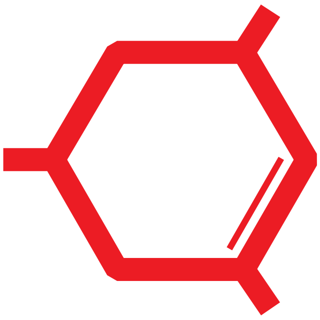


45th Austrian Chemistry Olympiad
National Competition

Theoretical Tasks
May 30th, 2019

Solutions

Problem 1 **25 bp ≙ 7 rp**

Mendeleev and the Elements

A. Mendeleev and his Rare Element

1.1 Calculate the binding energy of the ^{45}Sc nucleus in MeV

$$21 \cdot {}_{1}^{1}p + 24 \cdot {}_{0}^{1}n \rightarrow {}_{21}^{45}Sc$$

$$\Delta m = (21 \cdot 1.0072 + 24 \cdot 1.0087) - 44.9559 = 0.4041u = 6.712 \cdot 10^{-28} kg$$

$$E = \Delta m \cdot c^2 = (6.712 \cdot 10^{-28}) \cdot (2.998 \cdot 10^8)^2 = 6.033 \cdot 10^{-11} J = 3.764 \cdot 10^8 eV = 376 MeV$$

2 bp

1.2 Calculate the coordination number of Scandium.

12 **0.5 bp**

1.3 Determine the number of atoms in the unit cell.

$8 \cdot \frac{1}{8} + 1 \cdot 1 = 2$ **0.5 bp**

1.4 Calculate the density of Scandium.

$$\rho = \frac{Number\ of\ Atoms\ per\ UC \cdot M}{N_a \cdot V} = \frac{2 \cdot 45}{6.022 \cdot 10^{23} \cdot 5 \cdot 10^{-23}} = 2.989 g/cm^3$$

1 bp

1.5 Add empirical formulae, names and general product names to the table below.

Name incl. oxidation no. of the cation	Formula	Product
Scandium(III) nitrate **0.5 bp**	$Sc(NO_3)_3$	Salt **0.5 bp**
Scandium(III) oxide	Sc_2O_3 **0.5 bp**	a Salt
Hexafluoridoscandate(III) **0.5 bp**	$[ScF_6]^{3-}$	Complex **0.5 bp**
Trioxalatoscandate(III)	$[Sc(C_2O_4)_3]^{3-}$ **0.5 bp**	Chelate complex **0.5 bp**

1.6 Formulate a balanced equation for this reaction.

$2\ ScF_3 + 3\ Ca \rightarrow 2\ Sc + 3\ CaF_2$ **1 bp**

1.7 Determine the molar mass of Pretulite.

$$m = \frac{4M}{N_A} \rightarrow n = \frac{m}{M} = \frac{4M}{N_A} \cdot \frac{1}{M} = \frac{4}{N_A} \rightarrow \frac{m}{M} = \frac{4}{N_A}$$

$$\rho = \frac{m}{V} = \frac{4 \cdot M}{N_A} \cdot \frac{1}{a^2 \cdot c}$$

$$M = \frac{\rho \cdot N_A \cdot a^2 \cdot c}{4} = \frac{3.7 \cdot 6.022 \cdot 10^{23} \cdot (6.5806 \cdot 10^{-8})^2 \cdot (5.806 \cdot 10^{-8})}{4} = 140 g/mol$$

3 bp

1.8 Elementary analysis revealed that Pretulite contains 32% (m/m) Scandium. Determine the empirical formula of Pretulite.

$$\frac{0.32 \cdot 140}{45} = 1\ Sc$$

$$\Delta M = 95 g/mol \ \rightarrow PO_4{}^{3-}$$

$Sc[PO_4]$ **2 bp**

1.9 Formulate an equation for this nuclear transformation.

${}^{45}_{21}Sc + {}^{1}_{0}n \rightarrow {}^{45}_{20}Ca + {}^{1}_{1}p$ or ^{45}Sc(n,p)^{45}Ca **1 bp**

1.10 Formulate the equation for this nuclear decay and state the type of decay.

${}^{46}_{21}Sc \rightarrow {}^{46}_{22}Ti + {}^{0}_{-1}e + \bar{\nu}$

β^- decay **1.5 bp**

B. From Scandium to Titanium

1.11 Label the Pauli valence binding diagram and complete it for the given complex.

↑			↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
3 d					4 s		4 p	

2 bp

1.12 Determine hybridization of the central atom.

d^2sp^3 **0.5 bp**

1.13 Specify the magnetic behavior of the complex.

Paramagnetic **0.5 bp**

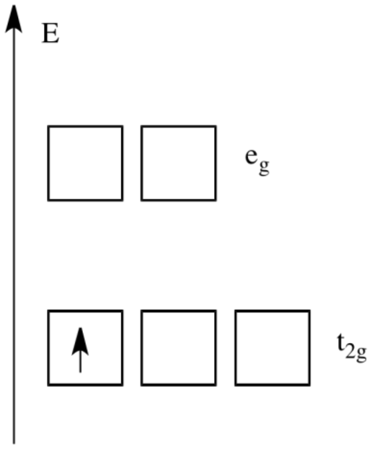
1.14 Specify the spatial structure of the complex.

Octahedral **0.5 bp**

1.15 Name the complex.

Hexaaquatitanium(III) **0.5 bp**

1.16 Draw the energy level diagram showing the configuration of the d electrons of the metal ion in the complex and denominate the respective types of the energy states.



1 bp

1.17 Calculate the wavelength of the light the complex absorbs.

$$\Delta_O = \frac{N_A \cdot hc}{\lambda}$$

$$234 \cdot 10^3 = \frac{6.022 \cdot 10^{23} \cdot 6.626 \cdot 10^{-34} \cdot 2.998 \cdot 10^8}{\lambda}$$

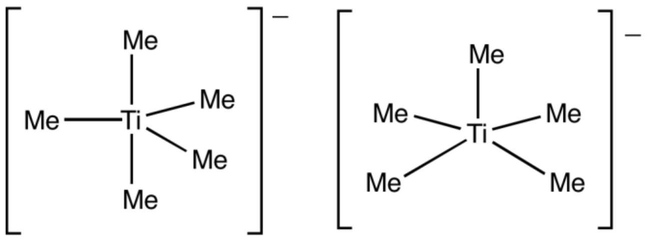
$$\lambda = 511 nm$$

1.5 bp

1.18 Determine the color of an aqueous solution of this complex.

Reddish purple **0.5 bp**

1.19 Sketch two possible spatial structures of [TiMe$_5$]$^-$ (Me ... Methylide anion). Name the respective geometrical shapes.



