

# 49. Austrian Chemistry Olympiad National Competition

## Theoretical Part 24<sup>th</sup> May 2023

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## Problem 1 (W. Faber)

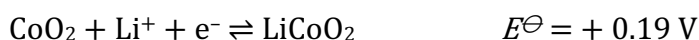
25.5 bp = 8 Points

## Applications of lithium

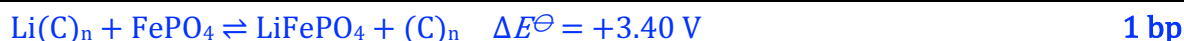
## A. Lithium rechargeable batteries

In technically used lithium rechargeable batteries, the negative electrode usually consists of lithium embedded in a graphite structure. The positive electrode can be made of different materials. In the case of lithium-ion batteries, it is usually made of lithium cobalt(III) oxide, while in the case of lithium iron phosphate batteries, the positive electrode consists of lithium iron(II) phosphate.

Reactions involved:



1.1 Write down the overall chemical equation for discharging a lithium iron phosphate battery and calculate the standard potential difference for this reaction.



The lithium iron phosphate battery achieves in practice a maximum energy density of  $160 \text{ Wh} \times \text{kg}^{-1}$ .

1.2 Calculate what percentage of the theoretically possible maximum energy density was thus achieved. Assume a value of  $n = 6$  for this calculation.

$$M(Li(C)_6 + FePO_4) = 229.82 \text{ g} \times \text{mol}^{-1}$$

$$n = \frac{1000 \text{ g}}{229.82 \text{ g} \times \text{mol}^{-1}} = 4.351 \text{ mol}$$

$$Q_{\max} = n \times z \times F = 4.351 \times 1 \times 96485 = 419829 \text{ As} = 116.62 \text{ Ah}$$

$$W = U \times Q = 3.40 \text{ V} \times 116.62 \text{ Ah} = 396.50 \text{ Wh}$$

$$\frac{160}{396.5} \times 100 = 40.35\%$$

**3 bp**

For the production of a lithium iron phosphate battery, among other things, an aluminium carrier foil is used to which a thin layer of lithium iron(II) phosphate is applied on one side. The carrier foil has a thickness of 15.0  $\mu\text{m}$ , the lithium iron(II) phosphate layer a thickness of 68.0  $\mu\text{m}$ . The purity of the lithium iron(II) phosphate used is 93%, the density is 1765  $\text{kg m}^{-3}$ . The film has a format of 241 mm x 200 mm

1.3 Calculate the maximum capacity of such a film in milliamperere hours mAh.

$$V = 0.241 \times 0.2 \times 68 \times 10^{-6} = 3.278 \times 10^{-6} \text{ m}^3$$

$$m = \rho \times V = 1765 \times 3.278 \times 10^{-6} = 5.785 \times 10^{-3} \text{ kg} = 5.785 \text{ g}$$

$$m_{\text{rein}} = 5.785 \times 0.93 = 5.380 \text{ g}$$

$$M(\text{LiFePO}_4) = 157.76 \text{ g} \times \text{mol}^{-1}$$

$$n = \frac{5.380 \text{ g}}{157.76 \text{ g} \times \text{mol}^{-1}} = 0.0341 \text{ mol}$$

$$Q = n \times z \times F = 0.0341 \times 1 \times 96485 = 3290 \text{ As} = 914 \text{ mAh}$$

3 bp

## B. Lithium carbonate

Lithium carbonate ( $M = 73.89 \text{ g mol}^{-1}$ ) is significantly less soluble than the carbonates of the other alkali metals. At 20.0°C the solubility is 13.3  $\text{g L}^{-1}$ , at 100°C 7.2  $\text{g L}^{-1}$ .

1.4 Calculate the molar enthalpy of solution of lithium carbonate. Assume that the enthalpy is constant in the temperature interval considered.

$$n_{20^\circ\text{C}} = \frac{13.3 \text{ g}}{73.89 \text{ g} \times \text{mol}^{-1}} = 0.180 \text{ mol}$$

$$n_{\text{CO}_3^{2-}} = n_1 = 0.180 \text{ mol}$$

$$n_{\text{Li}^+} = 2 \times n_1 = 0.360 \text{ mol}$$

$$K_L^{20^\circ\text{C}} = [\text{Li}^+]^2 \times [\text{CO}_3^{2-}] = 0.360^2 \times 0.180 = 1.166 \times 10^{-2}$$

$$n_{100^\circ\text{C}} = \frac{7.2 \text{ g}}{73.89 \text{ g} \times \text{mol}^{-1}} = 0.0974 \text{ mol}$$

$$n_{\text{CO}_3^{2-}} = n_1 = 0.0974 \text{ mol}$$

$$n_{\text{Li}^+} = 2 \times n_1 = 0.1949 \text{ mol}$$

$$K_L^{100^\circ\text{C}} = [\text{Li}^+]^2 \times [\text{CO}_3^{2-}] = 0.1949^2 \times 0.0974 = 7.402 \times 10^{-3}$$

$$\ln \frac{K_L^{100^\circ\text{C}}}{K_L^{20^\circ\text{C}}} = -\frac{\Delta_R H^\ominus}{R} \times \left( \frac{1}{373.15} - \frac{1}{293.15} \right)$$

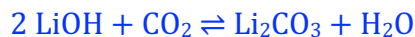
$$\Delta_R H^\ominus = -\frac{R \times \ln \frac{K_L^{100^\circ\text{C}}}{K_L^{20^\circ\text{C}}}}{\frac{1}{373.15} - \frac{1}{293.15}} = -5170 \text{ J/mol}$$

4 bp

**C. Lithium hydroxide**

In the Apollo space program, lithium hydroxide was used to remove the exhaled carbon dioxide from the air.

1.5 Give a balanced chemical equation for the reaction of lithium hydroxide with carbon dioxide.



1 bp

1.6 Calculate the maximum volume of carbon dioxide gas that can be bound by 1.00 g of pure lithium hydroxide at 25°C and 1.00 bar pressure.

$$M(\text{LiOH}) = 23.95 \text{ g} \times \text{mol}^{-1}$$

$$n_{\text{LiOH}} = \frac{1.00 \text{ g}}{23.95 \text{ g} \times \text{mol}^{-1}} = 0.04175 \text{ mol}$$

$$n_{\text{CO}_2} = \frac{n_{\text{LiOH}}}{2} = 0.02088 \text{ mol}$$

$$V = \frac{n \times R \times T}{p} = \frac{0.02088 \text{ mol} \times 0.083145 \text{ L} \times \text{bar} \times \text{K}^{-1} \times \text{mol}^{-1} \times 298.15 \text{ K}}{1.00 \text{ bar}} = 0.5175 \text{ L}$$

1.5 bp

Lithium hydroxide reacts slowly with carbon dioxide in the air to form lithium carbonate. Its purity can be determined via titration. For this purpose, a first titration first carried out with HCl and methyl orange, whereby both lithium hydroxide and lithium carbonate react. In a second titration, an excess of barium chloride is first added to precipitate the carbonate. Then HCl is used again to titrate the hydroxide using phenolphthalein as an indicator.

