, whether the orbital in question belongs to the t_{2g}- or the e_g- orbitals.



e_g	t_{2g}	e_g	t_{2g}	t_{2g}

0.5 each → **2.5 bp**

3.8 Fill up the d-orbital scheme of Cr^{3+} by using arrows for each electron in the usual way.



3 bp

3.9 Give equations for both nuclear reactions of ^{24}Al decay.

$^{24}_{13}Al \rightarrow {}^{24}_{12}Mg + e^+$

$^{24}_{12}Mg \rightarrow {}^{20}_{10}Ne + {}^{4}_{2}He$ **2 bp**

3.10 Write the nuclear reaction scheme for this electron capture process.

$^{26}_{13}Al + e^- \rightarrow {}^{26}_{12}Mg$ **1 bp**

Task 4 **29.5 bp ≙ 8 rp**

Aluminium, Chemical Bonds and Thermochemistry

4.1 Calculate the minimum temperature needed for the equilibrium to lie on the side of the product.

$\Delta_r H° = 3 \cdot (-51.46) + 584.59 + 3 \cdot 10.56 = 409.09 \cdot 10^3 \text{Jmol}^{-1}$ **1 bp**

$\Delta_r S° = 3 \cdot 227.95 - 314.44 - 2 \cdot 39.55 = 290.31\ \text{JK}^{-1}\text{mol}^{-1}$ **1 bp**

$T = \frac{\Delta_r H°}{\Delta_r S°} = 1409\ \text{K}\ (1136°\text{C})$ **1 bp**

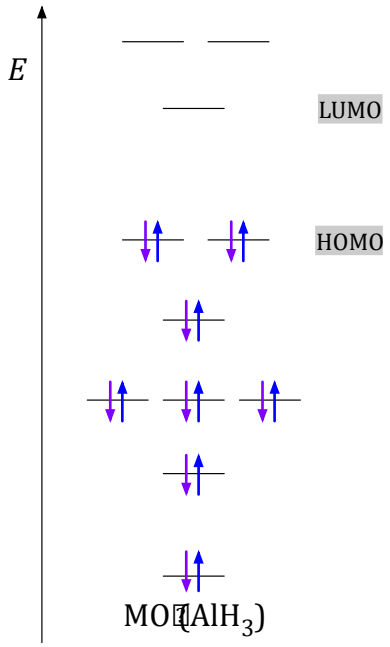
4.2 Write down a balanced equation for this reaction:

$AlCl_3 + 3\ LiAlH_4 \rightarrow 4\ AlH_3 + 3\ LiCl$ **1.5 bp**

4.3 Tick the right configuration of AlH_3 according to VSEPR

X trigonal planar **1 bp**

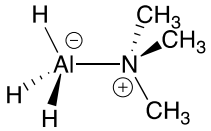
4.4 The figure shows an empty MO-scheme for AlH_3. Fill in all (!) electrons of AlH_3 using arrows.
Indicate HOMO and LUMO und tick the appropriate magnetic behavior.



X diamagnetic *O paramagnetic*

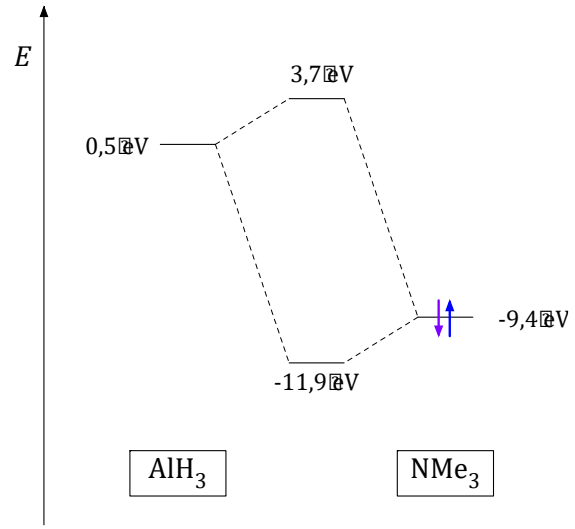
correct number of e- **1 bp**, correct occupation **1 bp**, HOMO/LUMO **1 bp**, magnetic **1 bp**