trigonal-bipyramidal and quadratic pyramidal, respectively

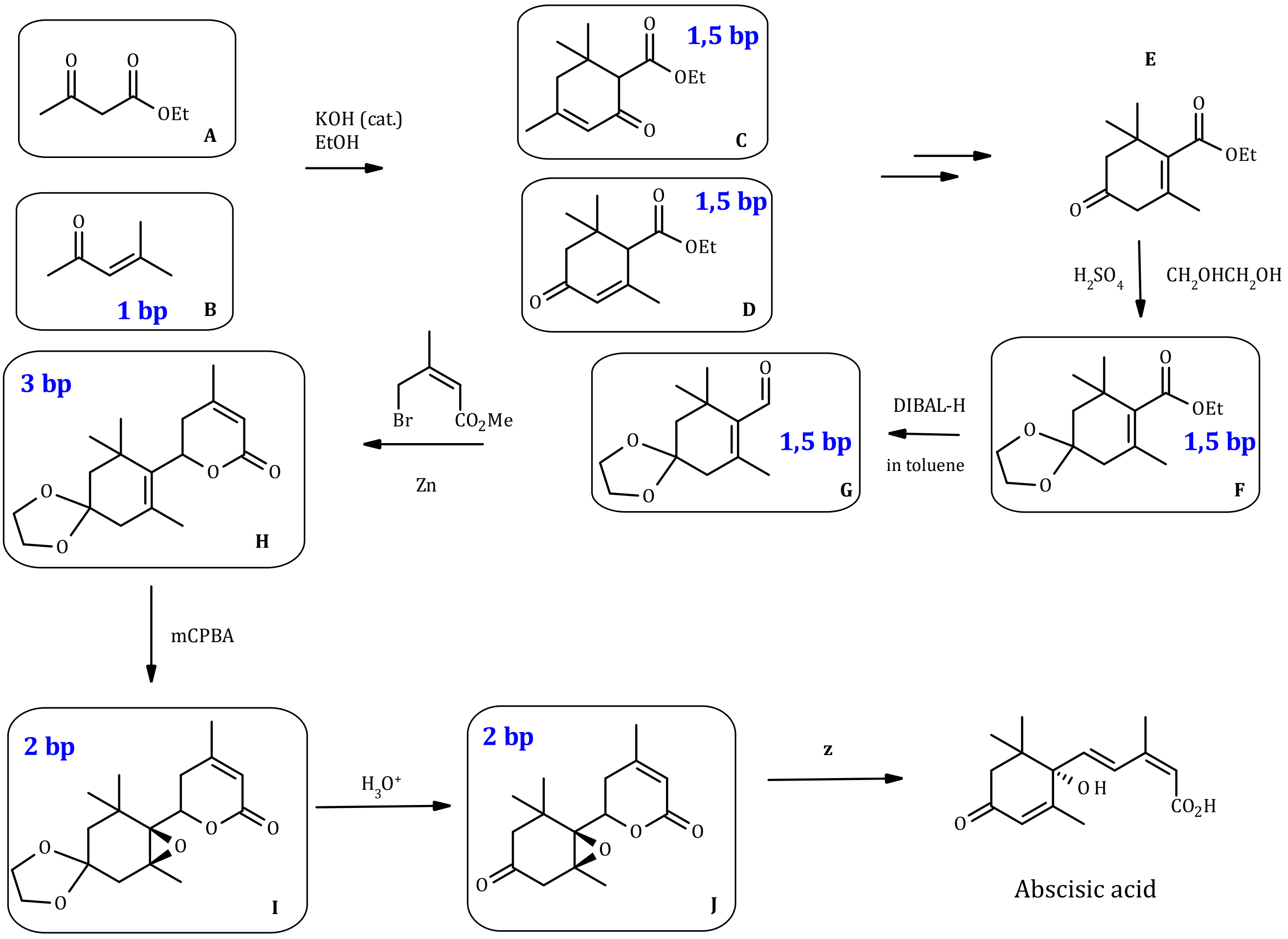
2 bp

Problem 2 **87 bp ≙ 21 rp**

Organic Chemistry and Music

A. AB(B)A – „Take a Chance on Me“

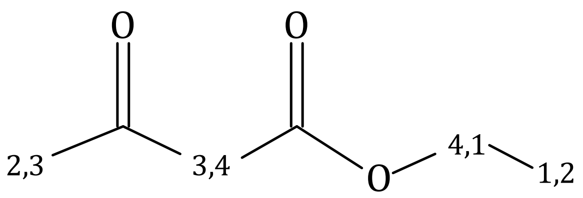
A.1. Synthesis of ABA (refer to the scheme on the next page):

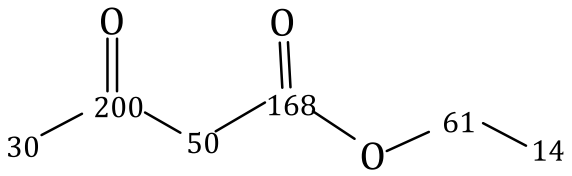


mCPBA ... meta-chloroperbenzoic acid

DIBAL-H ... Diisobutyl aluminium hydride

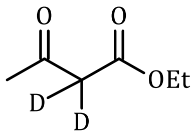
*2.1 Determine the structural formula of **A** (reaction scheme) and assign both ^1H- and ^{13}C-shifts to the respective atoms.*





5 bp

*2.2 Draw the structural formula of **A** when using a 1:1 mixture of D_2O/CD_3CN as the solvent during NMR measurements.*



2 bp

*2.3 Give the empirical formula of **J**.*

$C_{15}H_{20}O_4$ **2 bp**

*2.4 Determine the structural formulae **B** to **J**. Keep the correct stereochemistry in mind (reaction scheme).* ***14 bp***

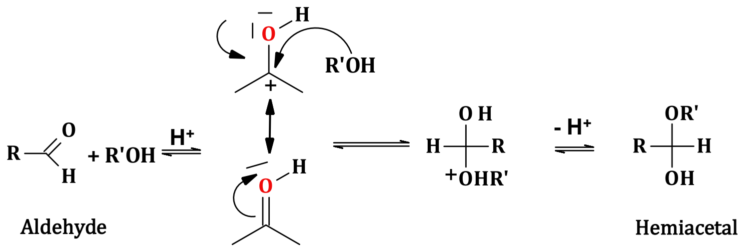
*2.5 Suggest a reagent **z** to transform **J** to Abscisic acid (reaction scheme).*

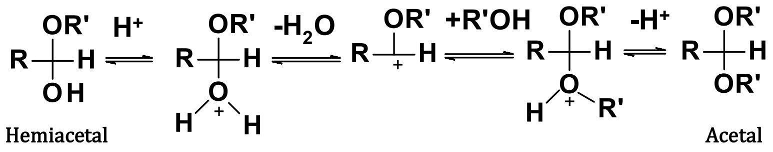
NaOH **1bp**

*2.6 The step from **E** to **F** comprises introducing a widely used protective group. Which concrete reaction during the following reaction process does it prevent from happening?*

A_N with metalloorganic compounds from **G** to **H** / Oxidation of the ketone to the ester by mCPBA **2bp**

*2.7 Demonstrate the reaction mechanism leading from **E** to **F**. Do not draw the entire molecule, but only the respective functional group and the corresponding residues.*





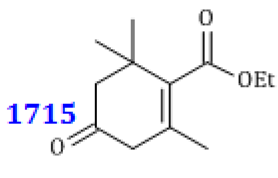
4bp

2.8 Which reaction mechanism do the two reactions below follow? Use standard acronyms.

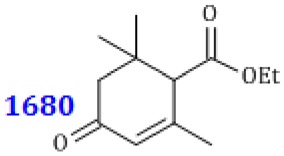
F→G: Red **G→H**: A_N / El *2 bp*

2.9 Assign the respective wave numbers to the corresponding functional group by writing them to the correct position of the respective structure of each of the three isomers.