The sample is a mixture of lithium hydroxide and lithium carbonate. To prepare a stock solution, 2.500 g of this mixture are transferred to a 500 mL volumetric flask, dissolved in water, filled up and homogenized. Then 25.00 mL of this stock solution is titrated with HCl (0.100 mol L<sup>-1</sup>) and methyl orange, consuming 48.5 mL to the equivalence point. Barium chloride is added to another 25.00 mL of the stock solution until no precipitate is formed. The following titration with HCl (0.100 mol L<sup>-1</sup>) and phenolphthalein as indicator results in a consumption of 41.7 mL.

1.7 Calculate the masses of lithium hydroxide and lithium carbonate in this sample.

$$n_{\text{OH}^-} = 0.0417 \times 0.1 = 0.00417 \text{ mol}$$

$$n_{\text{OH}^-}^{\text{tot}} = 20 \times n_{\text{OH}^-} = 0.0834 \text{ mol}$$

$$m_{\text{LiOH}} = n_{\text{OH}^-}^{\text{tot}} \times M_{\text{LiOH}} = 0.0834 \text{ mol} \times 23.95 \text{ g} \times \text{mol}^{-1} = 1.997 \text{ g}$$

$$m_{\text{Li}_2\text{CO}_3} = 2.5 \text{ g} - 1.997 \text{ g} = 0.503 \text{ g}$$

2 bp

In order to be able to estimate the accuracy of this titration method, you should now perform the following calculation:

Assume to have a carbonate concentration of  $0.0100 \text{ mol L}^{-1}$  in the  $25.00 \text{ mL}$  sample solution. Add  $3.00 \text{ mL}$  of a barium chloride solution with a concentration of  $0.100 \text{ mol L}^{-1}$ . The solubility product of barium carbonate is  $2.58 \times 10^{-9}$ .

**1.8** Calculate the concentration of carbonate ions in the solution after the addition of the barium chloride.

$$[\text{Ba}^{2+}] = \frac{0.003 \times 0.1 - x}{0.028}$$

$$[\text{CO}_3^{2-}] = \frac{0.025 \times 0.01 - x}{0.028}$$

$$K_L = [\text{Ba}^{2+}] \times [\text{CO}_3^{2-}] = \frac{0.003 \times 0.1 - x}{0.028} \times \frac{0.025 \times 0.01 - x}{0.028} = 2.58 \times 10^{-9}$$

$$(0.0003 - x) \times (0.00025 - x) = 2.0227 \times 10^{-12}$$

$$\text{solve for: } x = 2.499596 \times 10^{-4} \text{ mol}$$

$$[\text{CO}_3^{2-}] = \frac{0.025 \times 0.01 - x}{0.028} = 1.44 \times 10^{-6} \text{ mol} \times \text{L}^{-1}$$

6 bp

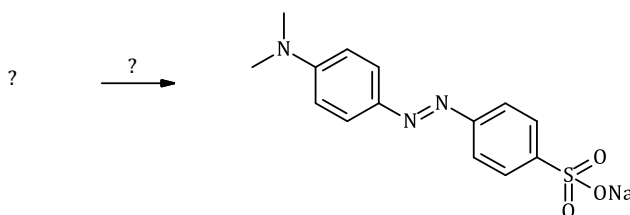
A second titration method for the given mixture starts with the same titration with HCl and methyl orange as indicator as the first method. However, the second titration is carried out with HCl and an indicator which has its transition point at a pH value of 8.2.

**1.9** Give the ionic equation for the reaction of the carbonate ion in the second titration.

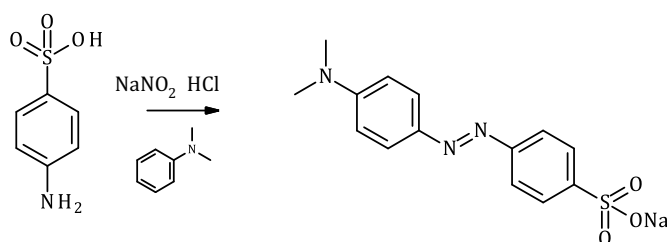


1 bp

The indicator methyl orange is synthetically accessible by azo coupling:



**1.10** Draw the constitutional formulas of the reactants and give the sum formulas of the reagents leading to this indicator. Name the type of reaction in the above coupling.



electrophilic substitution

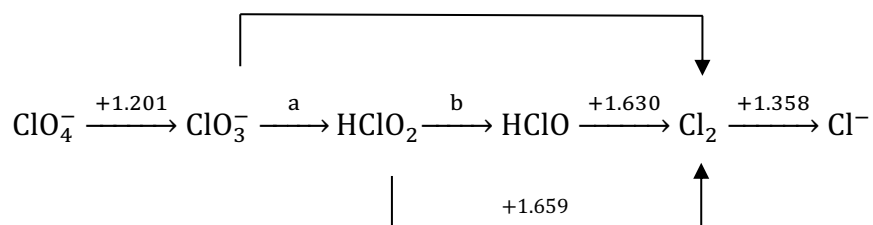
3 bp

## Problem 2 (W. Faber)

13 bp = 4 Points

## Oxygen-chlorine-compounds

The Latimer diagram of the oxygen-chlorine compounds at pH = 0 is given. All species are given here in the form in which they exist at pH = 0.



