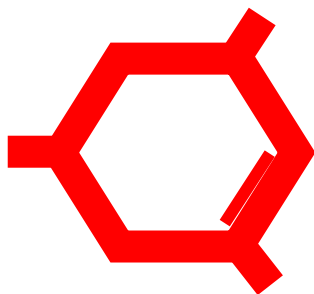


42nd Austrian Chemistry Olympiad

National Competition



SOLUTIONS

Theoretical Competition

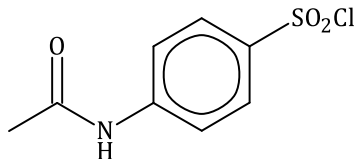
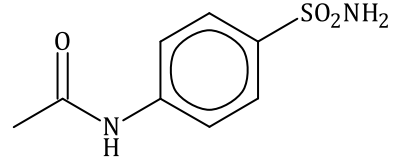
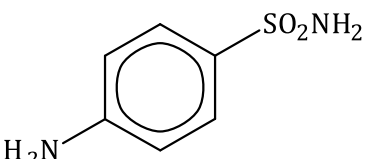
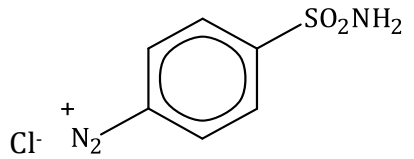
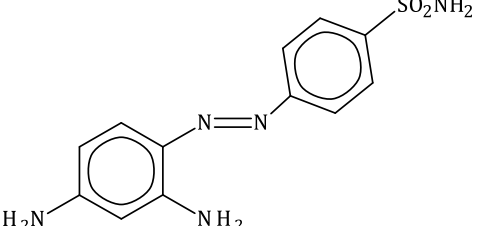
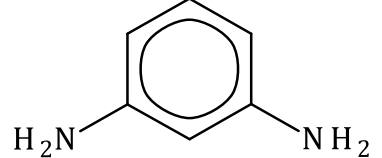
Task 1

11
41.5

41.5 bp $\triangleq$ 11 rp; $f =$

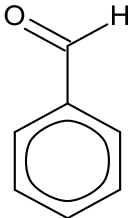
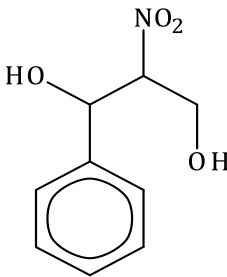
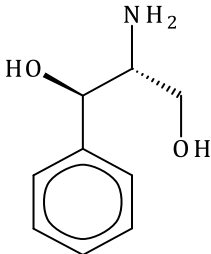
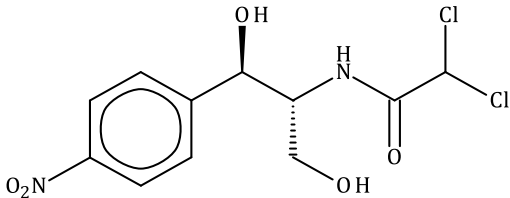
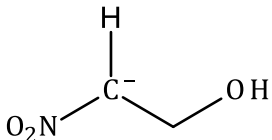
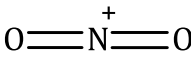
Some antibiotics

A. Prontosil

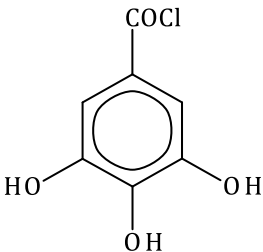
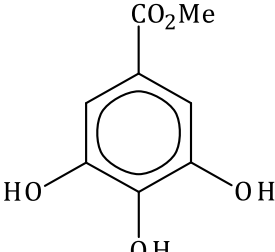
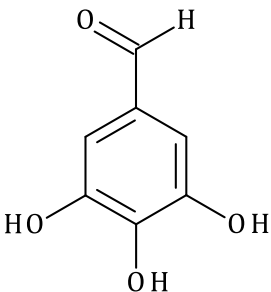
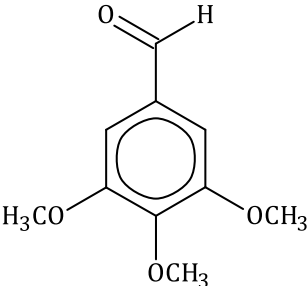
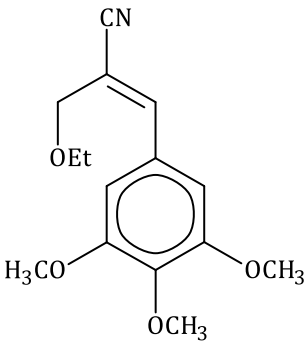
1.1. Draw the constitutional formulae of the compounds <i>B</i> , <i>C</i> , <i>D</i> , <i>E</i> , <i>F</i> and benzene-1,3-diamine.	
<i>B</i>  2bp	<i>C</i>  1.5bp
<i>D</i>  1.5bp	<i>E</i>  2bp
<i>F</i>  2bp	benzene-1,3-diamine  0.5bp

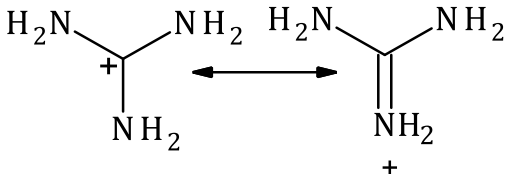
1.2. Why is the step <i>E</i> → <i>F</i> impossible when benzene is used instead of benzene-1,3-diamine?	
verbal justification: diazonium ion is a weak electrophile, benzenediamine is more reactive than benzene, caused by the +M-effect of the amino groups of benzenediamine; 1.5bp	
1.3. What type of stereoisomerism can occur in <i>F</i> ?	
diastereomerism	1bp

B. Chloramphenicol

1.4. Draw the constitutional formulae of the compounds A and B and the configurational formulae of C and E .	
A  0.5bp	B  2bp
C  2bp	E  2bp
1.5. Draw the structural formulae of the reactive species in the reaction A → B and D → E and name the respective reaction mechanism of each.	
A→B  1.5bp 1bp reaction mechanism: A_N	D→E  1.5bp 1bp reaction mechanism: S_E
1.6. Name substance C according to IUPAC.	
(2R, 3R) - 2-amino-3-phenylpropane-1,3-diol 1.5bp	

C. Trimethoprim

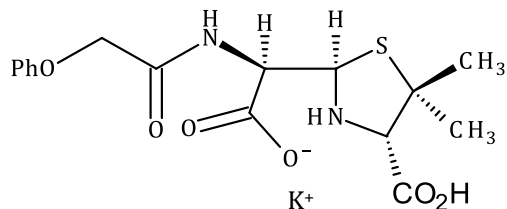
1.7. Draw the constitutional formulae of the compounds B , C , D and E and write down the molecular formula of X .	
A  1.5bp	B  1bp
C  2bp	D  1.5bp
E  2 bp	X CH₃OH 0.5 bp

1.8. Which effect in protonated guanidine is responsible for this? Draw at least two structural formulae in order to show this.	
<i>mesomeric effect</i> 0.5 bp <i>structural formulae:</i> 1.5bp	 etc.