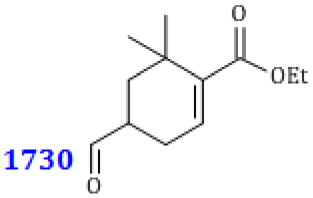
E



E'



E''



1050-1250: C-O-C

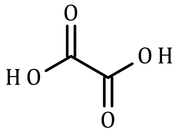
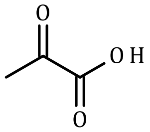
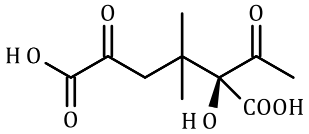
2 bp

2.10 Well-known effects in Organic chemistry cause the differences in the spectral range at 1700 cm^{-1}. Which of the following statements is true, and which one is false? Write "t" for "true" and "f" for "false".

t / f	Statement
f	Band shift to wavenumber 1730 cm^{-1} is a consequence of the –I effect.
t	C=O groups binding to two Alkyl groups absorb at lower wavenumbers, than C=O groups binding to one alkyl group.
f	Band shift to wavenumber 1680 cm^{-1} is a consequence of the –I effect.
f	Band shift to wavenumber 1730 cm^{-1} is a consequence of the +M effect.
t	Band shift to wavenumber 1680 cm^{-1} is a consequence of the +M effect.
f	Conjugation shifts wavenumbers to higher values.
f	An absorption band of $F_2C=O$ occurs at lower wavenumbers, than that of $(CH_3)_2C=O$.
t	Conjugation shifts wavenumbers to lower values.

2 bp

A.2. Determining the structure of ABA:

*2.11 Calculate the empirical formula of ozonolysis product **X**.*	
$C_{10}H_{14}O_7$	**2.5 bp**
*2.12 Give the structural formulae of ozonolysis products **X**, **Y** and **Z**.*	
 Z  Y  X	**4.5 bp**

2.13 Write the stereodescriptor(s) of Abscisic acid into the figure.	
S, 2Z, 3E	**1.5 bp**
2.14 How many enantiomers of Abscisic acid exist?	
2 enantiomers	**1 bp**
2.15 How many stereoisomers exist for the constitutional formula of Abscisic acid?	
$2^3 = 8$ stereo isomers	**1.5 bp**

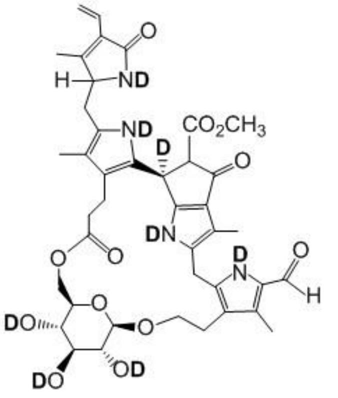
A.3. ABA Mechanism of action

*2.16 Name the functional groups labeled with **1**, **2**, and **3**, respectively.*	
1 = Lactam, 2 = Ester, 3 = Acetal	**1.5 bp**
*2.17 Determine the stereo descriptors of the C atoms labeled **a** and **b**.*	
a:R b: S	**3bp**
2.18 Determine the number of stereogenic centers and label them with an asterisk (*) in the structural formula.	
8 stereogenic centers	**1 bp**

2.19 Calculate the maximum number of possible stereoisomers of this catabolite based on the assumption that glucose is always present in its D-configuration and can only form different anomers.	
$2^4 = 16$ stereo isomers (all stereo centers in glucose are fixed, except for the anomeric C atom; plus three further chiral centers → 4 chiral centers)	**2 bp**

2.20 Assign the numbered signals in the 600 MHz-NMR-Spektrum to the respective structure by writing the numbers to the respective protons. It is not possible to assign all 7 signals explicitly.	
4,5,6 and 7: Protons of the four methyl groups 3: Protons of the methoxy group 2: Protons af the vinyl group 1: Proton of the aldehyde function	**2 bp**

2.21 The structure contains hydrogen atoms, whose signals are not visible when recording the NMR spectrum in a protic deuterated solvent, such as CD_3OD. Mark those hydrogen atoms by encircling them in the structural formula.



2 bp

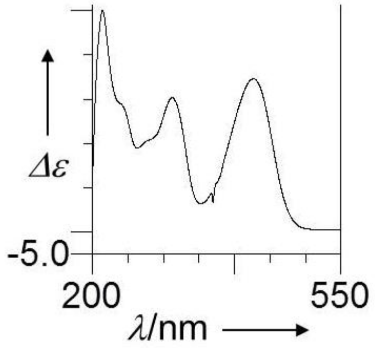
2.22 Determine the stereodescriptor at the position of the arrow.

Z configuration **1 bp**

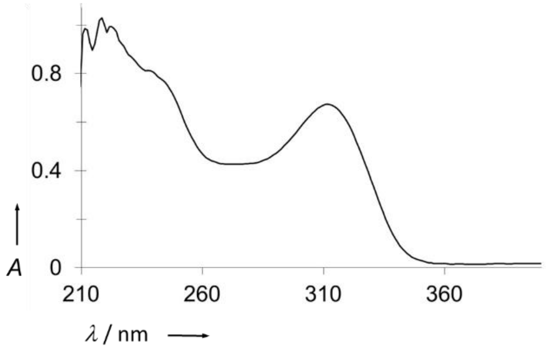
2.23 State which type of isomerism is present.