4.5 Complete the Natta projection for the adduct. Indicate formal charges if necessary.



2.5 bp

4.6 Write AlH_3 and NMe_3 respectively into the boxes
4.7 Draw arrows for the electron pair of the Lewis base on the correct HOMO.



box correct **2.5 bp**, e-pair **0.5 bp**

4.8 Calculate the enthalpy of reaction for the formation of the adduct in kJ/mol

$\Delta E = (-11.9) - (-9.4) = -2.5\ eV$ per electron **1 bp**

$\Delta_r H° = 2 \cdot (-2.5\ \text{eV}) \cdot \frac{1.602 \cdot 10^{-19}\text{J}}{\text{eV}} \cdot 6.022 \cdot 10^{23}\text{mol}^{-1} = -482\ \text{kJmol}^{-1}$ **1.5 bp**

4.9 Calculate the wavelength corresponding to the transition between the bonding (-11.9 eV) and the antibonding (3.7 eV) MO.

$\Delta E = 15.6\ eV = 2.499 \cdot 10^{-18} J = \frac{hc}{\lambda}$

$\Rightarrow \lambda = \frac{hc}{2.499 \cdot 10^{-18}\text{J}} = 79.5\ \text{nm}$ **1.5 bp**

4.10 Calculate the mass of aluminium that had to be used for such a flash.

$E = Pt = 8000 \frac{\text{J}}{\text{s}} \cdot \frac{1}{30}\text{s} = 266.7\text{J}$

$m = Mn = 26.98\ \text{gmol}^{-1} \cdot 4 \cdot \frac{266.7\text{J}}{3351.4\ \text{kJmol}^{-1}} = 8.6\ \text{mg}$ **2 bp**

4.11 Calculate the lattice energy for Al_2O_3 in kJ/mol.

5.986 eV ≙ 577.5 $\frac{\text{kJ}}{\text{mol}}$ 18.83 eV ≙ 1817 $\frac{\text{kJ}}{\text{mol}}$ 28.45 eV ≙ 2745 $\frac{\text{kJ}}{\text{mol}}$ **1 bp**

from 4 Al $_{(s)}$ + 3 $O_{2\ (g)}$ → 2 $Al_2O_{3\ (s)}$ we have

$$\Delta_r H° = 4\Delta_{sub}H° + 4 \cdot (IE1 + IE2 + IE3) + 3\Delta_{Diss}H°(O_2) + 6(EA1 + EA2) + 2\Delta_{latt}H°$$

$-3351.4 = 1320 + 20558 + 1480.8 + 9831.6 + 2\ \Delta_{latt}H°$

$\Delta_{latt}H° = -18271\ \text{kJmol}^{-1}$ **4 bp**

4.12 Calculate the time required for the electrolytic production of the aluminium apex in days.

height of the Al-pyramid: 169.26-169.04m = 22 cm **0.5 bp**

$V = \frac{a^2 \cdot h}{3} = \frac{12^2 \cdot 22}{3} = 1056\ cm^3$ $m = \rho \cdot V = 2.699 \cdot 1056 = 2850\ \text{g}$ **1 bp**

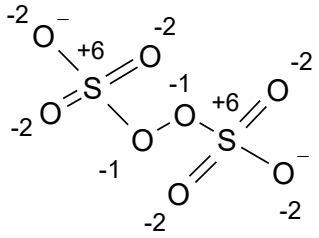
$t = \frac{m \cdot z \cdot F}{M \cdot I \cdot \eta} = \frac{2850 \cdot 3 \cdot 96485}{26.98 \cdot 2 \cdot 0.8} \approx 19110145\ \text{s} = 5308\ \text{h} = 221.2\ \text{d}$ **2 bp**