D. Penicillin V

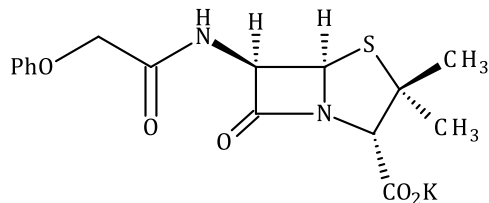
1.9. Draw the configurational formulae of the compounds **A** and **B**.

A



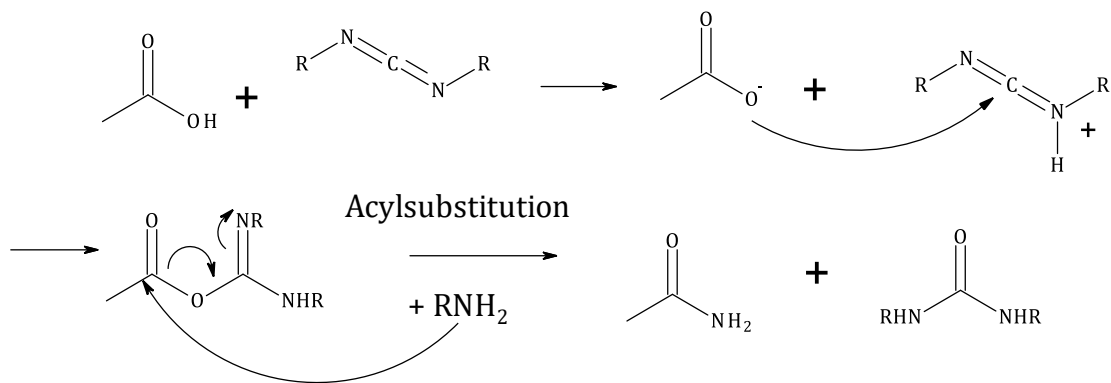
1 bp

B



2bp

1.10. Write the mechanism of the reaction **A**→**B** with structural formulae and „arrows“ for the attacking species. Draw only the parts of the molecules that are involved in this step. For all other parts write „R“ for rest in the usual way.



2.5bp

1.11. Write down the name of the functional group that is formed in reaction **A**→**B**.

lactam

0.5bp

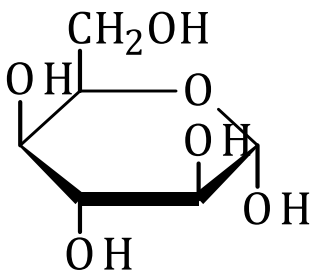
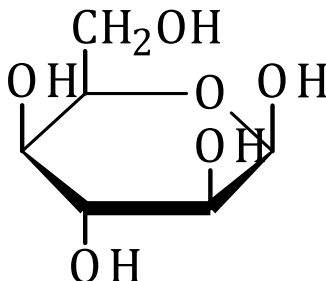
Task 2

$$16 \text{ bp} \triangleq 4 \text{ rp}; f = \frac{4}{16}$$

Birch sugar

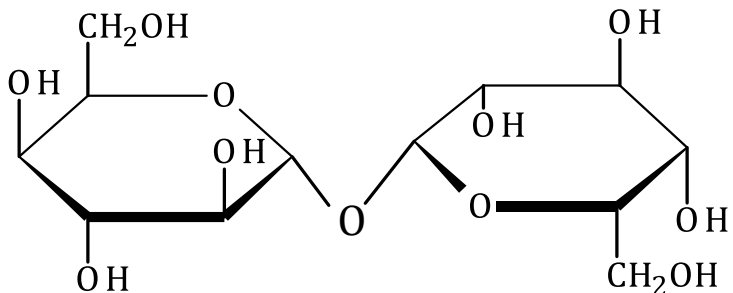
2.1. Draw the structural formulae of <i>A – F</i> in Fischer projection.	
A <pre> CHO H ——— ——— OH HO ——— ——— H H ——— ——— OH CH₂OH </pre> 1bp	B <pre> CH₂OH H ——— ——— OH HO ——— ——— H H ——— ——— OH CH₂OH </pre> 1.5bp
C <pre> CN H ——— ——— OH H ——— ——— OH HO ——— ——— H H ——— ——— OH CH₂OH </pre> 1bp	D <pre> CN HO ——— ——— H H ——— ——— OH HO ——— ——— H H ——— ——— OH CH₂OH </pre> 1bp
E <pre> CHO H ——— ——— OH H ——— ——— OH HO ——— ——— H H ——— ——— OH CH₂OH </pre> 1bp	F <pre> CHO HO ——— ——— H H ——— ——— OH HO ——— ——— H H ——— ——— OH CH₂OH </pre> 2bp

2.2. Draw the two formed pyranose sugars F_1 and F_2 in the Haworth projection and name both monosaccharides.

F_1  α-D-idopyranose 1.5bp	F_2  β-D-idopyranose 1.5bp
---	---

2.3. Name the special isomeric relationship between F_1 and F_2 .	
epimers / anomers	1bp

2.4. Draw the structural formula of the disaccharide in the Haworth projection that is formed through the combination of F_1 and F_2 . This substance shows a negative reaction with Fehling's solution.

 2.5bp

2.5. How many stereoisomers exist for B ?	
4 (32)	2bp

Task 3

33 bp $\triangleq$ 9 rp; $f =$

$\frac{9}{33}$

A journey through the world of metals

3.1. Determine which metal the mentioned metal *Y* is and provide your calculation below.

Supposing 100g:

$$69.75\text{g O} \quad n = m/M = 4.359 \text{ mol}$$

$$30.25\text{g Y} \quad 1:1 \Rightarrow n = 4.359 \text{ mol}$$

$$M(\text{Y}) = 30.25/4.359 = 6.94 \text{ g}\cdot\text{mol}^{-1} \Rightarrow \text{Li}$$

2bp

3.2. Write down the exact total formula of substance *Z*.



1bp

3.3. Calculate into which cubic lattice the metal *Y* crystallises.

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

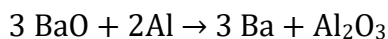
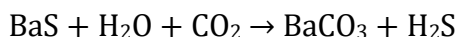
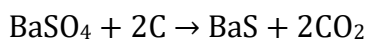
$$\text{Atoms/EC} = \frac{\rho \cdot N_A \cdot a^3}{M}$$

$$\text{Atoms/EC} = 2$$

$\Rightarrow$ cubic body centred

3bp

3.4. Write down balanced reaction equations for the four discussed processes. 1 bp each

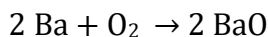
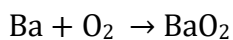


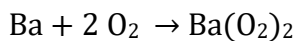
3.5. Specify the coordination numbers of the metal and oxide ions in the crystal structure.

CN = 6 for both

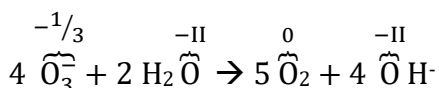
1bp

3.6. Write down balanced reaction equations for the formation of the three metal oxides from their elements. 0.5 bp each





3.7. Write down the balanced reaction equation for the reaction of the ozonide ions with water. Assign oxidation states to all atoms.