Diastereomerism, geometrical isomerism **1 bp**

2.24 Correctly assign „Catabolite 1“ and „Oxidation product“ to the spectra.



Oxidation product



Catabolite 1 **2 bp**

2.25 Deduce the color of each derivative.

Oxidation product: yellow Catabolite 1: colorless

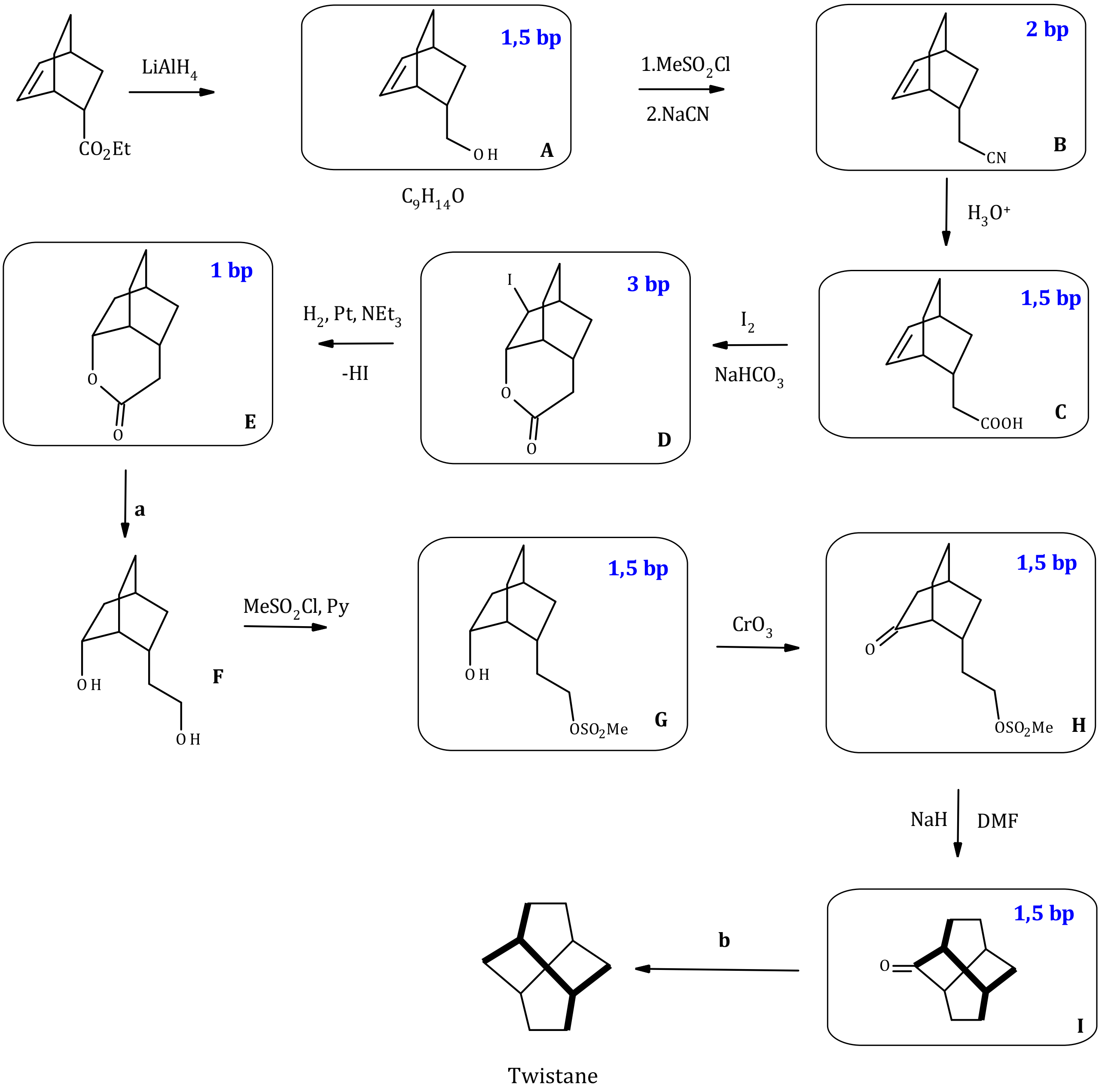
2 bp

2.26 One of the two compounds requires less energy for electronic excitation. Calculate the the energy of the photon that excites at the absorption maximum. Explicitly state the wavelength underlying your calculation. State the color of the exciting light.

$$E = \frac{h\cdot c}{\lambda} = \frac{6.6267015\cdot 10^{-34}\cdot J\cdot s\cdot 299792458\cdot m\cdot s^{-1}}{4.4\cdot 10^{-7}\cdot m} = 4.51\cdot 10^{-19}\cdot J$$

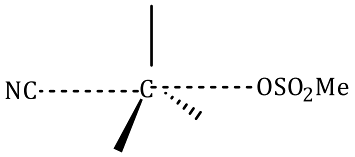
Excitation light: blue **1.5 bp**

B. „Let´s twist again“



*2.27 Determine the structural formulae **A-E** and **G-I** (reaction scheme) taking into account correct stereochemistry.* ***13.5 bp***

*2.28 Name the reaction mechanism in the second step of **A→B**! Draw the structure of the transition state.*



S_N2

2.5 bp

*2.29 Suggest reagents **b** for transforming **I** to Twistane; How is this name reaction called und what is the underlying mechanism (first step)?*

N_2H_4 / *KOH*

Wolff-Kishner reduction

A_N **2 bp**

*2.30 What role does NaH play during step **H→I**? Tick the correct answer(s).*

☐	Oxidant
☐	Reductant
☐	Acid
■	**Base**
☐	Protective group
☐	Catalyst

1 bp

2.31 Determine the symmetric elements of Twistane.

C2 axis, inversion center **2 bp**

Problem 3 **14 bp ≙ 4 rp**

Electrochemistry: Copper and Other Metals

A. Composition of a 10-cent coin.

3.1 Formulate balanced equations for dissolving the soluble components of the coin in diluted hydrochloric acid.

$2\ Al + 6\ H_3O^+ \rightarrow 2\ Al^{3+} + 3\ H_2 + 6\ H_2O$

$Zn + 2\ H_3O^+ \rightarrow Zn^{2+} + H_2 + 2\ H_2O$

$Sn + 2\ H_3O^+ \rightarrow Sn^{2+} + H_2 + 2\ H_2O$ **1.5 bp**

3.2 Specify the electrolyzed metal and calculate its mass fraction in the alloy.

Copper

$n(\mathrm{Cu}) = 0{,}0574\ \mathrm{mol}$

$$m\ (Cu) = \frac{M \cdot I \cdot t \cdot \eta}{z \cdot F} = \frac{63.55\ g\ mol^{-1} \cdot 13\ A \cdot 16.71\ min \cdot 60 s min^{-1} \cdot 0.85}{2 \cdot 96485 Asmol^{-1}} = 3.649\ g$$

Cu: $\frac{3.649}{4.100} = 89.0\%$ **2.5 bp**

3.3 Calculate the mass fraction of tin in the coin.

$$n(Komplex) = \frac{m}{M} = \frac{0.213}{616.11} = 0.0003457\ mol = n\ (Sn)$$

$$m(Sn) = n\ (Sn) \cdot M(Sn) = 3.457 \cdot 10^{-4} \cdot 118.71 \approx 0.0410\ g$$

Sn: $\frac{0.041}{4.100} = 1.0\%$ **1.5 bp**

3.4 Calculate the mass fractions of the remaining two metals in the coin.

$$n(H_2) = \frac{p \cdot V}{R \cdot T} = \frac{1.013 \cdot 10^5 Pa \cdot 363.9 \cdot 10^{-6}\ m^3}{8.314\ Jmol^{-1}K^{-1} \cdot 298\ K} \approx 0.01488\ mol$$

$n(H_2)$ from Zn and Al: $n(H_2)_{\mathrm{total}} - n(Sn) = 0.01453$ mol

$n(H_2)$ from Zn: x ; and $n(H_2)$ from Al: 1.5 y => x + 1.5 y = 0.01453

m(Zn) + m(Al) = 0.41 g => 65.41 x + 26.98 y = 0.41

From these two equations x and y can be calculated as:

$x = 3.13 \cdot 10^{-3}$ mol Zn ⇒ $m(Zn) = 3.13 \cdot 10^{-3} \cdot 65.41 = 0.205$ g

$y = 7.60 \cdot 10^{-3}$ mol Al ⇒ $m(Al) = 7.60 \cdot 10^{-3} \cdot 26.98 = 0.205$ g

Zn: $\frac{0.205}{4.100} = 5.0\%$ Al: $\frac{0.205}{4.100} = 5.0\%$ **4.5 bp**

B. Electrochemistry of Real Gold

$$\begin{tikzcd}
Au^{3+} \arrow[r, "x"] \arrow[rr, bend right, "+1.51"'] & Au^{+} \arrow[r, "+1{,}83"] & Au
\end{tikzcd}$$