Task 5 **27.5 bp ≙ 7 rp**

Sulfur Compounds, Kinetics and Electrochemistry

A. . Peroxodisulfate as oxidising agent

5.1 Draw a valence bond formula of the peroxodisulfate ion including formal charges.



structure **2 bp**
formal charges **0.5 bp**

5.2 Assign the correct oxidation number to all atoms in the structure. **1 bp**

5.3 Specify the smallest integer values of the coefficients a, b, c, and d.

a = 1, b = 2, c = 2, d = 1; 1 $S_2O_8^{2-}$ + 2 I^- → 2 SO_4^{2-} + 1 I_2 **1 bp**

5.4 Write down the rate law for the reaction (R1) and specify the overall reaction order.

$v = k \cdot c(S_2O_8^{2-})^x \cdot c(I^-)^y$

measurements (1) and (2): $c_0(I^-)_{(2)} = c_0(I^-)_{(1)}$; $c_0(S_2O_8^{2-})_{(2)} / c_0(S_2O_8^{2-})_{(1)} = 1.4$; $v_{0(2)} / v_{0(1)} = 1.4$ => $x = 1$ **1 bp**

measurements (1) and (3): $c_0(I^-)_{(3)} / c_0(I^-)_{(1)} = 1.5$; $c_0(S_2O_8^{2-})_{(3)} / c_0(S_2O_8^{2-})_{(1)} = 1.8$; $v_{0(3)} / v_{0(1)} = 2.7 = 1.8 \cdot 1.5$ => $y = 1$ **1 bp**

$v = k \cdot c(S_2O_8^{2-}) \cdot c(I^-)$ **0.5 bp**

overall reaction order: 2 **0.5 bp**

5.5 Calculate the reaction rate constant k from the values given above.

$k = v / c(S_2O_8^{2-}) \cdot c(I^-) = 1.1 \cdot 10^{-8} / (0.1 \cdot 10^{-3} \cdot 1.10^{-2}) = 0.011\ L \cdot mol^{-1} \cdot s^{-1}$ **1.5 bp**

5.6 Calculate the temperature (in °C), which must be chosen, in order to increase the reaction rate tenfold under otherwise identical conditions.

Use Arrhenius law: $\frac{k_1}{k_2} = e^{\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$

with $k_1/k_2 = 1/10$

$\Rightarrow ln\frac{1}{10} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow \frac{1}{T_2} = \frac{R}{E_a} \cdot ln\frac{1}{10} + \frac{1}{T_1} \Rightarrow T_2 = 345\ K \sim 72^oC$ **2.5 bp**

5.7 Write down a balanced equation for the reduction of iodine with thiosulfate.

2 $S_2O_3^{2-}$ + I_2 ⇄ 2 I^- + $S_4O_6^{2-}$ **0.5 bp**

5.8 Write down the rate law for this variant of the reaction (R1).

The iodide concentration remains constant, because the iodine being formed is quickly reduced to iodide by thiosulfate, the latter being in excess

→ reaction pseudo-first order: $v = k' \cdot c(S_2O_8^{2-})$ **2 bp**

B. Peroxodisulfate in the iodine clock reaction

5.9 Derive an equation for the rate of formation of I_3^-. Use the steady state approximation for all reaction intermediates.

$$v = \frac{d[I_3^-]}{dt} = k_4 \cdot [I_2] \cdot [I^-]$$

$$\frac{d[I_2]}{dt} = k_3 \cdot [I^+] \cdot [I^-] - k_4 \cdot [I_2] \cdot [I^-] = 0 \Rightarrow v = k_4 \cdot [I_2] \cdot [I^-] = k_3 \cdot [I^+] \cdot [I^-]$$

$$\frac{d[I^+]}{dt} = k_2 \cdot \left[IS_2O_8^{3-}\right] - k_3 \cdot [I^+] \cdot [I^-] = 0 \Rightarrow v = k_3 \cdot [I^+] \cdot [I^-] = k_2 \cdot \left[IS_2O_8^{3-}\right]$$

$$\frac{d\left[IS_2O_8^{3-}\right]}{dt} = k_1 \cdot \left[S_2O_8^{2-}\right] \cdot [I^-] - k_2 \cdot \left[IS_2O_8^{3-}\right] = 0 \Rightarrow v = k_2 \cdot \left[IS_2O_8^{3-}\right] = k_1 \cdot \left[S_2O_8^{2-}\right] \cdot [I^-]$$

$$v = \frac{d[I_3^-]}{dt} = k_1 \cdot \left[S_2O_8^{2-}\right] \cdot [I^-]$$ **4 bp**