1,5bp for ON

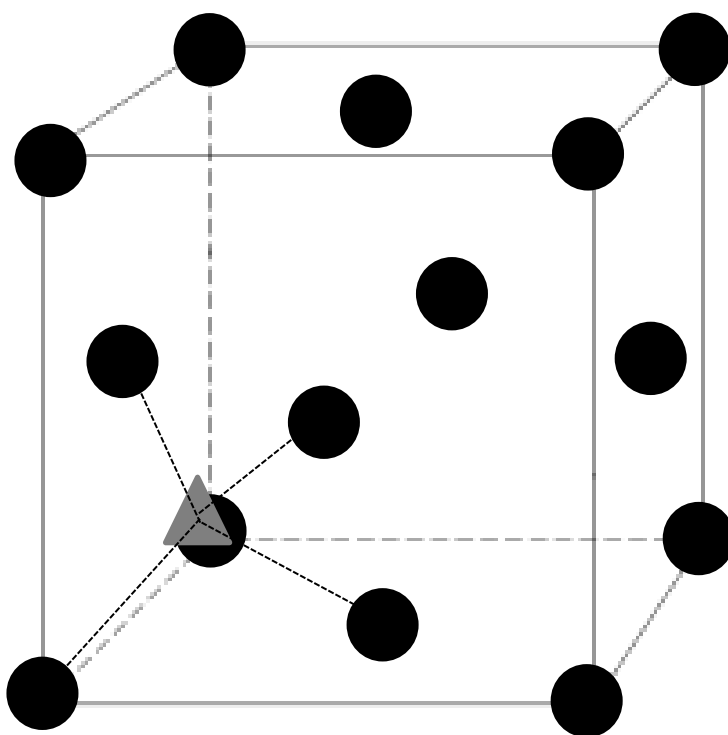
4bp for RE

3.8. Calculate the amount of hydrogen in Mg_2NiH_4 in percent by mass.

$$\text{mass content} = (4 \cdot 1.01) / (2 \cdot 24.31 + 58.69 + 4 \cdot 1.01) = 0.03628 = 3.628 \%$$

1bp

3.9. Draw all nickel atoms (without H atoms) as coloured balls, and one magnesium ion, which you can choose freely, as a triangle into the given unit cell. Indicate the tetrahedron for the chosen magnesium ion with dashed lines.



4bp

3.10. How many tetrahedron gaps and how many octahedron gaps are there per unit cell?

tetrahedron gaps: 8

1bp

octahedron gaps: 4

1bp

3.11. Write down the amount of formula units of Mg_2NiH_4 in one unit cell.

$$8 \cdot \frac{1}{8} + 6 \cdot \frac{1}{2} = 4$$

1bp

3.12. Calculate the lattice parameter a_0 of the unit cell.

$$n \cdot \lambda = 2d \cdot \sin \theta$$

$$\text{with } n = 1, \lambda = 1.542 \text{ \AA}, \theta = 11.92^\circ$$

$$d = \frac{1 \cdot 1.542 \cdot 10^{-10}}{2 \cdot \sin(11.92^\circ)} = 3.733 \cdot 10^{-10} \text{ m}$$

d is the distance between the planes, $3d$ the length of the body diagonal in the cell

$$a \cdot \sqrt{3} = 3d$$

$$a = \frac{3 \cdot 3.733 \cdot 10^{-10}}{\sqrt{3}} \text{ m} = 6.465 \cdot 10^{-10} \text{ m}$$

4bp

3.13. Calculate the density of Mg_2NiH_4 powder in g/cm^3 .

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

$$\rho = \frac{4 \cdot 111.34 \text{ g} \cdot \text{mol}^{-1}}{6.022 \cdot 10^{23} \text{ mol}^{-1} \cdot (6.465 \cdot 10^{-8} \text{ cm})^3}$$

$$\rho = 2.737 \text{ g} \cdot \text{cm}^{-3}$$

3 bp

Task 4

24 bp $\triangleq$ 6 rp; $f = \frac{6}{24}$

Something „Gschmackig's“ (= tasty) from Tyrol

A. The „Tiroler Zelten“

4.1. Calculate the exact total formula of substance **W**.

$$m(\text{C}) = 70.56 \text{ g} \rightarrow n(\text{C}) = 5.875 \text{ mol}$$

$$m(\text{H}) = 5.93 \text{ g} \rightarrow n(\text{H}) = 5.871 \text{ mol}$$

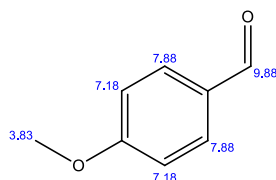
$$m(\text{O}) = 23.51 \text{ g} \rightarrow n(\text{O}) = 1.469 \text{ mol}$$

$$\rightarrow \text{empirical formula: } \text{C}_4\text{H}_4\text{O}$$

$$\text{MS} \rightarrow \text{total formula: } \text{C}_8\text{H}_8\text{O}_2$$

2bp

4.2. Draw the exact structural formula of substance **W**.



2bp

4.3. Calculate the exact total formula of substance **X**.

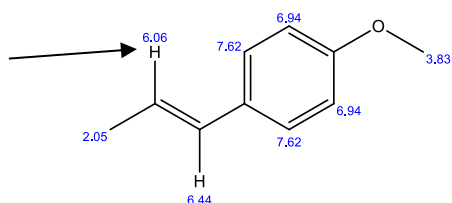
$$m(\text{C}) = 2.4020 \text{ g} \rightarrow 81.03\% \text{ C} \rightarrow n(\text{C}) = 6.7468 \text{ mol}$$

$$m(\text{H}) = 0.2424 \text{ g} \rightarrow 8.17\% \text{ H} \rightarrow n(\text{H}) = 8.0891 \text{ mol}$$

$m(O) = 0.3200\text{g} \rightarrow 10.80\% O \rightarrow n(O) = 0.6750\text{ mol}$
 $\rightarrow$ total formula: $C_{10}H_{12}O$

3bp

4.4. Draw the structural formula of substance **X** and mark which H atom is responsible for the signal at 6.06 ppm with an arrow.



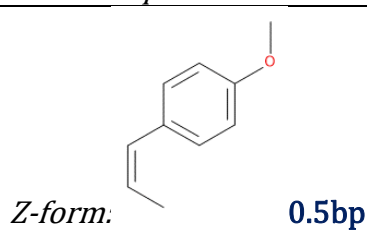
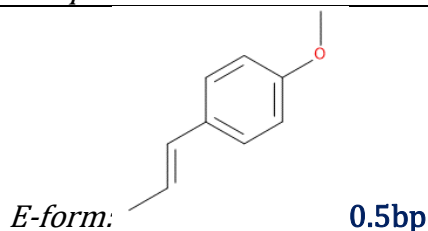
2.5bp

4.5. Write down the IUPAC name of substance **X** without stereo descriptors.

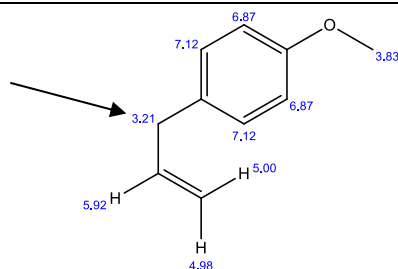
1-methoxy-4-(prop-1-en-1-yl)-benzene

2bp

4.6. Denote the both configurations of **X** by drawing their structural formulae in the boxes provided below and indicate eventual stereo descriptors.