3.6 Calculate the missing potential x.

$x = \frac{3\cdot 1.517 - 1.83}{2} = 1.36\ \text{V}$ **1 bp**

3.7 Calculate the complex forming constant of [AuCl₄]⁻ at 298 K from the given standard potentials.

(1) $Au^{3+} + 3\ e^{-} \rightarrow Au$ $E_1^O = +1.517\ \text{V}$ $\Delta G_1^O = -439.1\ \text{kJ/mol}$

(2) $[AuCl_4]^{-} + 3\ e^{-} \rightarrow Au + 4\ Cl^{-}$ $E_2^O = +1.002\ \text{V}$ $\Delta G_2^O = -290.0\ \text{kJ/mol}$

One needs to calculate the equilibrium (=complex forming)constant β for the reaction:

(3) $Au3^{+} + 4\ Cl^{-} \rightleftarrows [AuCl_4]^{-}$

(3) = (1) – (2) => $\Delta E^0 = 1.517\ \text{V} - 1.002\ \text{V} = 0.515\ \text{V}$

$\Delta G_3^O = -3\cdot F\cdot 0.515 = -1.545\cdot F\ \text{J / mol} = -149.1\ \text{kJ/mol}$

$\Delta G_3^O = -R\cdot T \ln\beta \Rightarrow \ln\beta = \frac{1.545\cdot F}{R\cdot T} = 60.17$ **3 bp**

$\beta = 1.35\cdot 10^{26}$

Problem 4 **32 bp ≙ 10 rp**

Energy and Conjugated Systems

A. Propene

4.1 Calculate $\Delta_rH°$, $\Delta_rS°$, and $\Delta_rG°$, as well as K_p at 298K..

$$\Delta_r H° = 2 \cdot 20.4 - 52.4 + 7.7 = -3{,}9\ kJmol^{-1}$$
$$\Delta_r S° = 2 \cdot 266.8 - 219.3 - 301.0 = 13.3\ Jmol^{-1}K^{-1}$$
$$\Delta_r G° = -3900 - 298 \cdot 13{,}3 = -7863 Jmol^{-1} = -7.9\ kJmol^{-1}$$
$$\mathrm{Kp} = e^{-\frac{\Delta_R G}{RT}} = 23.9$$

4 bp

4.2 Calculate the heat that is set free at isobaric conditions when producing 1000kg Propene at 436K.

$$\Delta_r C_p = 2 \cdot 64.3 - 80.2 - 42.9 = 5.5 Jmol^{-1}K^{-1}$$
$$\Delta_r H°_{436} = \Delta_r H°_{298} + \Delta_r C_p \cdot (436 - 298) = -3141 Jmol^{-1}$$
$$M_{Propen} = 42.09 gmol^{-1} \Rightarrow 1000kg \mathrel{\widehat{=}} 2.376 \cdot 10^4 mol$$
$$0.5 \cdot 2.376 \cdot 10^4 \mathrm{mol} \cdot -3141 \mathrm{Jmol}^{-1} \Rightarrow 3.73 \cdot 10^7 \mathrm{J}\ \text{set free.}$$

3.5 bp

4.3 Calculate $\Delta_rH°$ and $\Delta_rU°$ for for this reaction at 298K.

$C_3H_{8(g)} + 5\ O_2$	→	$3\ CO_{2(g)} + 4\ H_2O_{(l)}$	$\Delta_c H^°_{Propane}$
$3\ CO_{2(g)} + 4\ H_2O_{(l)}$	→	$C_3H_{6(g)} + 4{,}5\ O_2$	$-\ \Delta_c H^°_{Propene}$
$H_2O_{(l)}$	→	$H_2(g) + ½\ O_2(g)$	$-\ \Delta_c H^°_{H2O}$
$C_3H_{8(g)}$	→	$C_3H_{6(g)} + H_{2(g)}$	$\Delta_r H^°$

$$\Delta_r H° = -2220 + 2058 + 286.5 = 124.5 kJmol^{-1}$$
$$\Delta_r U° = \Delta_r H° - \Delta_r nRT = 122 kJmol^{-1}$$

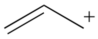
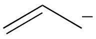
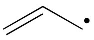
3.5 bp

B. Propene in Action – the Allyl System

4.4 State the hybridization of the C atoms in the backbone shown

☐ sp X sp^2 ☐ sp^3 ☐ sp^3d^2 ☐ die 3 C Atome sind verschiedene Hybride **0.5 bp**

4.5 State the number of π electrons

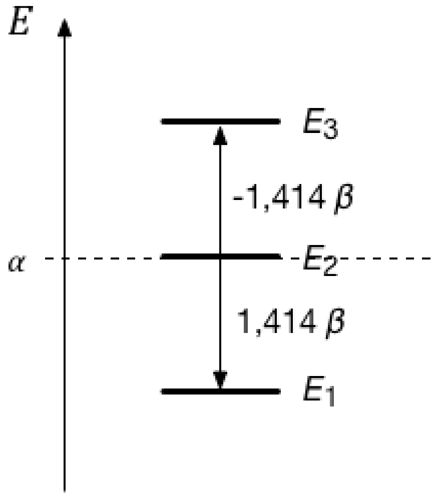
for  2 **0.5bp**	for  4 **0.5bp**	for  3 **0.5 bp**

4.6 State the number of antibonding nodal planes for the π molecular orbitals.

for φ_1 0 **0.5bp**	*for φ_2* 1 **0.5bp**	*for φ_3* 2 **1 bp**

4.7 Give the correct term for E_2, the energy of φ_2. Insert the energy levels E_1, E_2, and E_3 ,as well as the parameter β including its sign into the diagram. Label them clearly.

$E_2 = \alpha$ (2bp)



total **3.5 bp**

4.8 Calculate the charges q_1, q_2, q_3 at the C atoms C_1, C_2, and C_3

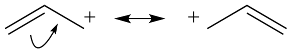
For the allyl cation

only φ_1 is occupied with 2 e

$$q_1 = 1 - 2 \cdot (0.500)^2 = 0.5$$
$$q_2 = 1 - 2 \cdot (0.707)^2 = 0.0003 \approx 0$$
$$q_3 = q_1 = 0.5$$

1.5 bp

Draw the mesomeric resonance structures for the allyl cation



0.5 bp

Charges at the mesomeric structures and the calculated values for q_1, q_2, q_3

X correspond ☐ do not correspond to each other **0.5 bp**

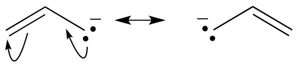
For the allyl anion:

φ_1 and φ_2 are occupied with 2 e each

$$q_1 = 1 - (2 \cdot (0.500)^2 + 2 \cdot (0.707)^2 = -0.5$$
$$q_2 = 1 - 2 \cdot (0.707)^2 - 2 \cdot 0 = 0.0003 \approx 0$$
$$q_3 = q_1 = -0.5$$

2 bp

Draw the mesomeric resonance structures for the allyl anion



0.5 bp

Charges at the mesomeric structures and the calculated values for q_1, q_2, q_3

X correspond ☐ do not correspond to each other **0.5 bp**

4.9 Calculate the bond orders I_{12} and I_{23} of the allyl radical.

φ_1 occupied with 2 e and φ_2 with 1 e

$$I_{12} = 2 \cdot (0.500) \cdot (0.707) + 1 \cdot (0.707) \cdot 0 = 0.707$$
$$I_{23} = 2 \cdot (0.707) \cdot (0.500) + 1 \cdot (0) \cdot (-0.707) = 0.707$$