C. Electrochemistry of sulfur compounds

$$HSO_4^- \xrightarrow{\boxed{-0.253}} S_2O_6^{2-} \xrightarrow{+0.569} H_2SO_3 \xrightarrow{\boxed{+0.400}} S_2O_3^{2-} \xrightarrow{+0.600} S \xrightarrow{+0.144} H_2S$$

5.10 Calculate the missing potentials x and y.

x = $\frac{2 \cdot 0.158 - 0.569}{1} = -0.253$ V **1 bp**

y = $\frac{3 \cdot 0.456 - 0.569}{2} = 0.400$ V **1 bp**

5.11 Prove by calculation that S(0) is stable against disproportionation.

S(0) is stable, because $E^O(S(0)|S(-\text{II})) < E^O(S(\text{II})|S(0))$ **1 bp**

5.12 Provide a balanced equation for the disproportionation of S(II) with the species indicated in the Latimer diagram.

$S_2O_3^{2-} \rightleftarrows SO_3^{2-} + S$ **1.5 bp**

5.13 Calculate the equilibrium constant for this disproportionation at 25 °C.

$\Delta E^O = 0.60 - 0.4 = 0.2$ V **1 bp**

$\Delta G^O = -z \cdot F \cdot \Delta E^O = -R \cdot T \cdot lnK \Rightarrow lnK = \frac{2 \cdot 96485 \cdot 0.2}{8.314 \cdot 298} = 15.58 \Rightarrow K = 5.8 \cdot 10^6$ **1.5 bp**

5.14 Does hydrogen peroxide react with $Na_2S_2O_8$ under standard conditions as a reducing or as an oxidising agent? Tick the correct answer.

x reducing agent *O oxidizing agent* **0.5 bp**

5.15 Write down the correct redox equation and calculate ΔE^0.

Red: $S_2O_8^{2-} + 2\ e^- \rightleftarrows 2\ SO_4^{2-}$ Ox: $H_2O_2 \rightleftarrows O_2 + 2\ H^+ + 2e^-$

$S_2O_8^{2-} + H_2O_2 \rightleftarrows 2\ SO_4^{2-} + O_2 + 2\ H^+$ **1.5 bp**

$\Delta E^0 = 1.96\ V - 0.69\ V = 1.27\ V$ **0.5 bp**

Task 6 **34 bp ≙ 7 rp**

Lead, Calcium and Equilibrium

6.1 Calculate the concentrations of Pb^{2+} and Ca^{2+} in the aqueous solution.

$$c_{Pb} = \frac{c_{EDTA} \cdot V_{EDTA}}{V_{Pb}} = \frac{0.01\frac{mol}{L} \cdot 0.0203\ L}{0.025\ L} = 0.00812\ \text{mol/L}$$ **1.5 bp**

$$c_{Ca} = \frac{c_{EDTA} \cdot V_{EDTA}}{V_{Pb}} = \frac{0.01\frac{mol}{L} \cdot 0.0134\ L}{0.025\ L} = 0.00536\ \text{mol/L}$$ **1.5 bp**

6.2 Calculate the concentration of free lead ions in the solution at the end of the first titration. Assume that in this calculation only the ions Pb^{2+}, $EDTA^{4-}$ and $[PbEDTA^{2-}]$ have to be considered. It is possibly necessary to make another assumption and to check if it is reasonable.