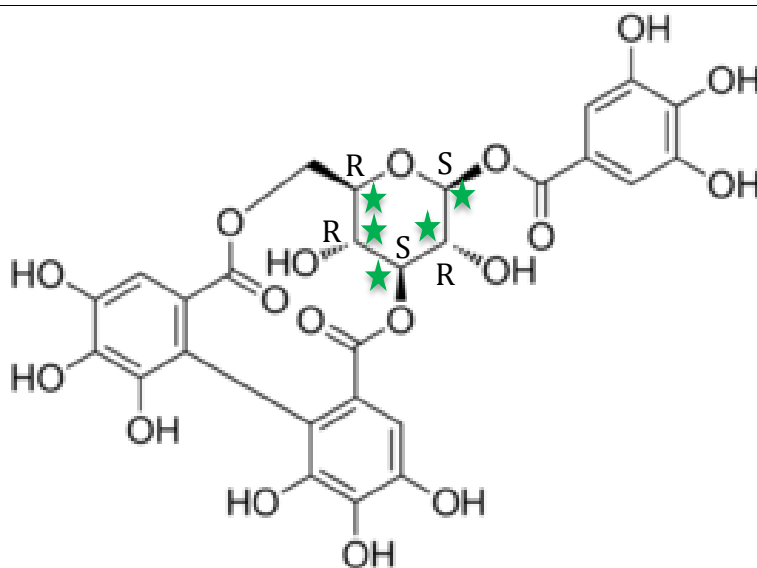
4.7. Draw the structural formula of estragole and mark which H atom(s) are responsible for the signal at 3.21 ppm.



2.5bp

B. A mug of mulled wine

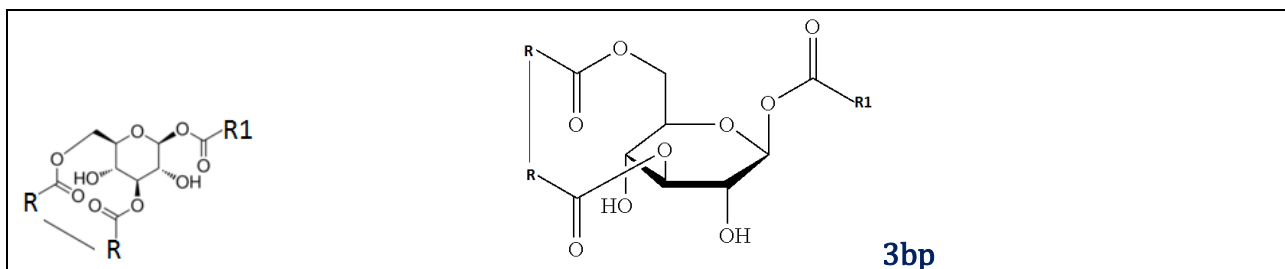
4.8. Mark all chiral centres with an asterisk (*) in the corilagin molecule depicted below and precisely indicate their absolute configuration by labelling the atoms with their stereo descriptors.



marking **1bp**
configuration: **5bp**

picture: corilagin

4.9. Provide a drawing of the heterocyclic compound of corilagin in the Haworth projection. Simplify the structure as depicted below.



Task 5

35 bp $\triangleq$ 10 rp; f =

$\frac{10}{35}$

Little A to G of Nickel Complexes

5.1. Hereunder some names of complexes are given. If you find some of the ones specified above, fill in the corresponding letter. (Note: Whereas there will be no negative marks for this part of the task in total, wrong answers will lead to deduction of points.)

hexaamminenickel(III) ____	hexaaquanickel(II) C
hexaethyldiaminonickel(II) ____	hexanitratonickel(II) ____
diamminetetraaquanickel(II) D	tetraaquaethyldiaminonickel(II) E
tetracarbonylnickel(II) ____	tetracarbonylnickel(0) G

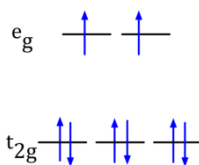
every correct assignment +0.5bp, wrong assignments – 0.5 bp, min 0 bp

5.2. Write down the complete electron configuration of the central atom in these complexes.

Ni^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$

1bp

5.3. Draw a diagram showing the splitting of the d-orbitals of Ni in the octahedral complex. Decide which magnetic properties you expect.



X paramagnetic

O diamagnetic

2bp
0.5bp

5.4. Fill in the missing values for Δ_o . Into the first row write the letter (A, B, C) for the corresponding complex.

complex	C	A	B
Δ_o/cm^{-1}	8500	10800	13000
Δ_o/eV	1.05	1.34	1.61
$\Delta_o/\text{kJ mol}^{-1}$	101.68	129.20	155.51

assignment of complexes first row 1.5 bp, energy values 1bp each

5.5. Calculate the ligand field stabilization energy for the complex with $\Delta_o = 10800 \text{ cm}^{-1}$ in eV.

$$\text{LFSE} = 6 \cdot 0.4 \Delta_o - 2 \cdot 0.6 \Delta_o = 1.2 \Delta_o = 1.2 \cdot 1.34 = 1.61 \text{ eV}$$

2bp

5.6. In this calculation you did not have to consider the pairing energy P because ... (tick right answer/s)

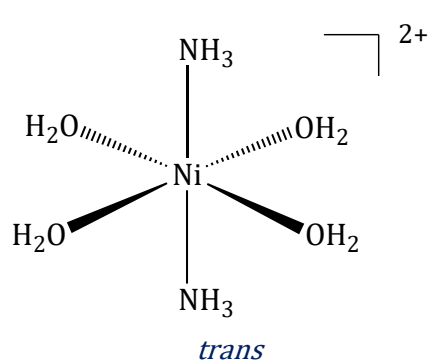
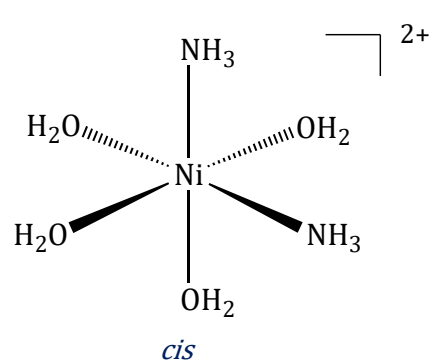
- ☐ ... it is only an approximation, P is negligible.
☐ ... you only have to consider P in orbitals that lie higher in energy as the others.
☒ ... the Ni central atom in the spherical ligand field has the same number of paired spins.
☐ Not true at all. One has to consider P and I did that.