2.1 Give the values of  $a$  and  $b$  and justify your answers by calculation.

$$5 \times 1.468 = 3 \times 1.659 + a \times 2$$

$$a = 1.1815$$

$$3 \times 1.659 = 2 \times b + 1.630$$

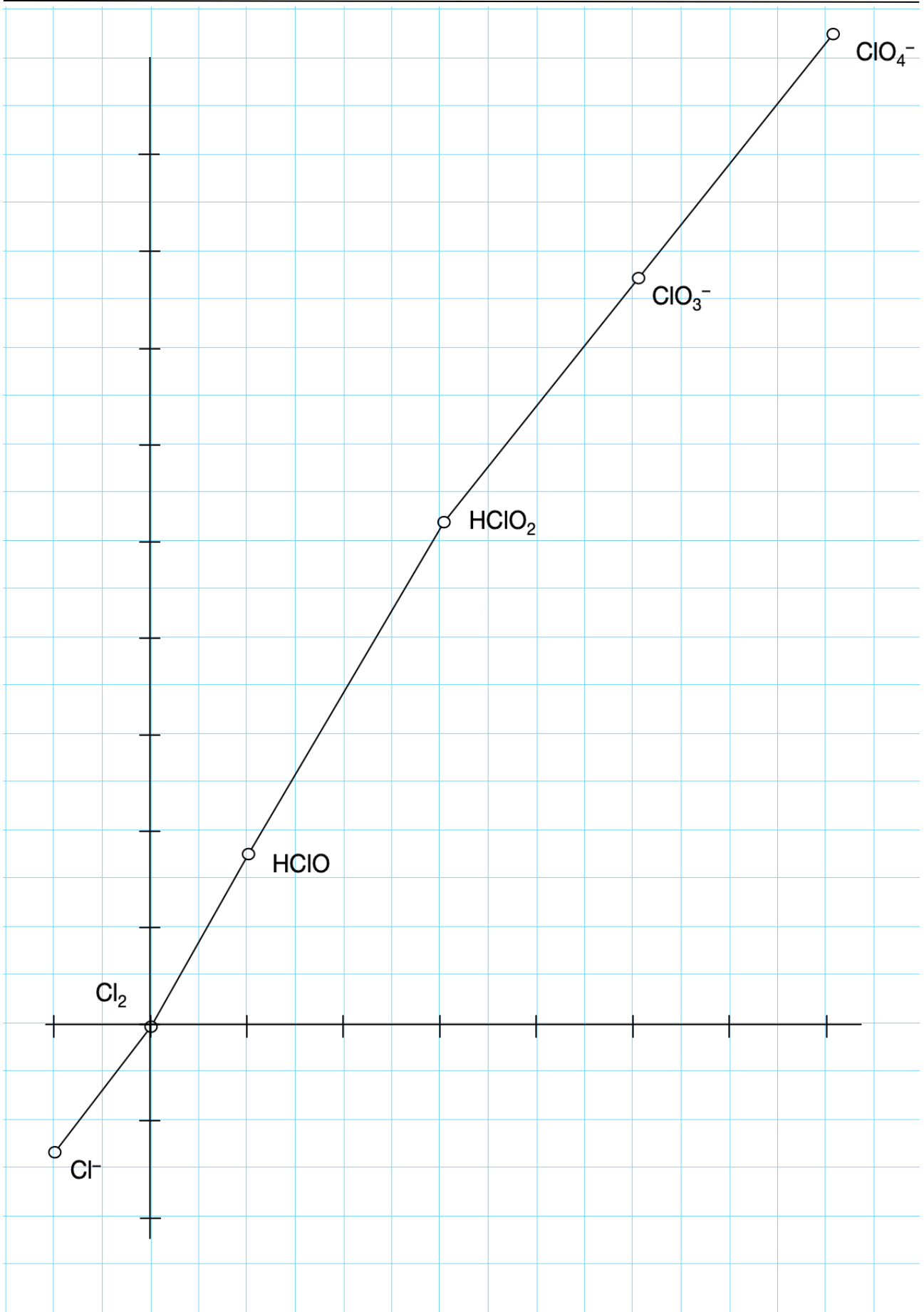
$$b = 1.6735$$

2 bp

2.2 Draw the Frost diagram of the oxygen-chlorine compounds at pH = 0 on the following page and note in the table below the coordinates of the plotted points.

	Coordinate on the horizontal axis	Coordinate on the vertical axis
Cl <sup>-</sup>	-1	-1.358
Cl <sub>2</sub>	0	0
HClO	1	1.63
HClO <sub>2</sub>	3	4.978
ClO <sub>3</sub> <sup>-</sup>	5	7.34
ClO <sub>4</sub> <sup>-</sup>	7	9.742

6 bp





One of the given oxygen-chlorine compounds tends to disproportionate under the given conditions.

2.3 Write down the sum formula of this compound.	
HClO <sub>2</sub>	1 bp
2.4 Write down a possible balanced chemical equation for this process under acidic conditions.	
$2 \text{HClO}_2 \rightleftharpoons \text{H}^+ + \text{ClO}_3^- + \text{HClO}$	1 bp
2.5 Calculate the reduction potential of $\text{ClO}_4^-/\text{ClO}_3^-$ at $\text{pH} = 14$ and give the chemical equation of the reduction at that pH.	
<p>reduction at <math>\text{pH} = 0</math>:</p> $\text{ClO}_4^- + 2 \text{e}^- + 2 \text{H}^+ \rightleftharpoons \text{ClO}_3^- + \text{H}_2\text{O}$ $E = E^\ominus - \frac{RT}{zF} \ln \left( \frac{1}{(10^{-14})^2} \right) = 1.201 - \frac{8.3145 \times 298.15}{2 \times 96485} \times \ln(10^{28}) = 0.373 \text{ V}$ <p>reduction at <math>\text{pH} = 14</math>:</p> $\text{ClO}_4^- + 2 \text{e}^- + \text{H}_2\text{O} \rightleftharpoons \text{ClO}_3^- + 2 \text{OH}^-$	
	3 bp

## Problem 3 (H. Wachtler)

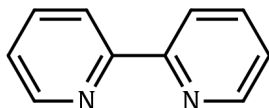
26 bp = 8 Points

## Inorganic? Of course!

## A. Synthesis of hydrogen

2,2'-Bipyridine (bpy) is a chemical compound from the group of bipyridines with the sum formula  $C_{10}H_8N_2$ . It consists of two pyridine rings, which are linked to each other in the  $\alpha$ -position.

3.1 Draw the structural formula of 2,2'-bipyridine (bpy).

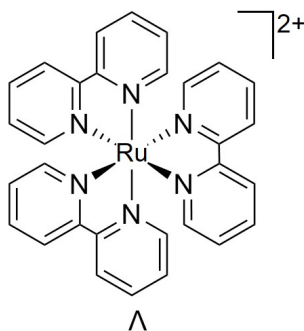
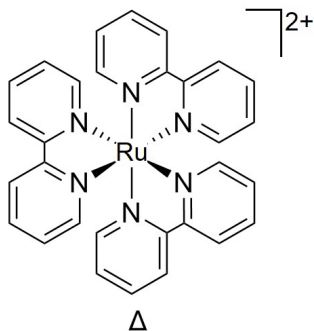


1 bp

The compound can be used as a bidentate chelating ligand, coordinating through the nitrogen atoms. Abbreviations bpy or bipy are used frequently. Stable complexes are formed with many transition metals. In octahedral complex geometry, two complex species are formed.

Tris(bipyridine)ruthenium(II) chloride is a coordination compound with the formula  $[Ru(bpy)_3]Cl_2$ . This polypyridine complex is a red crystalline salt which is obtained as a hexahydrate. All the interesting properties are due to the cation  $[Ru(bpy)_3]^{2+}$ , which has attracted much attention because of its special optical properties.

3.2 Draw the structures and name the two isomers of the cation  $[Ru(bpy)_3]^{2+}$ . Name the type of isomerism.

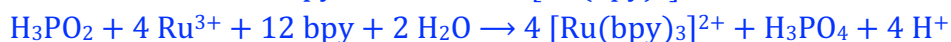


configurational isomers (enantiomers)

3 bp

Tris(bipyridine)ruthenium(II) chloride is prepared by treating an aqueous solution of ruthenium(III) chloride with 2,2'-bipyridine. Ru(III) is reduced to Ru(II) using hypophosphorous acid ( $H_3PO_2$ ) as a reducing agent.