$$K_\beta = \frac{[[PbEDTA^{2-}]]}{[Pb^{2+}] \cdot [EDTA^{4-}]} = 10^{18.04}$$

$$c_{Pb}^{Total} = [Pb^{2+}] + \left[[PbEDTA^{2-}]\right] = \frac{0.00812\frac{mol}{L} \cdot 0.025\ L}{0.1278\ L} = 1.5884 \cdot 10^{-3}\ \text{mol/L}$$ **2 bp**

assumption: $[Pb^{2+}] \ll \left[[PbEDTA^{2-}]\right] \Rightarrow$ **1 bp**

$\left[[PbEDTA^{2-}]\right] \cong 1.5884 \cdot 10^{-3}$ mol/L **1 bp**

$[Pb^{2+}] = [EDTA^{4-}] \Rightarrow K_\beta = \frac{1.5884 \cdot 10^{-3}}{[Pb^{2+}]^2} = 10^{18.04}$ **2 bp**

$[Pb^{2+}] = \sqrt{\frac{1.5884 \cdot 10^{-3}}{10^{18.04}}} = 3.806 \cdot 10^{-11}$ mol/L ⇒ assumption is correct **2 bp**

6.3 Show by calculation that no precipitation occurs. For $[Pb^{2+}]$, use the result of 6.2. If you were not able to get a result in 6.2, use $[Pb^{2+}] = 3.0 \cdot 10^{-11}$ mol/L. Use $[Ca^{2+}]$ at the beginning of the 2nd titration.

$[Pb^{2+}]_{Max} = \frac{K_L}{[OH^-]^2} = \frac{4.2 \cdot 10^{-15}}{(10^{-2})^2} = 4.2 \cdot 10^{-11}$ mol/L **2 bp**

$[Pb^{2+}]_{Max} > 3.806 \cdot 10^{-11} \Rightarrow$ no precipitation **1 bp**

$[Ca^{2+}]_{Max} = \frac{K_L}{[OH^-]^2} = \frac{3.9 \cdot 10^{-6}}{(10^{-2})^2} = 3.9 \cdot 10^{-2}$ mol/L **1 bp**

$[Ca^{2+}] = \frac{0.00536\frac{mol}{L} \cdot 0.025\ L}{(0.1278 + 0.0223)L} = 8.93 \cdot 10^{-4}$ mol/L **1 bp**

$[Ca^{2+}]_{Max} > 8.93 \cdot 10^{-4} \Rightarrow$ no precipitation **1 bp**

6.4 Calculate the concentrations of all EDTA species at pH = 6.00 without simplification. The autoprotolysis of water does not have to be considered, the activity coefficients of all ions are equal to 1.

$C_{Total} = 0.0100$ mol/L; $pH = 6.00$ ⇒ $[H^+] = 10^{-6}$ mol/L

Simplified variable names:

$[H_4EDTA] = e_0$; $[H_3EDTA^-] = e_1$; $[H_2EDTA^{2-}] = e_2$; $[HEDTA^{3-}] = e_3$; $[EDTA^{4-}] = e_4$

Equations:

(1) $e_0 + e_1 + e_2 + e_3 + e_4 = 0.01$ **1 bp**

(2) $K_{A_1} = \frac{e_1 \cdot [H^+]}{e_0}$ **1 bp**

(3) $K_{A_2} = \frac{e_2 \cdot [H^+]}{e_1}$ **1 bp**

(4) $K_{A_3} = \frac{e_3 \cdot [H^+]}{e_2}$ **1 bp**

(5) $K_{A_4} = \frac{e_4 \cdot [H^+]}{e_3}$ **1 bp**

Calculations:

$e_3 = \frac{e_4 \cdot [H^+]}{K_{A_4}}$ **1 bp**

$e_2 = \frac{e_3 \cdot [H^+]}{K_{A_3}} = \frac{e_4 \cdot [H^+]^2}{K_{A_3} \cdot K_{A_4}}$ **1 bp**

$e_1 = \frac{e_2 \cdot [H^+]}{K_{A_2}} = \frac{e_4 \cdot [H^+]^3}{K_{A_2} \cdot K_{A_3} \cdot K_{A_4}}$ **1 bp**

$e_0 = \frac{e_1 \cdot [H^+]}{K_{A_1}} = \frac{e_4 \cdot [H^+]^4}{K_{A_1} \cdot K_{A_2} \cdot K_{A_3} \cdot K_{A_4}}$ **1 bp**