0.5bp

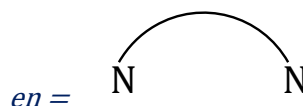
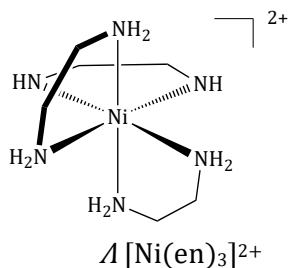
5.7. Tick the right answers a) which complex is thermodynamically more stable. b) the name of the effect causing this stability.			
a)	0 complex D $[\text{Ni}(\text{NH}_3)_2(\text{OH}_2)_4]^{2+}$	X complex E $[\text{Ni}(\text{en})(\text{OH}_2)_4]^{2+}$	0.5bp
b)	0 inert-pair-effect 0 resonance	X chelate effect 0 trans effect	0.5bp

5.8. Calculate the reaction entropies $\Delta_R S^\circ$ for (1) and (2).			
for reaction (1)			
	$\Delta_R G^\circ = -RT \ln K_c = -8.314 \cdot 298 \cdot 11.6 = -28740 \text{ J}$		0.5bp
	$\Delta_R S^\circ = \frac{\Delta_R H^\circ - \Delta_R G^\circ}{T} = \frac{-33500 + 28740}{298} = -15.97 \text{ J K}^{-1}$		1.5bp
for reaction (2)			
	$\Delta_R G^\circ = -RT \ln K_c = -8.314 \cdot 298 \cdot 17.78 = -44051 \text{ J}$		0.5bp
	$\Delta_R S^\circ = \frac{\Delta_R H^\circ - \Delta_R G^\circ}{T} = \frac{-37200 + 44051}{298} = 22.99 \text{ J K}^{-1}$		1.5bp

5.9. For reaction (3) calculate $\Delta_R H^\circ$, $\Delta_R S^\circ$ and $\Delta_R G^\circ$.			
reactions: (3) = (2) - (1)			1.5bp
	$\Delta_R H^\circ_{(3)} = \Delta_R H^\circ_{(2)} - \Delta_R H^\circ_{(1)} = -37.2 + 33.5 = -3.7 \text{ kJ}$		1bp
	$\Delta_R G^\circ_{(3)} = \Delta_R G^\circ_{(2)} - \Delta_R G^\circ_{(1)} = -44.05 + 28.74 = -15.31 \text{ kJ}$		1bp
	$\Delta_R S^\circ_{(3)} = \Delta_R S^\circ_{(2)} - \Delta_R S^\circ_{(1)} = 22.99 + 15.97 = 38.96 \text{ J K}^{-1}$		1bp

5.10. Complex D $[\text{Ni}(\text{NH}_3)_2(\text{OH}_2)_4]^{2+}$ has two stereo isomers. Draw them using the octahedral skeletons. Assign the appropriate stereodescriptors.			
 <i>trans</i>  <i>cis</i>			
			1.5bp each 0.5bp each

5.11. Draw the Λ -isomer of complex **F** $[\text{Ni}(\text{en})_3]^{2+}$ using the skeleton. Draw en in the way shown below.



3bp

5.12. In the VB-scheme for complex **G** ...

- a) draw the electrons (electron pairs) of the Ni central atom with $\uparrow$ and $\uparrow\downarrow$ respectively 1.5bp
b) mark the orbitals occupied by electron pairs from the ligands with an X. 0.5bp

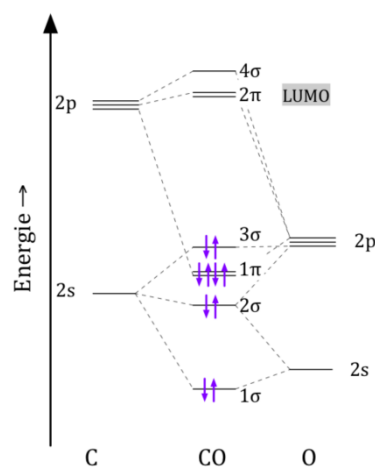
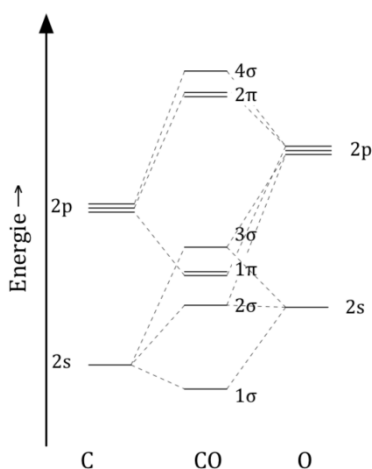
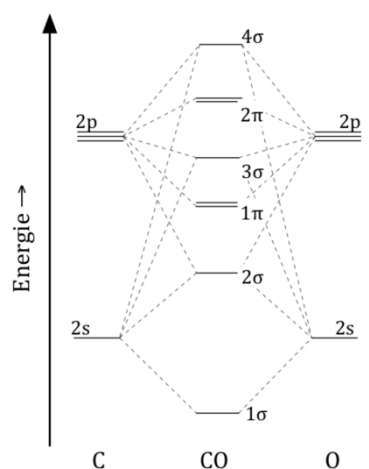
3d					4s	4p				4d				
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	X	X	X	X						

5.13. Denote the hybridization of the Ni central atom in complex **G** and choose the geometrical shape resulting of this hybridization.

hybrid: sp^3 shape: ☐ octahedral ☒ tetrahedral
☐ square planar ☐ trigonal prismatic

1bp

5.14. One of the following MO-schemes shows the energies for the molecular orbitals of CO in correct sequence. Choose the right scheme by correctly „occupying“ it with electrons (arrows) and indicating the LUMO.