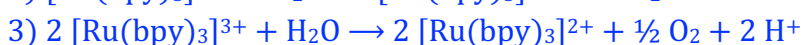
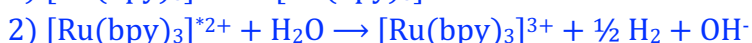
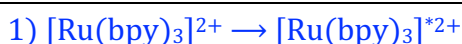
3.3 Write down a balanced ionic equation for the synthesis of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ .



1 bp

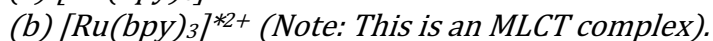
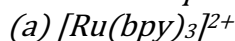
The photoionization of  $[\text{Ru}(\text{bpy})_3]^{2+}$  is the archetype of a class of reactions that could enable photochemical water splitting: After photochemical excitation at **452 nm**, which produces the metal-to-ligand charge-transfer (MLCT) complex  $[\text{Ru}(\text{bpy})_3]^{*2+}$  as the catalytic intermediate, the knocked-out electron reacts with  $\text{H}_2\text{O}$ . The remaining complex  $[\text{Ru}(\text{bpy})_3]^{3+}$  is now thermodynamically capable of oxidizing water.

3.4 Describe this process by writing down three balanced ionic equations.

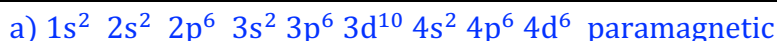


2.5 bp

3.5 Give the complete electron configurations for the central atoms in



Determine if each complex is "paramagnetic" or "diamagnetic".



0,5 bp



1 bp

3.6 The standard potential for water splitting is  $\Delta E = +1.23 \text{ V}$ . Calculate the maximum wavelength of a photon in nm with which the reaction still can be performed.

$$E = UIt = UQ = 1.23 \text{ V} \times 1.6 \times 10^{-19} \text{ As} = 1.97 \times 10^{-19} \text{ J}$$

$$E = h\nu = hc/\lambda$$

$$\lambda = hc/E = 1.009 \times 10^{-6} \text{ m} = 1009 \text{ nm}$$

1.5 bp

3.7 Assumption: the excess energy of the incident photon for the above reaction is not converted into heat, but into another photon. Calculate the wavelength of the "excess energy photon"  $\lambda_{\text{ex}}$  in nm.

$$E_{\text{inc}} = hc/\lambda = hc/(452 \times 10^{-9}) = 4.39 \times 10^{-19} \text{ J}$$

$$E_{\text{ex}} = 4.39 \times 10^{-19} \text{ J} - 1.97 \times 10^{-19} \text{ J} = 2.42 \times 10^{-19} \text{ J}$$

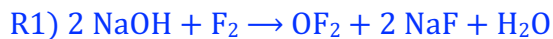
$$\lambda_{\text{ex}} = hc/E = 8.19 \times 10^{-7} \text{ m} = 819 \text{ nm}$$

1.5 bp

**B. Fluorine – fluorinating agent**

The reaction of fluorine gas with sodium hydroxide produces compound **A** ( $\text{OF}_2$ ), a salt and water (**R1**). In the presence of UV light, two different radicals are formed from **A** (**R2**), each of them dimerizes with an identical radical when heated to form **B** and **C** (**R3**). **C** is a reactive gas which reacts spontaneously with almost all elements.

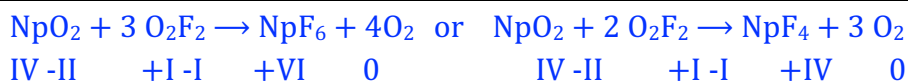
3.8 Write down the balanced chemical equations (**R1**) – (**R3**).



2 bp

$\text{O}_2\text{F}_2$  is a very strong fluorinating agent and reacts with neptunium(IV) oxide under oxidation. In addition to the binary neptunium compound, only oxygen is formed in the process

3.9 Write down a redox equations and note down all oxidation numbers.



2 bp

3.10 Which of the following reactions occurs in this reaction? Tick the correct answers.

 Comproportionation

 Disproportionation

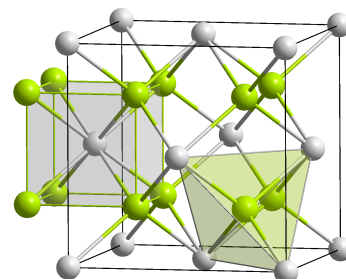
 Lewis acid base reaction

 none of the mentioned

comproportionation

0.5 bp

Neptunium(IV) oxide has a cubic crystal structure, it has the space group  $\text{Fm}\bar{3}\text{m}$  (No. 225), the elementary cell has as lattice constant  $a = 544 \text{ pm}$ , the structure type is  $\text{CaF}_2$  type (fluorite). The density is  $11.10 \text{ gcm}^{-3}$ .



3.11 Write down the empirical formula and the formula of the unit cell of neptunium(IV) oxide.



1 bp

3.12 From the lattice constant and density of neptunium(IV) oxide, calculate its molar mass.

$$m(4\text{NpO}_2) = \rho \cdot V = 11.10 \cdot (544 \times 10^{-10})^3 = 1.79 \times 10^{-21} \text{ g}$$

$$m(\text{NpO}_2) = 4.47 \times 10^{-22} \text{ g}$$

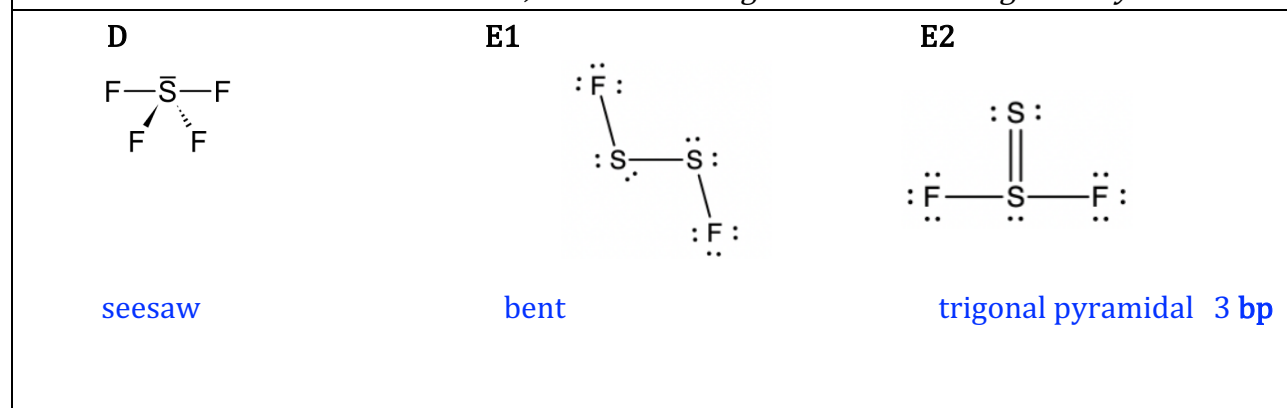
$$M(\text{NpO}_2) = N_A \times m(\text{NpO}_2) = 269 \text{ g/mol}$$