1.5 bp

C. Hexatriene

4.10 Specify the following points for hexatriene:

Total number of all atomic p-orbitals (attention: e.g. 3p are three orbitals)	∞	**1 bp**
Number of atomic p-orbitals relevant for the Hückel approximation	6	**0.5 bp**
Number of resulting π – molecular orbitals	6	**0.5 bp**

4.11 Energies of the three orbitals increase as follows (Tick the correct one):

☐ $\varphi_a, \varphi_b, \varphi_c$ ☐ $\varphi_b, \varphi_c, \varphi_a$ ☐ $\varphi_c, \varphi_b, \varphi_a$ X $\varphi_b, \varphi_a, \varphi_c$ **1 bp**

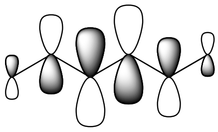
4.12 Does one of the images show one of the orbitals mathematically expressed above? If yes, specify, which one ($\varphi_a, \varphi_b, \varphi_c$).

A shows _________ B shows _________ C shows φ_a **0.5 bp**

4.13 Specify the numbers of antibonding nodes.

A 2 B 0 C 3 **0.5 bp**

4.14 Draw the most energy-rich π-molecular orbital of Hexatriene in analogy to the pictures above.



Backbone with number of nodes correct 1bp; also size ratios visible: **2.5 bp**

Problem 5 **27 bp ≙ 7 rp**

Tartar Equilibrium

5.1 Give the empirical formula and the molar mass of potassium hydrogentartrate.

$M(KC_4H_5O_6) = 188.19\ g/mol$ **1 bp**

5.2 Calculate the solubility product of this salt at those conditions.

$$c_{KC_4H_5O_6} = \frac{2.50 g/L}{188.19 g/mol} = 0.0133\ mol/L$$

$$K_{SP}^{17^\circ} = c_{KC_4H_5O_6}^2 = 0.000176$$

2 bp

5.3 Calculate the molar concentration of potassium hydrogentartrate in this wine. For your calculation assume that the density of wine remains constantly at 1000 g/L despite changing temperature.

$$c_{KC_4H_5O_6} = \frac{1.13 g/L}{188.19 g/mol} = 0.00600\ mol/L$$

1 bp

5.4 How much – i.e. which mass – potassium hydrogencarbonate could one add to the wine in Problem 5.3 per liter after partially removing potassium hydrogentartrate, before one could expect that solid potassium hydrogentartrate forms anew. To simplify the problem, assume that adding potassium hydrogencarbonate to the wine does not substantially change the pH of wine and that hence the molar concentration of hydrogentartrate ions does not change either. Use the solubility product calculated in Problem 5.2. If you did not achieve a result there, use the value $K_{SP}^{17^\circ} = 0.0002$.

$$K_{SP}^{17^\circ} = [K^+] \cdot [C_4H_5O_6{}^-] = 0.000176$$

$$[K^+]_{\max} = \frac{0.000176}{0.006} = 0.0294\ mol/L$$

$$[K^+]_{neu} = [K^+]_{\max} - c_{KC_4H_5O_6} = 0.0294 - 0.00600 = 0.0234\ mol/L$$

$$m_{KHCO_3} = [K^+]_{neu} \cdot M(KHCO_3) = 0.0234 \cdot 100.12 = 2.34\ g$$

4 bp

5.5 Calculate the sum of concentrations of all tartaric acid species in this wine.

$$c_{KC_4H_5O_6} = \frac{2.50 g/L}{188.19 g/mol} = 0.0133 \frac{mol}{L} = [C_4H_5O_6^-]$$

$$K_{A1} = \frac{[C_4H_5O_6^-]\cdot[H_3O^+]}{[C_4H_6O_6]} = 10^{-2.98} \quad \Rightarrow \quad 10^{-2.98} = \frac{0.0133\cdot 10^{-3.1}}{[C_4H_6O_6]}$$

$$\Rightarrow \quad [C_4H_6O_6] = 0.0101\ \mathrm{mol/L}$$

$$K_{A2} = \frac{[C_4H_4O_6^{2-}]\cdot[H_3O^+]}{[C_4H_5O_6^-]} = 10^{-4.34} \quad \Rightarrow \quad 10^{-4.34} = \frac{[C_4H_4O_6^{2-}]\cdot 10^{-3.1}}{0.0133}$$

$$\Rightarrow \quad [C_4H_4O_6^{2-}] = 0.000764\ \mathrm{mol/L}$$

$$c_{\mathrm{total}} = [C_4H_5O_6^-] + [C_4H_6O_6] + [C_4H_4O_6^{2-}] = 0.0241\ mol/L$$

6 bp

5.6 *Calculate the concentrations of all tartaric acid species at this pH without considering precipitation reactions. In case you did not get a result for the total concentration of all tartaric acid species in Problem 5.5, use* $c_{tot} = 0.03\ mol/L$ *for your calculations.*

$c_{\text{tot}} = 0.0241\ mol/L$

$[C_4H_6O_6] = s \qquad [C_4H_5O_6^-] = h \qquad [C_4H_4O_6^{2-}] = t$

$$K_{A1} = \frac{[C_4H_5O_6^-]\cdot[H_3O^+]}{[C_4H_6O_6]} = 10^{-2.98} \quad \Rightarrow \quad 10^{-2.98} = \frac{h\cdot 10^{-3.45}}{s} \quad (1)$$

$$K_{A2} = \frac{[C_4H_4O_6^{2-}]\cdot[H_3O^+]}{[C_4H_5O_6^-]} = 10^{-4.34} \quad \Rightarrow \quad 10^{-4.34} = \frac{t\cdot 10^{-3.45}}{h} \quad (2)$$

$$s + h + t = 0.0241 \quad (3)$$

$$s = h\cdot\frac{10^{-3.45}}{10^{-2.98}} = \text{h}\cdot 0.339$$

$$t = h\cdot\frac{10^{-4.34}}{10^{-3.45}} = h\cdot 0.129$$

h·0.339 + h + h·0.129 =0.0241

h = $[C_4H_5O_6^-]$ = 0.0164 mol/L s = $[C_4H_6O_6]$ = 0.00557 mol/L

t = $[C_4H_4O_6^{2-}]$ = 0.00212 mol/L **8 bp**

5.7 *Now, calculate the mass of solid potassium hydrogen tartrate precipitating after adding potassium hydrogencarbonate in Problem 5.6. For the sake of simplicity, assume that no hydrogentartrate is formed or consumed from other tartaric acid species during this process. Furthermore, assume that all potassium that was initially present in the wine originates from potassium hydrogentartrate.*
Use the solubility product calculated in Problem 5.2. If you did not achieve a result there, use the value $K_{SP}^{17°} = 0.0002$.

$$n_{K_{gesamt}} = 0.0133 mol + \frac{1.5g}{100.12g/mol} = 0.0283\ mol$$

$$K_{SP}^{17°} = 0.000176 = (0.0283 - x)\cdot(0.0164 - x)$$

x = 0.007811

m = 0.007810·188.19 = 1.470 g **5 bp**

Problem 6 **17 bp ≙ 5 rp**

Kinetics

6.1 Determine the order of the reaction regarding the three species. Demonstrate your line of thoughts.

1st order for $[I^-]$; Comparing lines 1 and 2;