$0.01 = e_4 + e_3 + e_2 + e_1 + e_0$

$0.01 = e_4 + \frac{e_4 \cdot [H^+]}{K_{A_4}} + \frac{e_4 \cdot [H^+]^2}{K_{A_3} \cdot K_{A_4}} + \frac{e_4 \cdot [H^+]^3}{K_{A_2} \cdot K_{A_3} \cdot K_{A_4}} + \frac{e_4 \cdot [H^+]^4}{K_{A_1} \cdot K_{A_2} \cdot K_{A_3} \cdot K_{A_4}}$ **2 bp**

$e_4 = \frac{0{,}01}{1 + \frac{[H^+]}{K_{A_4}} + \frac{[H^+]^2}{K_{A_3} \cdot K_{A_4}} + \frac{[H^+]^3}{K_{A_2} \cdot K_{A_3} \cdot K_{A_4}} + \frac{[H^+]^4}{K_{A_1} \cdot K_{A_2} \cdot K_{A_3} \cdot K_{A_4}}} = 2.247 \cdot 10^{-7}\text{mol/L}$ **2 bp**

$e_3 = \frac{e_4 \cdot [H^+]}{K_{A_4}} = 4.088 \cdot 10^{-3}\text{mol/L}$ **1 bp**

$e_2 = \frac{e_3 \cdot [H^+]}{K_{A_3}} = 5.909 \cdot 10^{-3}\text{mol/L}$ **1 bp**

$e_1 = \frac{e_2 \cdot [H^+]}{K_{A_2}} = 2.764 \cdot 10^{-6}\text{mol/L}$ **1 bp**

$e_0 = \frac{e_1 \cdot [H^+]}{K_{A_1}} = 2.764 \cdot 10^{-10}$ mol/L **1 bp**

Task 7 **28.5 bp ≙ 7 rp**

Fuel and Otto engine

7.1 Indicate the molar masses:

Hep: 100.23 $gmol^{-1}$ Oct: 114.26 $gmol^{-1}$ **0.5 bp**

7.2 Calculate the standard enthalpy of combustion $\Delta_c H°$ for heptane in the units given below.

$C_7H_{16} + 11\ O_2 \rightarrow 7\ CO_2(g) + 8\ H_2O\ (g)$

$\Delta_c H° = \Delta_r H° = 8 \cdot (-241.8) + 7 \cdot (-393.5) + 224.4 = -4464.5\ kJmol^{-1}$

$\Delta_c H° = \frac{-4464.5\ kJmol^{-1}}{0.10023\ kgmol^{-1}} = -44543\ kJkg^{-1}$

$\Delta_c H° = -44543\ kJkg^{-1} \cdot 0.680\ kg\ L^{-1} = -30289\ kJL^{-1}$

$-4464.5\ kJmol^{-1}$ $-44543\ kJkg^{-1}$ $-30289\ kJL^{-1}$ **3 bp**

7.3 Calculate the standard enthalpy of formation $\Delta_f H°$ of iso-octane in kJ/mol.

$C_8H_{18} + 12.5\ O_2 \rightarrow 8\ CO_2(g) + 9\ H_2O\ (g)$

$\Delta_c H° = -44328\ kJkg^{-1} \cdot 0.11426\ kgmol^{-1} = -5064.9\ kJmol^{-1}$
$\Delta_c H° = 8\Delta_f H°\ (CO_2) + 9\Delta_f H°\ (H_2O) - \Delta_f H°(Oct)$

$\Delta_f H° = 8 \cdot (-393.5) + 9 \cdot (-241.8) - (-5064.9) = -259.3\ kJmol^{-1}$ **1.5 bp**