$$M(\text{Np}) = 237 \text{ g/mol}$$

2.5 bp

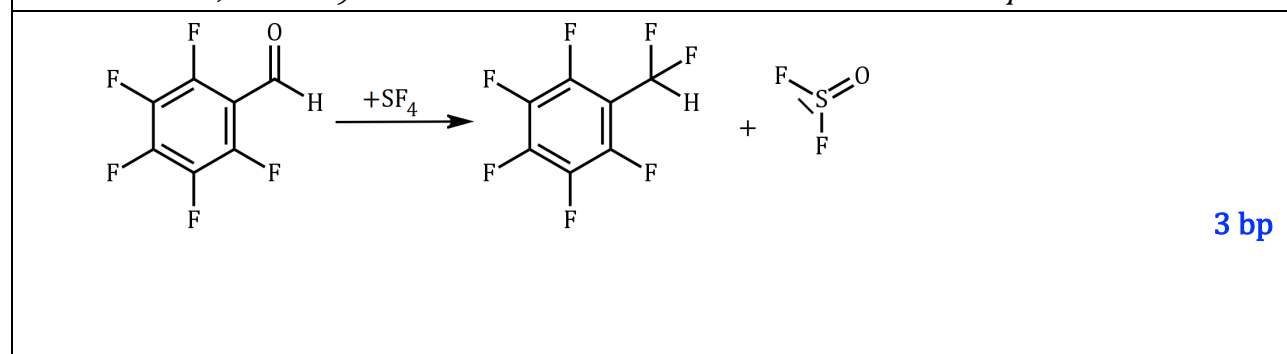
In addition to oxygen fluorides, there are a number of different sulphur fluorides.  $\text{SF}_4$  (**D**) and  $\text{S}_2\text{F}_2$  (**E**) are unstable fluorides. **E** occurs in two isomeric forms **E1** and **E2**.

3.13 Draw the Lewis structures of **D**, **E1** and **E2** and give the molecular geometry of each.



**D** is a selective fluorinating reagent that can transform a carbonyl group selectively to a  $\text{CF}_2$  group.

3.14 What products are formed from an arylcarbonyl compound (42.879% C, 0.514% H, 8.16% O, rest is F) with **D**? Draw the structural formulas of all compounds.



## Problem 4 (G. Schellander)

25 bp = 7.5 Points

Some thermodynamics of NO<sub>x</sub>

Since the oxygen source for combustion processes usually is air, nitrogen inevitably also enters the respective combustion chamber. Thus, equilibria of for the formation of nitrogen oxides have to be considered:



In the following tasks let us assume that only NO is formed and that no other nitrogen oxides are produced.

	$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J mol}^{-1} \text{K}^{-1}$	$C_p / \text{J mol}^{-1} \text{K}^{-1}$
N <sub>2(g)</sub>	0.0	191.6	29.1
NO <sub>(g)</sub>	91.3	210.8	29.9
O <sub>2(g)</sub>	0.0	205.2	29.40

Thermodynamische Daten aus dem CRC-Handbook

4.1 Determine  $\Delta_R G^\ominus_{298}$  and  $K_p$  (at 298 K) for the reaction (R1).

$$\Delta_R S^\ominus = 2 \times 210.8 - 191.6 - 205.2 = 24.8 \text{ JK}^{-1} \text{mol}^{-1}$$

$$\Delta_R G^\ominus = 2 \times 91.3 - 298 \times 0.0248 = 175.2 \text{ kJmol}^{-1}$$

$$K_p = e^{-\frac{\Delta_R G^\ominus}{RT}} = 1.95 \times 10^{-31}$$

2 bp

4.2 Determine  $\Delta_f G^\ominus$  of nitrogen(II) oxide.

$$\Delta_f G^\ominus = 175.2/2 = 87.6 \text{ kJmol}^{-1}$$

1.5 bp

Let us assume in the following that  $\Delta_R H^\ominus$ , and  $\Delta_R S^\ominus$  are temperature independent. It is known that:

$$K_p = \frac{p_{\text{NO}}^2}{p_{\text{O}_2} \times p_{\text{N}_2}}$$

4.3 Derive an expression from  $K_p$  that gives  $p_{\text{NO}}$  as a function of  $T$ ,  $p_{\text{O}_2}$ ,  $p_{\text{N}_2}$ ,  $\Delta_R H^\ominus$  and  $\Delta_R S^\ominus$ .

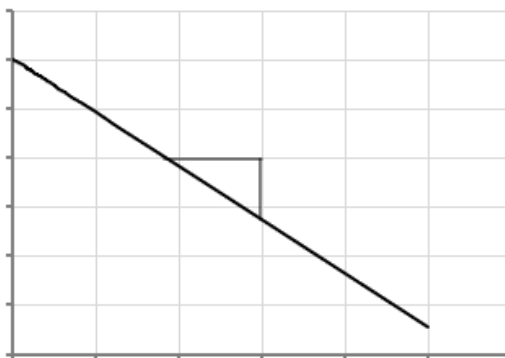
$$\begin{aligned} \ln K_p &= 2 \ln p_{\text{NO}} - \ln(p_{\text{O}_2} p_{\text{N}_2}) = -\frac{\Delta_R G^\ominus}{RT} = -\frac{\Delta_R H^\ominus}{RT} + \frac{\Delta_R S^\ominus}{R} \\ \Rightarrow \ln p_{\text{NO}} &= -\frac{\Delta_R H^\ominus}{2RT} + \frac{\Delta_R S^\ominus}{2R} + \frac{1}{2} \ln(p_{\text{O}_2} p_{\text{N}_2}) \end{aligned}$$

2.5 bp

4.4 Based on your previous results, tick the correct answers:

With increasing temperature   $p_{\text{NO}}$  increases.   $p_{\text{NO}}$  decreases.   $p_{\text{NO}}$  inc. 1 bp

The correctly derived expression for  $p_{\text{NO}}$  as a function of temperature can be represented as a linear function:



4.5 For this graph, give the correct expressions for ...

... labeling of the ordinate (y-axis):  $\ln p_{\text{NO}}$

... labeling of the abscissa (x-axis):  $1/T$

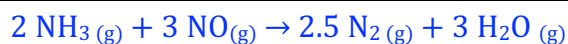
... slope:  $-\frac{\Delta_R H^\ominus}{2R}$

... ordinate section (section on the y-axis)  $\frac{\Delta_R S^\ominus}{2R} + \frac{1}{2} \ln(p_{\text{O}_2} p_{\text{N}_2})$

2 bp

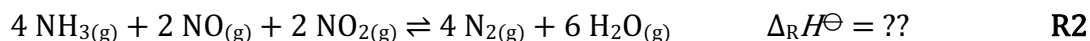
Since nitrogen oxides are known to be environmental pollutants (next to a few other hazards), attempts are being made to keep their emission low by removing them from the exhaust gas stream after combustion. One method of doing this is selective catalytic reduction (SCR), in which nitrogen monoxide reacts with ammonia at elevated temperatures to produce nitrogen.