2nd order for $[IO_3^-]$; Comparing lines 1 and 3;

2nd order for $[H^+]$; Comparing lines 1 and 4; **2 bp**

6.2 Specify the rate law and calculate the rate constant k.

$v = k\,[I^-]^1\,[IO_3^-]^2\,[H^+]^2 = k\cdot 0.01\cdot(0.1)^2\cdot(0.01)^2 = 0.60$

$k = 0.60/1\cdot 10^{-8} = 6.0\cdot 10^7\ \text{mol}^{-4}\cdot\text{L}^4\cdot\text{s}^{-1}$ **1.5 bp**

6.3 The activation energy of the reaction above at 25°C is E_A=84 kJ·mol^{-1}. Calculate by which factor the reaction rate increases, if one decreases the activation energy (e.g. with a catalyst) by 10 kJ·mol^{-1}.

before: $k_1 = A\cdot e^{-E_{A1}/RT}$; $\ln k_1 = \ln A - E_{AI}/RT$

after: $k_2 = A\cdot e^{-E_{A2}/RT}$; $\ln k_2 = \ln A - E_{A2}/RT$

$\ln (k_2/k_1) = -E_{A2}/RT + E_{A1}/RT = -74000/(8.314\cdot 298) + 84000/(8.314\cdot 298)$

$= -29.87 + 33.90 = 4.03$

$k_2/k_1 = 56.3$

The reaction proceeds 56.3 times faster! **2 bp**

6.4 Show that these assumptions allow you to derive the expression $[ES] = \frac{[E]_{tot}\cdot[S]}{K_M+[S]}$, where the Michaelis-Menten constant is $K_M = \frac{k_{-a}+k_b}{k_a}$.

Because of the steady state in ES one can write:

$$\frac{d[ES]}{dt} = 0 = k_a[E][S] - k_{-a}[ES] - k_b[ES] = 0$$

$$[E_{tot}] = [E] + [ES] \rightarrow [E] = [E_{tot}] - [ES]$$

$$k_a([E_{tot}] - [ES])[S] = (k_{-a} + k_b)[ES]$$

$$[E_{tot}][S]k_a - [ES][S]k_a = (k_{-a} + k_b)[ES]$$

$$[E_{tot}][S]k_a = [ES](k_{-a} + k_b + k_a[S])$$

$$[ES] = \frac{[E_{tot}][S]k_a}{(k_{-a} + k_b + k_a[S])}$$

$$[ES] = \frac{[E_{tot}][S]}{\frac{k_{-a}+k_b}{k_a} + [S]}$$

$$[ES] = \frac{[E_{tot}][S]}{K_M+[S]}$$

4 bp

6.5 Show that the maximum reaction rate is $\left(\frac{d[P]}{dt}\right)_{max} = v_{max} = k_b \cdot [E]_{tot}$.

$$v = \left(\frac{d[P]}{dt}\right) = [ES] \cdot k_b$$

as the maximum case is that all E is present as ES, it follows that [ES]max = [E]tot => $v_{max} = k_b \cdot [E]_{tot}$

1 bp

6.6 Derive the Michaelis-Menten equation $v = \frac{v_{max} \cdot [S]}{K_M + [S]}$ *from 6.4 and 6.5.*

$$v = \left(\frac{d[P]}{dt}\right) = [ES] \cdot k_b$$

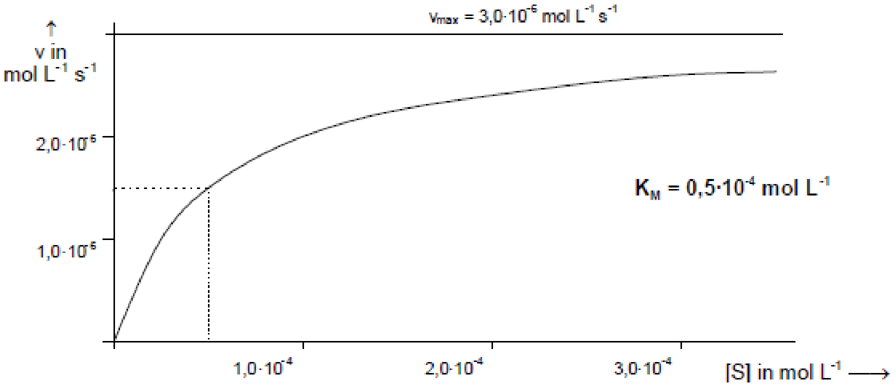
nach 6.4: $[ES] = \frac{[E_{tot}][S]}{K_M + [S]}$ => $v = \frac{k_b [E_{tot}][S]}{K_M + [S]}$

nach 6.5: $v_{max} = k_b \cdot [E]_{tot}$ => $v = \frac{v_{max} \cdot [S]}{K_M + [S]}$ **1.5 bp**

6.7 Read the value for K_M from the curve below showing v = f([S]).

If $v = ½ \cdot v_{max}$ in equation 6.6, it follows that $K_M = [S]$,

Hence one has to read the [S] value corresponding to $v = 1.5 \cdot 10^{-6}$ mol $L^{-1} s^{-1}$.



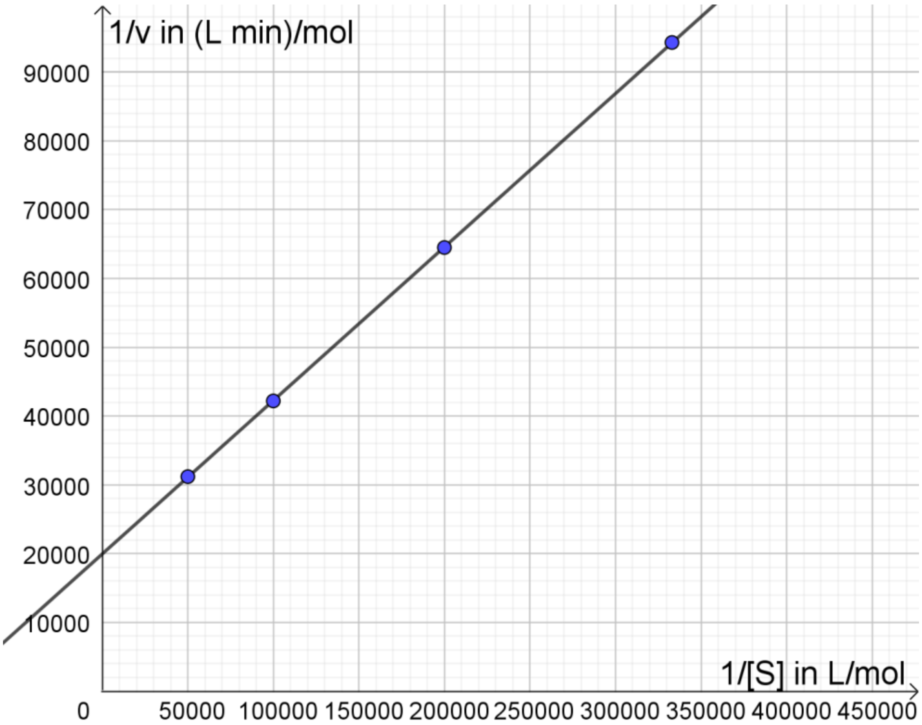
1 bp

6.8 Show that $\frac{1}{v} = \frac{K_M}{v_{max}} \cdot \frac{1}{[S]} + \frac{1}{v_{max}}$.

From eq. 6.6: $v = \frac{v_{max} \cdot [S]}{K_M + [S]}$ => $\frac{1}{v} = \frac{K_M + [S]}{v_{max} \cdot [S]}$ => $\frac{1}{v} = \frac{K_M}{v_{max}} \cdot \frac{1}{[S]} + \frac{1}{v_{max}}$ **0.5 bp**