Task 6

18 bp $\triangleq$ 5 rp; f =

$\frac{5}{18}$

Bombastic Calorimetry

6.1. Give a balanced equation for the combustion including the symbols for the states of matter.		
$\text{C}_8\text{H}_{18}(\text{l}) + 10 \text{O}_{2(\text{g})} \rightarrow 8 \text{CO}_{2(\text{g})} + 4 \text{H}_2\text{O}(\text{l})$		1bp
6.2. Calculate the molar standard enthalpies of combustion $\Delta_c H^\circ$ of A and B.		
for compound A $M(\text{C}_8\text{H}_8) = 104.16 \text{ g mol}^{-1}$ $0.7834 \text{ g} \triangleq 0.007521 \text{ mol}$		
$\Delta U = Q - Q_{\text{wire}} = -34181 - (-30) = 34151 \text{ J}$		0.5bp
$\Delta U^\circ = \frac{-34.151 \text{ kJ}}{0.007521 \text{ mol}} = -4541 \text{ kJ mol}^{-1}$		1bp
$\Delta_c H^\circ = \Delta_c U^\circ + p\Delta V = \Delta_c U^\circ + \Delta nRT = -4541 + \frac{-2 \cdot 8.314 \cdot 298}{1000} = -4546 \text{ kJ mol}^{-1}$		2bp
for compound B $0.6548 \text{ g} \triangleq 0.006286 \text{ mol}$		
$\Delta U = Q - Q_{\text{wire}} = -27623 + 30 = 27593 \text{ J}$		0.5bp
$\Delta U^\circ = \frac{-27.593 \text{ kJ}}{0.006286 \text{ mol}} = -4390 \text{ kJ mol}^{-1}$		1bp
$\Delta_c H^\circ = \Delta_c U^\circ + p\Delta V = \Delta_c U^\circ + \Delta nRT = -4390 + \frac{-2 \cdot 8.314 \cdot 298}{1000} = -4395 \text{ kJ mol}^{-1}$		2bp
6.3. Calculate the molar standard enthalpies of formation $\Delta_f H^\circ$ of A and B. In case you did not get a result in 6.2. use $\Delta_c H^\circ_A = -4581 \text{ kJ mol}^{-1}$ and $\Delta_c H^\circ_B = -4431 \text{ kJ mol}^{-1}$.		
für Verbindung A		
$\Delta_c H^\circ(\text{A}) = 8 \cdot \Delta_f H^\circ(\text{CO}_2) + 4 \cdot \Delta_f H^\circ(\text{H}_2\text{O}(\text{l})) - \Delta_f H^\circ(\text{A})$		
$\Delta_f H^\circ(\text{A}) = 8 \cdot \Delta_f H^\circ(\text{CO}_2) + 4 \cdot \Delta_f H^\circ(\text{H}_2\text{O}(\text{l})) - \Delta_c H^\circ(\text{A}) =$		
$= 8 \cdot (-393.5) - 4 \cdot (285.8) + 4546 = 254.8 \text{ kJ mol}^{-1} \quad (289.8 \text{ kJ mol}^{-1})$		1.5bp
für Verbindung B		
$\Delta_f H^\circ(\text{B}) = 8 \cdot \Delta_f H^\circ(\text{CO}_2) + 4 \cdot \Delta_f H^\circ(\text{H}_2\text{O}(\text{l})) - \Delta_c H^\circ(\text{B}) =$		
$= 8 \cdot (-393.5) - 4 \cdot (285.8) + 4546 = 103.8 \text{ kJ mol}^{-1} \quad (139.8 \text{ kJ mol}^{-1})$		1.5bp
6.4. According to the standard enthalpies of formation, one of the substances should be more stable with regard to dissociation in the elements than the other. This is... (tick the right circle!).		
☐ compound A	☒ compound B	1bp
6.5. According to Hückel's rule one compound is aromatic. Into the brackets write the number of π -Elektrons of the ring systems and mark the aromatic compound.		
☐ Cyclooctatetraene (8)	☒ styrene (6)	1.5bp
6.6. Assign which compound was which sample by correctly filling in A or B respectively.		

A was cyclooctatetraene

B was styrene

0.5bp

6.7. For styrene calculate the standard enthalpy of combustion according to the incremental system.

$$\begin{aligned}\Delta_c H^\circ &= 8 \cdot \Delta_c H_f^\circ(\text{C-H}) + 4 \cdot \Delta_c H_f^\circ(\text{C-C}) + 3 \cdot \Delta_c H_f^\circ(\text{C}=\text{C}_{2\text{C}}) + \Delta_c H_f^\circ(\text{C}=\text{C}_{3\text{C}}) + \Delta_c H_f^\circ(\text{Ring}) + \Delta_{\text{vap}} H^\circ = \\ &= 8 \cdot (-226.1) - 4 \cdot (206.4) - 3 \cdot (491.5) - 484.4 - 4.2 + 43.5 = \\ &= -4554 \text{ kJ}\end{aligned}$$

3bp

6.8. For both hydrocarbons calculate the stabilization energy through a comparison between the calculated and the measured enthalpies of combustion.

for cyclooctatetraene

$$\Delta E = \Delta_c H^\circ_{\text{theor}} - \Delta_c H^\circ = -4561.5 + 4546 = -15.5 \text{ kJ} \quad (19.5 \text{ kJ})$$

(opposite sign accepted likewise)

0.5bp

for styrene

$$\Delta E = \Delta_c H^\circ_{\text{theor}} - \Delta_c H^\circ = -4554 + 4395 = -159 \text{ kJ} \quad (-123 \text{ kJ})$$

(opposite sign accepted likewise)

0.5bp

Task 7

26 bp $\triangleq$ 7 rp; $f = \frac{7}{26}$

A kinetic mixture

A. Nitrogen oxides

7.1. Put a cross into the box where the factor of the change in rate matches the concentration change.

Change of concentration	The rate changes with the factor								
	1	2	4	8	16	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$
[O ₂] quadrupled, [NO] unchanged			×						
[O ₂] unchanged, [NO] quadrupled					×				
[O ₂] unchanged, [NO] halved							×		
[O ₂] halved, [NO] quadrupled				×					
[O ₂] quadrupled, [NO] halved	×								

Lines 1 -3: 0.5 bp each; Lines 4 and 5: 1 bp each

7.2. Calculate the activation energy of the reaction.

All initial concentrations are halved $\Rightarrow \frac{1}{8}$ of the former rate 1.5bp
 $\Rightarrow k(T_2):k(T_1) = 8:1$

$$\ln \frac{k(T_2)}{k(T_1)} = \frac{E_A}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \Rightarrow R \cdot \ln 8 \cdot \left(\frac{1}{733} - \frac{1}{873} \right) = E_A \Rightarrow E_A = 79.0 \text{ kJ}$$

1bp

B. The iodination of acetone

7.3. Calculate the amount of acetone in 1.00 L (= „concentration of Ac“).

$$M(\text{Ac}) = 58.09 \text{ g} \cdot \text{mol}^{-1}; 1 \text{ L has } 790 \text{ g} \Rightarrow c(\text{Ac}) = 13.6 \text{ mol} \cdot \text{L}^{-1}$$

1.5bp

7.4. Fill the missing values into the table, calculate the individual initial concentrations and the reaction rates of the four experiments.

Try	$c(\text{H}_3\text{O}^+) \text{ mol} \cdot \text{L}^{-1}$	$c(\text{I}_2) \text{ mol} \cdot \text{L}^{-1}$	$c(\text{acetone}) \text{ mol} \cdot \text{L}^{-1}$	$v \text{ in } \text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
1	0.784	$1.515 \cdot 10^{-3}$	1.36	$3.86 \cdot 10^{-5}$
2	0.392	$1.515 \cdot 10^{-3}$	1.36	$1.89 \cdot 10^{-5}$
3	0.784	$1.010 \cdot 10^{-3}$	1.36	$3.89 \cdot 10^{-5}$
4	0.784	$1.515 \cdot 10^{-3}$	1.02	$2.86 \cdot 10^{-5}$

For each (different concentration): 0.25bp; for each v : 0.5bp

7.5. Write down an equation for the differential reaction rate of the iodination of acetone using the right integer reaction orders.

$$v = k \cdot [\text{Ac}] \cdot [\text{H}_3\text{O}^+]$$

2bp

7.6. Calculate a mean value of the rate constant with the right units.

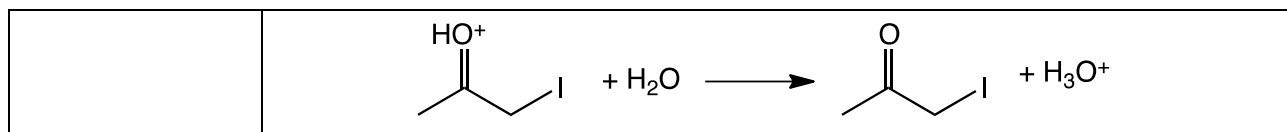
$$\left. \begin{array}{l} k = 3.38 \cdot 10^{-5} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \\ k = 3.55 \cdot 10^{-5} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \\ k = 3.64 \cdot 10^{-5} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \\ k = 3.57 \cdot 10^{-5} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \end{array} \right\} \Rightarrow k = 3.54 \cdot 10^{-5} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

2bp

7.7. Put a cross (crosses) left of the reaction equation which corresponds to a possible RDS which matches the differential rate law.