4.6 Give a balanced chemical equation for this reaction including the states of matter.



1 bp

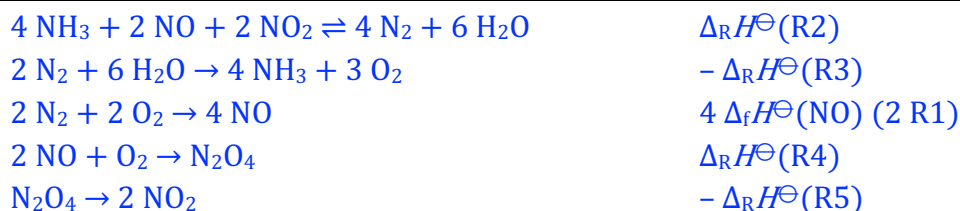
The reaction is faster if the exhaust gas stream contains nitrogen dioxide in addition to nitrogen monoxide. The reaction is often written like this:



In addition to the thermodynamic data already given at the beginning of this task, a few more reaction enthalpies are given below:



4.7 Calculate  $\Delta_{\text{R}}H^{\ominus}$  for (R2) by applying an appropriate thermodynamic circle.

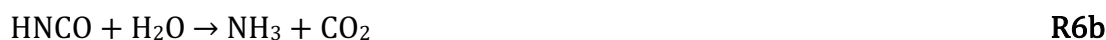


$$\text{R2} - \text{R3} + 2 \text{R1} + \text{R4} - \text{R5} = 0 \quad \Rightarrow \quad \text{R2} = \text{R3} - 2\text{R1} - \text{R4} + \text{R5}$$

$$\begin{aligned} \Delta_{\text{R}}H^{\ominus}(\text{R2}) - \Delta_{\text{R}}H^{\ominus}(\text{R3}) + 4 \Delta_{\text{f}}H^{\ominus}(\text{NO}) + \Delta_{\text{R}}H^{\ominus}(\text{R4}) - \Delta_{\text{R}}H^{\ominus}(\text{R5}) &= 0 \\ \Rightarrow \Delta_{\text{R}}H^{\ominus}(\text{R2}) &= \Delta_{\text{R}}H^{\ominus}(\text{R3}) - 4 \Delta_{\text{f}}H^{\ominus}(\text{NO}) - \Delta_{\text{R}}H^{\ominus}(\text{R4}) + \Delta_{\text{R}}H^{\ominus}(\text{R5}) \\ &= -1268 - 4 \times 91.3 + 171.5 - 55.3 = -1517 \text{ kJ/mol} \end{aligned}$$

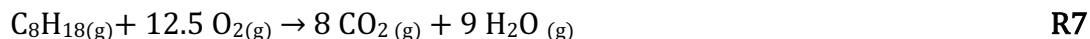
5 bp

If SCR is used in motor vehicles, ammonia is generated in situ from an aqueous urea solution (UWS urea water solution) by injecting it into the exhaust gas stream before it reaches the catalyst. In the process, the water evaporates and the urea is decomposed in two steps. In the first one isocyanic acid is produced.





Let's make a chemically based estimation of the consumption of UWS. Let us assume a fuel with a density of  $0.731 \text{ kg L}^{-1}$ , which consists only of *n*-octane and which combusts completely in the engine.



The combustion air consists only of  $\text{N}_2$  (79 %  $V/V$ ) and  $\text{O}_2$  (21 %  $V/V$ ). The exhaust gas shall be composed only of  $\text{N}_{2(\text{g})}$ ,  $\text{CO}_{2(\text{g})}$  and  $\text{H}_2\text{O}_{(\text{g})}$ .

**4.8** Calculate the amount of substance of this exhaust gas for one litre of the fuel.

$M(\text{C}_8\text{H}_{18}) = 114.26 \text{ g/mol}$ ;  $1\text{L} \rightarrow 731\text{g} \triangleq 6.398 \text{ mol}$   
 $12.5 \times 6.398 = 79.97 \text{ mol O}_2\text{-demand}$ ;  $6.398 \times (8+9) = 108.8 \text{ mol CO}_2 + \text{H}_2\text{O}$  are formed  
 $79.97 \times 0.79/0.21 = 300.9 \text{ mol N}_2$  go in as well  
 total  
 409.7 mol Abgas **3 bp**

Now – with unchanged amounts of nitrogen, carbon dioxide and water vapor – 1000 ppm  $\text{NO}_x$  shall be in the exhaust gas, where  $\text{NO}$  and  $\text{NO}_2$  shall be present in equal molar fractions. The catalyst can reduce the  $\text{NO}_x$  content by 80%, using a 32% urea solution (density  $1.09 \text{ kg L}^{-1}$ ).

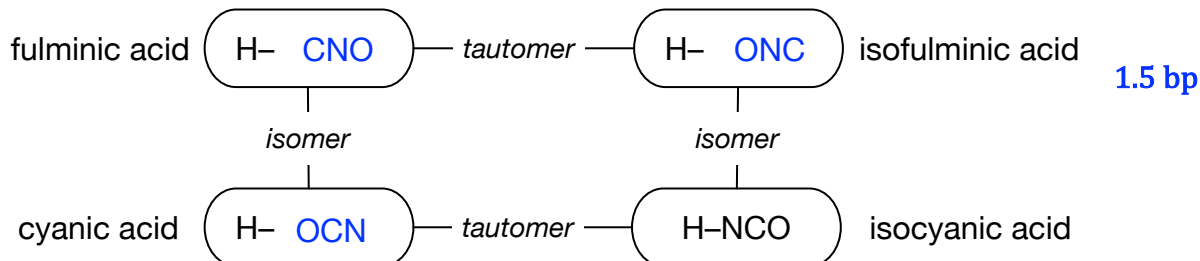
**4.9** Calculate the minimum volume of urea solution needed for 1 L of the fuel. Assume stoichiometric volumes of ammonia (reaction **R2**). Neglect the volume of water vapor from the urea solution.

If you don't have any result from 4.8, assume 300 mol exhaust gas.