6.9 Determine the Michaelis constant K_M and the rate constant k_b from the Lineweaver-Burk- plot.

$[S]_0 \cdot 10^{-6}$ in mol L^{-1}	$[S]_0^{-1}$ in mol^{-1} L	$v_0 \cdot 10^{-5}$ in mol $L^{-1} min^{-1}$	v_0^{-1} in mol^{-1} Lmin
3.0	$3.33 \cdot 10^5$	1.06	$9.43 \cdot 10^4$
5.0	$2.00 \cdot 10^5$	1.55	$6.45 \cdot 10^4$
10	$1.00 \cdot 10^5$	2.37	$4.22 \cdot 10^4$
20	$0.50 \cdot 10^5$	3.21	$3.12 \cdot 10^4$



$$\frac{1}{v} = \frac{K_M}{v_{max}} \cdot \frac{1}{[S]} + \frac{1}{v_{max}}$$

Intercept: $\frac{1}{[S]} = 0 \quad => \quad \frac{1}{v_{max}} = 2 \cdot 10^4 mol^{-1} L\ min => v_{\max} = 5 \cdot 10^{-5}$ mol $L^{-1}min^{-1}$

with $[E]_{tot} = 1{,}0 \cdot 10^{-9}$ mol L^{-1} it follows from 6.5 that: $k_b = 5 \cdot 10^4$ min^{-1}

The linear equation yields: $K_M = 1.1 \cdot 10^{-5}$ mol/L

2.5 bp

6.10 Calculate the fraction of enzyme molecules (f_{ES}) that bind substrate.

$$f_{ES} = \frac{v_0}{v_{max}} = \frac{[S]_0}{K_M + [S]_0} = \frac{3 \cdot 10^{-5} mol\ L^{-1}}{1.5 \cdot 10^{-5} mol\ L^{-1} + 3 \cdot 10^{-5} mol\ L^{-1}} = 0.67$$

1 bp

Problem 7 **21 bp ≙ 6 rp**

Evaporating and Cooling

7.1 Calculate the energy necessary to reheat the air in the room to 22°C (at atmospheric pressure).

$\bar{M} = 28.02 \cdot 0.79 + 32.00 \cdot 0.21 = 28.856 gmol^{-1}$; $V = 300m^3$

$n = \frac{pv}{RT} = \frac{101325 Jm^{-3} \cdot 300m^3}{8.314 Jmol^{-1}K^{-1} \cdot 268K} = 13642 mol$ cold air

$m_{air} = 13642 mol \cdot 28.856 gmol^{-1} = 393664 g$

$q = c_p \cdot m \cdot \Delta T = 1.008 \frac{J}{gK} \cdot 393664 g \cdot 27K = 1.071 \cdot 10^7 J = 10.7 MJ$ **3 bp**

7.2 Calculate the number of gas bubbles occurring per second, assuming a mean bubble diameter of 2mm.

$r = 1$mm → $V = \frac{4r^3\pi}{3} = 4.1888 mm^3$; $\rightarrow 0.18 Ls^{-1} = 1.8 \cdot 10^5 mm^3 s^{-1}$

Number of Bubbles $= \frac{1.8 \cdot 10^5 mm^3 s^{-1}}{4.1888 mm^3} = 42972 s^{-1}$ **1.5 bp**

7.3 Tick the correct boxes

When rising through the column, pressure in the gas
☐ increases
X decreases

☐ Work is performed on the bubbles.
X The bubbles perform work.

This work needs to be
X added
☐ subtracted
to/from the heat transferred by the gas to calculate the Enthalpy of Vaporization.

0.5pb each; **1.5 bp**

7.4 Calculate the Enthalpy of Vaporization $\Delta_{vap}H$ determined during the experiment above.

$\Delta_{vap}H = \frac{c_p \Delta T + \Delta p}{\rho_V} = \frac{1204 Jm^{-3}K^{-1} \cdot 32.5K + 4128 Jm^{-3}}{1.030 molm^{-3}} = 42.0\ kJmol^{-1}$ **1.5 bp**

7.5 Use calculation to decide, if air or nitrogen had been used for the experiment.

At p = 1atm = 101325 Pa and T = 21.5°C (294.65K), 1m^3 equals to 41.362 mol

$\frac{1204 Jm^{-3}K^{-1}}{41.362 molm^{-3}} = 29.1088 Jmol^{-3}K^{-1}$

$\frac{29.1088 Jmol^{-1}K^{-1}}{28.02 gmol^{-1}} = 1.039 Jg^{-1}K^{-1}$ or $\frac{29.1088 Jmol^{-1}K^{-1}}{28.865 gmol^{-1}} = 1.008 Jg^{-1}K^{-1}$

This figure corresponds to that of air. Hence air was used. **3.5 bp**

7.6 Calculate the ***vapor pressure of water above the salt solution*** *from the vapor density* ***at*** *temperature T_0.*

$$p = \frac{nRT}{V} = 1.03\frac{mol}{m^3} \cdot 8.314JK^{-1}mol^{-1} \cdot 294.65K = 2523Pa$$ **2 bp**

7.7 Calculate the ***vapor pressure of pure water*** *at T_o and tick the correct boxes.*

$$\Delta_{vap}H° = 2463\frac{J}{g} \cdot 18.02g/mol = 44383Jmol^{-1}$$

$$\ln p_1 = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \ln p_2$$

$$= -\frac{44383Jmol^{-1}}{8.314Jmol^{-1}K^{-1}}\left(\frac{1}{294.65K} - \frac{1}{289.15K}\right) + \ln(1818.8) = 7.8506 => p_1 = 2567Pa$$

X The vapor pressure of water decreases by adding salt. **3 bp**

7.8 Calculate the cooling power of the setup at this flow rate, i.e. at 150m³/h.

$$\frac{E}{V} = c_p\Delta T + \Delta p = 39130 + 4128 = 43258Jm^{-3}$$

$$P_{cool} = \frac{43258Jm^{-3} \cdot 150m^3h^{-1}}{3600sh^{-1}} = 1802.4\,W$$ **2.5 bp**

7.9 Calculate the mechanical power of the air blower.

$$P = 150m^3 \cdot (3600s)^{-1} \cdot 262mbar \cdot 100Jm^{-3}mbar^{-1} = 1092\,W$$ **1 bp**

7.10 Calculate the net cooling power of the setup (air blower + bubble evaporator).

2200 – 1092 = 1108 W generation of heat

Netto = Cooling – Heating = 1802 – 1108 = 694 W net cooling power. **1.5 bp**