7.4 Calculate the density of this test mixture in g/L.

$0.07 \cdot 0.68 + 0.93 \cdot 0.692 = 0.691\ gcm^{-3} = 691\ g/L$ **1 bp**

7.5 Calculate the standard enthalpy of combustion for the test mixture in kJ/mol.

Mass in 1000mL: 47.6 g Hep and 643.6 g Oct
Amount of substance in 1000mL: $\frac{47.6}{100.23} = 0.4749$ mol Hep and $\frac{643.66}{114.26} = 5.633$ mol Oct
Total amount of substance in 1000mL : 6.108 mol
Mole fractions: $x_{Hep} = 0.07775$ and $x_{Oct} = 0.9222$ **1.5 bp**
$\Delta_c H°(Mix) = x_{Hep} \cdot \Delta_c H°(Hep) + x_{Oct} \cdot \Delta_c H°(Oct)$
$= 0.07775 \cdot (-4464.5) + 0.9222 \cdot (-5064.9) \approx -5018\ kJmol^{-1}$
1.5 bp

7.6 Calculate the standard entropy and the standard Gibbs energy of mixing for 100 mL of the test mixture at 298 K.

100 mL are 0.6108 mol

$\Delta_{mix}G = nRT(x_{Hep}\ln x_{Hep} + x_{Oct}\ln x_{Oct}) = -414$ J **1.5 bp**

$\Delta_{mix}S = -nR(x_{Hep}\ln x_{Hep} + x_{Oct}\ln x_{Oct}) = 1.39$ JK^{-1} **1.5 bp**

7.7 In which of the four steps (A-B-C-D) no work is done?
Indicate the correct letter(s):

B, D **1 bp**

7.8 In one of the four steps (A-B-C-D) the combustion of the fuel takes place – so fast, that the Volume can be considered constant.
Indicate the correct letter:

B **0.5 bp**

7.9 In one of the four steps (A-B-C-D) the entropy of the working gas is lowered.
Indicate the correct letter:

D **0.5 bp**

7.10 Indicate V_1 and V_2.

$V_2 = 0.15\ V_1$ and $V_1 - 0.15V_1 = 1$L therefore $V_1 = \frac{1L}{0.85} = 1.176$ L **1 bp**

$V_2 = 0.1764$ L **0.5 bp**

7.11 Calculate T_2 and T_4.

$T_1 = 288$ K $T_3 = 2073$ K

$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \Rightarrow T_2 = 288\text{K}\left(\frac{1.176}{0.1764}\right)^{0.4} = 288\text{K} \cdot 2.14 = 616$ K

$T_4 = T_3\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{2073\text{ K}}{2.14} = 969$ K **3 bp**

7.12 Calculate the molar amount of air in the cylinder.

$n = \frac{pV}{RT} = \frac{100000\text{ Pa}\cdot 0.001176\text{ m}^3}{8.314\text{ J K}^{-1}\text{mol}^{-1}\cdot 288\text{ K}} = 0.04911$ mol **1 bp**

7.13 Calculate the changes in internal energy…	
… for step A ($\Delta_A U$)	
0.04911 mol air gives $C_V = 0.04911\ \text{mol} \cdot 20.85 = 1.024\ \text{JK}^{-1}$	**1 bp**
$\Delta_A U = C_V(T_2 - T_1) = 1.024\ \text{JK}^{-1} \cdot 328\text{K} = 335.9\ \text{J}$	**1 bp**
… for step B ($\Delta_B U$)	
$\Delta_\text{B} U = C_V(T_3 - T_2) = 1.024\ \text{JK}^{-1} \cdot 1457\text{K} = 1492\ \text{J}$	**1 bp**
… for step C ($\Delta_C U$)	
$\Delta_\text{C} U = C_V(T_4 - T_3) = 1.024\ \text{JK}^{-1} \cdot (-1104\text{K}) = -1130.5\ \text{J}$	**1 bp**
… for step D ($\Delta_D U$)	
$\Delta_\text{D} U = C_V(T_1 - T_4) = 1.024\ \text{JK}^{-1} \cdot (-681\text{K}) = -697.3\ \text{kJ}$	**1 bp**

7.14 Calculate the efficiency of the idealized Otto engine.	
$w = \Delta_\text{A} U + \Delta_C U = -794.6\ \text{J}$	**2 bp**
Only in step B energy is being added. Therefore	
$\eta = \frac{\lvert w \rvert}{q} = \frac{\lvert w \rvert}{\Delta_B U} = \frac{794.6}{1492.0} = 0.533$ bzw. 53.3%	**2 bp**