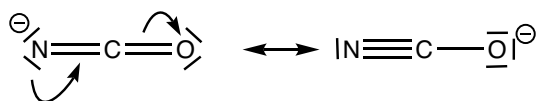
$1000\text{ppm NO}_x \triangleq 0.4097 \text{ mol NO}_x$ ; from that 80% (0.3278 mol) are converted;  
 according to R2 0.3278 mol  $\text{NH}_3$  are required  
 → according to R6 that means 0.1638 mol urea ( $M = 60.07 \text{ g/mol}$ ) or 9.84 g  
 these are contained in 30.8 g solution, corresponding to 28.2 mL **2 bp**

On the one hand, the name isocyanic acid suggests that several isomers of this compound exist. On the other hand, "cyanic" suggests a relation with the cyanide  $\text{CN}^-$ . In fact, there are 4 isomers, all of which contain a  $\text{CN}$  group. Two of each are tautomers. The fulminic acid contains a  $\text{C-H}$  bond.

4.10 Fill in the formulas in the boxes below (formula of isocyanic acid is already given).



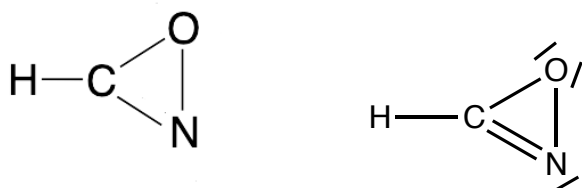
4.11 Draw two mesomeric Lewis structures for the isocyanate anion (including non-bonding pairs and formal charges) that show how the rearrangement between isocyanic acid and cyanic acid can proceed.



**1 bp**

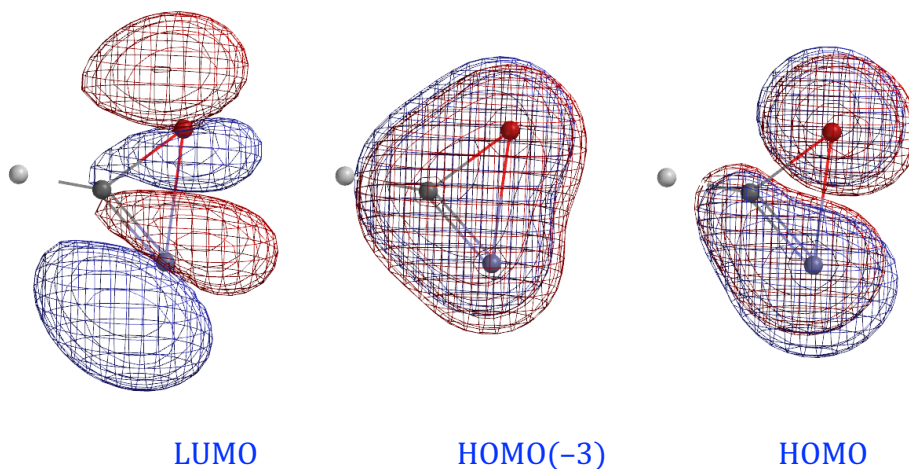
In addition, a non-linear geometry might be possible:

4.12 Draw the missing electron pairs into the Lewis structure.



**1 bp**

4.13 The figure shows three (calculated) molecular orbitals of the structure. Assign the designations "LUMO", "HOMO" and "HOMO (-3)", where the latter means an MO that is energetically three steps below the HOMO.



**1.5 bp**

## Problem 5 (G. Schellander, J. Novacek)

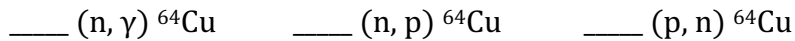
40 bp = 12 Points

## Copper-64

Throughout this problem use the scientific notation for numbers above 1000 and below 0.001.

Copper-64 can be prepared by various methods. By thermal neutrons in an (n,  $\gamma$ )-reaction, by fast neutrons in an (n, p)-reaction or in a cyclotron (accelerator for charged particles) by a (p, n)-reaction.

5.1 Specify the starting nuclides in each case.



$^{64}\text{Cu}$  can also be generated from natural zinc in a cyclotron. For this purpose, a (d, 2p)-reaction is used. Natural zinc consists of the stable isotopes  $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$ ,  $^{67}\text{Zn}$ ,  $^{68}\text{Zn}$  with proportions of 49.2%, 27.7%, 4.00%, 18.5%.

5.2 Give a balanced nuclear chemical equation (with all atomic and mass numbers) for this process.



In an experiment, a 15 MeV deuteron beam (i.e. a beam of  $^2\text{H}^+$  ions) was able to achieve a yield of  $1.195 \times 10^7 \text{ Bq } \mu\text{A}^{-1} \text{ h}^{-1}$ . Assume that the Zn target had a mass of 5 mg and that 1.00 % of the target were actually hit by the deuteron beam. Use the molar mass of Zn from the periodic table; the decay constant of  $^{64}\text{Cu}$  is  $\lambda = 1.516 \times 10^{-5} \text{ s}^{-1}$ .

5.3 For irradiation  $10^{-5} \text{ mol}$  of deuterons are used. Calculate the fraction of the Zn nuclide (considered for conversion) that was actually converted.

$$1 \mu\text{Ah}: n_{\text{d}} = \frac{It}{F} = \frac{10^{-6} \text{ A} \times 3600 \text{ s}}{96485 \text{ A s mol}^{-1}} = 3.73 \times 10^{-8} \text{ mol deuterons} \rightarrow$$

$$268 \mu\text{Ah} \triangleq 10^{-5} \text{ mol deuterons}$$

$5 \text{ mg} \triangleq 0.765 \times 10^{-5} \text{ mol Zn}$ , of which  $7.65 \times 10^{-7} \text{ mol}$  are hit,  
from that 49.2% or  $3.67 \times 10^{-7} \text{ mol}$  are  $^{64}\text{Zn}$

$$1.195 \times 10^7 \text{ Bq} / \mu\text{Ah} \triangleq 3.203 \times 10^9 \text{ Bq} / 268 \mu\text{Ah}$$

$$N = A / \lambda = 3.203 \times 10^9 \text{ Bq} / 1.516 \times 10^{-5} \text{ s}^{-1} = 2.113 \times 10^{14} \triangleq 3.508 \times 10^{-10} \text{ mol}$$

$$\text{fraction converted: } 3.508 \times 10^{-10} \text{ mol} / 3.76 \times 10^{-7} \text{ mol} = 9.32 \times 10^{-3}$$

**5 bp**

$^{64}\text{Cu}$  can decay in various ways:

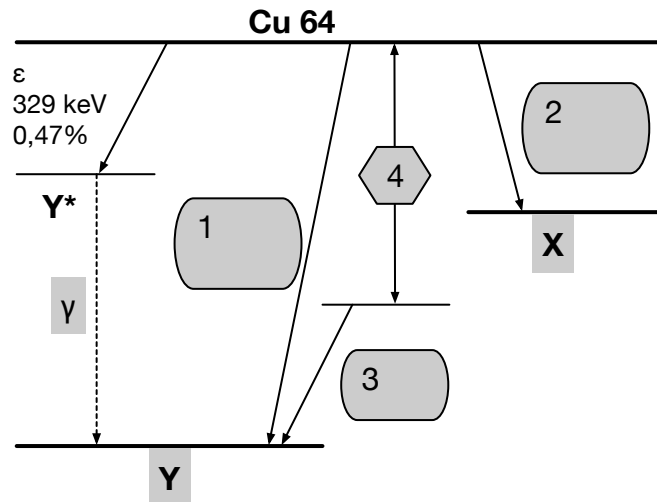
$\beta^-$ -decay, (38.48 %,  $E_{\max, \beta^-} = 579 \text{ keV}$ ) – daughter isotope **X**

$\beta^+$ -decay (17.52%,  $E_{\max, \beta^+}$ ) – daughter isotope **Y**

$\epsilon$  electron capture (329 keV, 0.47%) to an excited state **Y\***

$\epsilon$  electron capture (1.675 MeV, 43.53%) to the ground state of **Y**

The decomposition scheme demonstrates the situation, but some things highlighted in grey still need to be clarified.