2bp

X	$\text{CH}_3\text{COCH}_3 + \text{H}_3\text{O}^+ \longrightarrow \text{CH}_3\text{C}(\text{OH})^+\text{CH}_3 + \text{H}_2\text{O}$
	$\text{CH}_3\text{C}(\text{OH})\text{CH}_3 + \text{I}_3^- \longrightarrow \text{CH}_3\text{C}(\text{OH})\text{CH}_2\text{I} + 2 \text{I}^-$
X	$\text{CH}_3\text{C}(\text{OH})^+\text{CH}_3 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{C}(\text{OH})\text{CH}_3 + \text{H}_3\text{O}^+$



C. The Rice-Herzfeld-Mechanism

7.8. Write down a balanced equation for the pyrolysis reaction.	
$\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$	0.5bp

7.9. Write the formulae for the unstable particles of the propagation reactions into the two boxes.			
$\bullet\text{CH}_3$	1bp	$\text{CH}_3\text{CO}\bullet$	1bp

7.10. Give a proof for the differential rate law given above, assuming a steady state mechanism for the unstable particles of the propagation reactions.	
$\frac{d[\text{CH}_4]}{dt} = k_b \cdot [\text{CH}_3\text{CHO}] \cdot [\bullet\text{CH}_3]$	1bp
$\frac{d[\bullet\text{CH}_3]}{dt} = 0 = k_a \cdot [\text{CH}_3\text{CHO}] - k_b \cdot [\text{CH}_3\text{CHO}] \cdot [\bullet\text{CH}_3] + k_c \cdot [\text{CH}_3\text{CO}\bullet] - k_d \cdot [\bullet\text{CH}_3]^2$	1bp
$\frac{d[\text{CH}_3\text{CO}\bullet]}{dt} = 0 = k_b \cdot [\text{CH}_3\text{CHO}] \cdot [\bullet\text{CH}_3] - k_c \cdot [\text{CH}_3\text{CO}\bullet]$	1bp
Adding the last two equations: $0 = k_a \cdot [\text{CH}_3\text{CHO}] - k_d \cdot [\bullet\text{CH}_3]^2$	1.5bp
$[\bullet\text{CH}_3] = \left(\frac{k_a}{k_d} \cdot [\text{CH}_3\text{CHO}]\right)^{\frac{1}{2}}$ using the first equation leads to:	
$\frac{d[\text{CH}_4]}{dt} = k_b \cdot [\text{CH}_3\text{CHO}] \cdot \left(\frac{k_a}{k_d} \cdot [\text{CH}_3\text{CHO}]\right)^{\frac{1}{2}} = k_b \cdot \left(\frac{k_a}{k_d}\right)^{\frac{1}{2}} \cdot [\text{CH}_3\text{CHO}]^{\frac{3}{2}}$ q.e.d.	1bp

7.11. Write down a relation between k_{EXP} and the rate constants of the elemental steps.	
$k_{\text{EXP}} = k_b \cdot \left(\frac{k_a}{k_d}\right)^{\frac{1}{2}}$	1bp

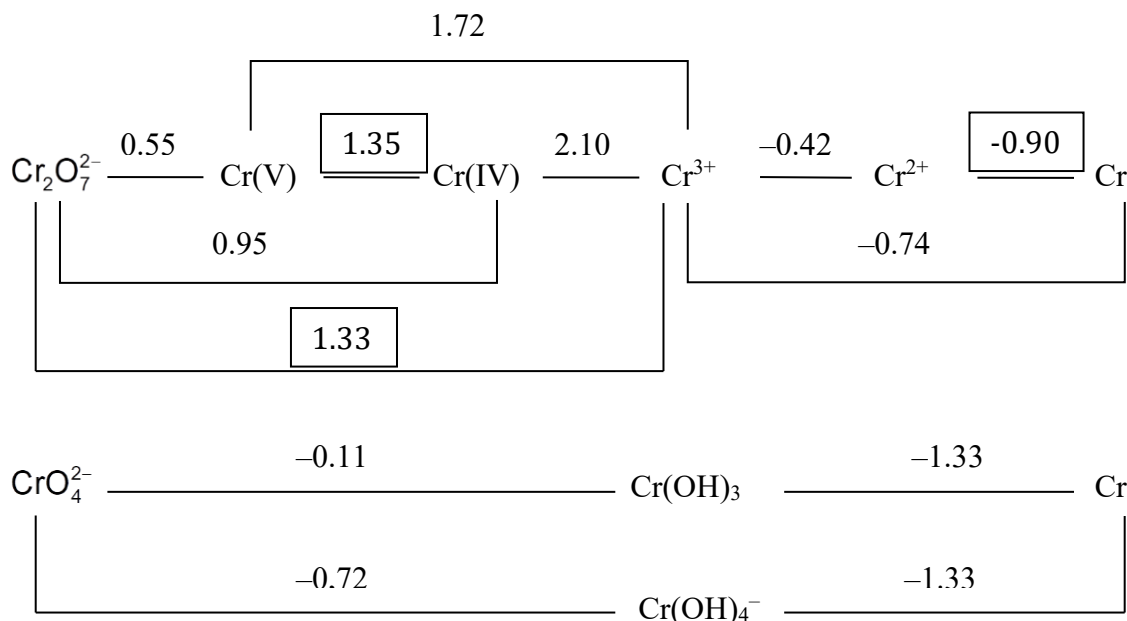
Task 8

$\frac{8}{31}$

31 bp $\triangleq$ 8 rp; $f =$

Another journey: electro chemistry and equilibrium

A. Another metal: Chromium



8.1. Calculate the three missing E^0 -values and write the respective results on the corresponding lines.

$$E^0(\{Cr(V)|Cr(IV)\}) = \frac{2 \cdot 0.95 - 0.55}{1} = 1.35 \text{ V}$$

$$E^0(\{Cr(II)|Cr(0)\}) = \frac{-3 \cdot 0.74 - (-0.42)}{2} = -0.90 \text{ V}$$

$$E^0(\{Cr(VI)|Cr(III)\}) = \frac{2 \cdot 0.95 + 2.10}{3} = 1.33 \text{ V}$$

3bp

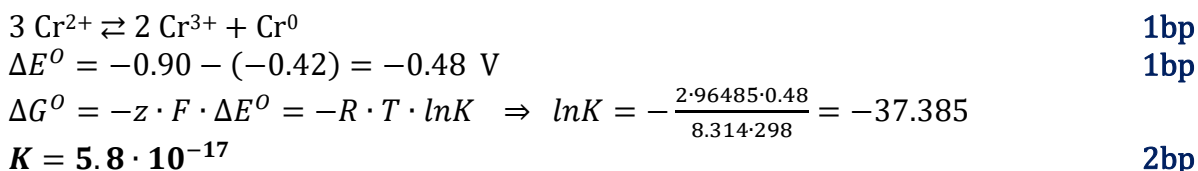
8.2. Are $Cr(V)$ and $Cr(IV)$ stable against disproportionation? Give reasoning for your answers using inequalities.

$Cr(V)$ not stable, because $E^0(\{Cr(V)|Cr(IV)\}) > E^0(\{Cr(VI)|Cr(V)\})$

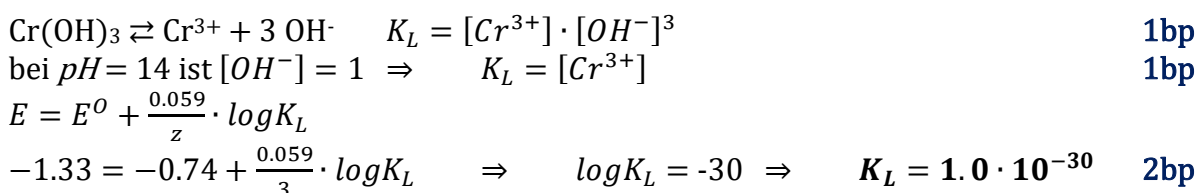
$Cr(IV)$ not stable, because $E^0(\{Cr(IV)|Cr(III)\}) > E^0(\{Cr(V)|Cr(IV)\})$

2bp

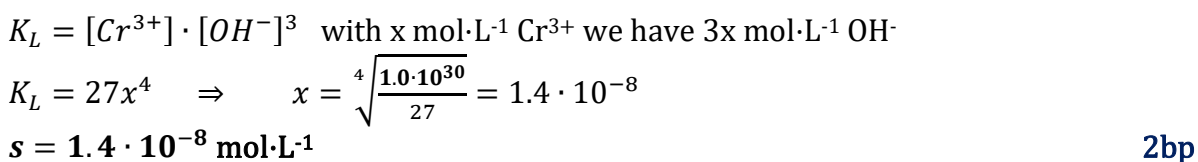
8.3. Calculate the equilibrium constant for the disproportionation of Cr(II) at 25°C.



8.4. Calculate the solubility product of Cr(OH)₃ at 25°C.

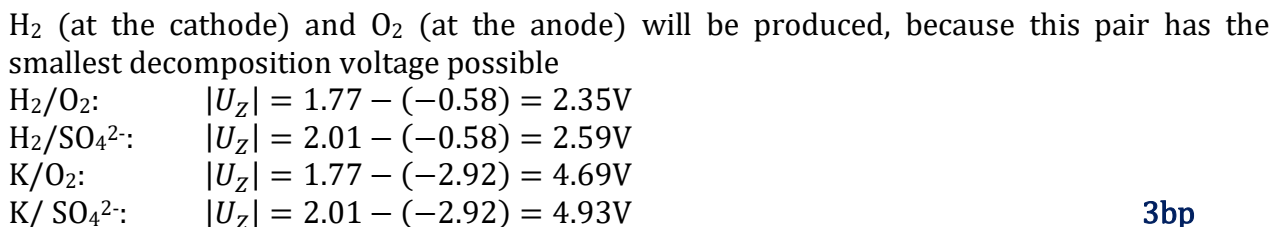


8.5. Calculate the solubility of Cr(OH)₃ at 25°C. If you didn't get a result in 8.4., you may use $1.0 \cdot 10^{-28}$ (this is not the correct value!).



B. The „Voltameter“

8.6. Which products deposit at the platinum-cathode and at the platinum-anode? Give your reasoning comparing all possible decomposition voltages.



8.7 Write down a balanced equation for the overall electrolysis reaction.



8.8. Calculate the amount of the deposited products, and from there the total volume of the gas in the left tube of the picture.

$$n(X) = \frac{I \cdot t \cdot \eta}{z \cdot F}$$

$$n(H_2) = \frac{0.805 \cdot 7 \cdot 60}{2 \cdot 96485} = 1.752 \cdot 10^{-3} \text{ mol} \quad \text{1bp}$$

$$n(O_2) = 0.5 \cdot (H_2) = 8.76 \cdot 10^{-4} \text{ mol} \quad \text{0.5bp}$$

$$V = \frac{n \cdot R \cdot T}{p} = \frac{2.628 \cdot 10^{-3} \cdot 8.314 \cdot 293}{99800} = 6.40 \cdot 10^{-5} \text{ m}^3 \quad \text{1bp}$$

$$V = \mathbf{64.0 \text{ mL}}$$

C. An acid constant and its consequences

8.9. Calculate the molar concentration of the saturated solution of benzoic acid using the unit $\text{mol} \cdot \text{cm}^{-3}$.

$$M(BA) = 122.1 \text{ g} \cdot \text{mol}^{-1}$$

$$c = \frac{2.90}{122.1} = 2.375 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1} = \mathbf{2.38 \cdot 10^{-5} \text{ mol} \cdot \text{cm}^{-3}} \quad \text{1bp}$$

8.10. Calculate the protolysis degree of benzoic acid and the protolysis constant of the acid.

$$\Lambda_0(BA) = \lambda_0(H^+) + \lambda_0(\text{Benzoat}) = 350 + 32.4 = 382.4 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \quad \text{1bp}$$

$$\Lambda_c(BA) = \frac{\kappa}{c} = \frac{0.453 \cdot 10^{-3}}{2.38 \cdot 10^{-5}} = 19.11 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \quad \text{1bp}$$

$$\alpha = \frac{\Lambda_c(BA)}{\Lambda_0(BA)} = \frac{19.11}{382.4} = \mathbf{5.00 \cdot 10^{-2}} \quad \text{1bp}$$

$$K_A = \left(\frac{\alpha^2}{(1-\alpha)} \right) \cdot c_0 = \frac{0.0025}{0.95} \cdot 2.375 \cdot 10^{-2} = \mathbf{6.25 \cdot 10^{-5}} \quad \text{1bp}$$

8.11. Calculate the volume of NaOH, which was titrated by the student, if the result of 8.9. is right.

$$n(BS) = n(NaOH)$$

$$10 \cdot 2.375 \cdot 10^{-2} = x \cdot 0.01 \Rightarrow x = \mathbf{23.75 \text{ mL}} \quad \text{1bp}$$

8.12. Calculate the pH of the solution at the end point of the titration.

There is only Na-benzoate present: $c_0 = \frac{10 \cdot 2.375 \cdot 10^{-2}}{10 + 23.75} = 7.04 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1} \quad \text{1bp}$

$$K_B(\text{Benzoat}) = \frac{1.0 \cdot 10^{-14}}{6.25 \cdot 10^{-5}} = 1.6 \cdot 10^{-10} \quad \text{1bp}$$

$$K_B = \frac{[OH^-]^2}{c_0 - [OH^-]} \cong \frac{[OH^-]^2}{c_0} \Rightarrow \mathbf{pH} = 14 - 0.5 \cdot (pK_B - \log c_0) = 14 - 0.5 \cdot (9.80 + 2.15) = \mathbf{8.02} \quad \text{2bp}$$