5.4 Write down the nuclides **X** and **Y**.

X:  $^{64}\text{Zn}$  Y:  $^{64}\text{Ni}$

1 bp

5.5 Note what has to be written in the fields **1**, **2** and **3**, orientate yourself for this on the already given  $\epsilon$ -decay. In particular, calculate the maximum energy  $E_{\beta^+}$  of the  $\beta^+$  decay. Do not forget the particle(s) whose mass energy corresponds to the field **4**.

**1:**  $\epsilon$  1.675 MeV, 43.53%

**2:**  $\beta^-$ , 579 keV, 38.48 %,

**3:**  $\beta^+$ , 17.52%,

$$E_{\max, \beta^+} = 1675 - 2m_{\text{e}}c^2 = 1675 - 1022 = 653 \text{ keV}$$

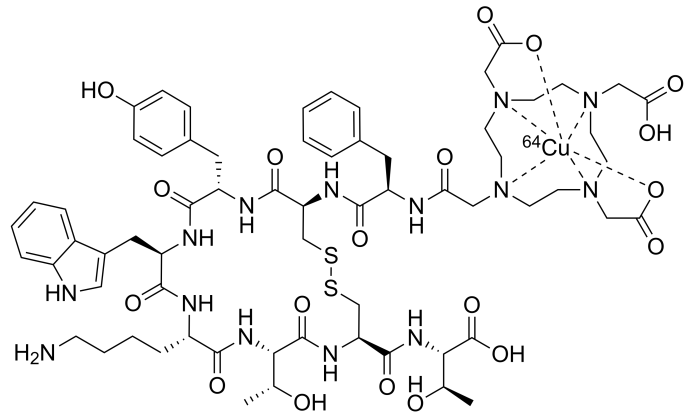
4 bp

5.6 Give the energy of the gamma photon  $\gamma$  in keV emitted at the transition **Y\***  $\rightarrow$  **Y**

$$\Delta E = 1675 - 329 = 1346 \text{ keV}$$

1bp

Due to its positron emission,  $^{64}\text{Cu}$  has recently been used as a radioactive pharmakon for positron emission tomography (PET). For this purpose, it is bound by a multidentate ligand ("DOTA"). The ligand is attached to a small polypeptide designed to allow binding to somatostatin receptors.



A US manufacturer claims about its product DETECTNET<sup>1</sup>: It is a sterile, colourless to slightly yellowish solution

with a total activity of  $37 \text{ MBq} \times \text{mL}^{-1}$  of  $^{64}\text{Cu}$ -Dotatate at the time of production indicated on the label. A table also indicates the decrease of activity to the attending physicians, because the usability is of course of limited duration.

5.7 Calculate the number of positrons emitted per second per mL of substance 9 hours after the time of production.

$$A(9\text{h}) = A_0 \times e^{-\lambda t} = 22.6 \text{ MBq}$$

$$A_{\beta^+} = 0.1752 \times A_{\text{ges}} = 3.967 \text{ MBq}$$

Per second  $3.97 \times 10^6$  positrons are emitted.

3 bp

A patient is treated with 3 mL of the above given substance, PET is performed, he is allowed to go home and radioactivity continues to decrease

5.8 Calculate the time (in days) after which the activity in the patient has decreased to 0.5% of the initial value. Assume that 7% of the administered  $^{64}\text{Cu}$  is excreted during this time.

$$\text{Decrease to 0.5\%: } N_t = 0.005 N_{\text{administered}}$$

$$N_t = N_0 e^{-\lambda t}; \text{ wegen Ausscheidung } N_0 = 0.93 N_{\text{administered}}$$

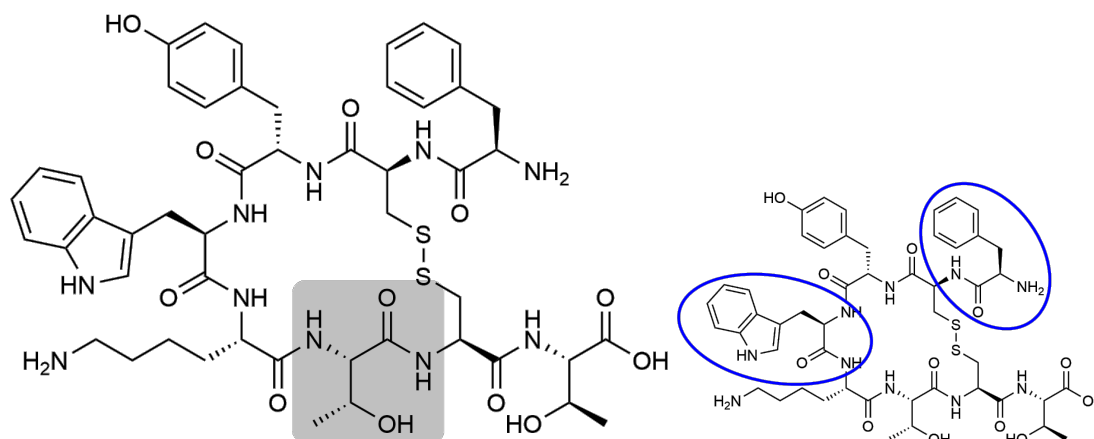
$$\Rightarrow 0.005 N_{\text{administered}} = 0.93 N_{\text{administered}} e^{-\lambda t}$$

$$\Rightarrow t = \frac{\ln 5.376 \times 10^{-3}}{-1.515 \times 10^{-5} \text{ s}^{-1}} = 3.449 \times 10^5 \text{ s} \approx 4 \text{ days}$$

2.5 bp

<sup>1</sup> (<https://dailymed.nlm.nih.gov/dailymed/drugInfo.cfm?setid=f898c8a7-beb7-4318-a8ea-6f058d69342b>, accessed 9.5.2023)

In the following, only the peptide backbone of the DOTATATE ligand (shown below) will be considered.



5.9 How many amino acids are in the peptide?		
8		1 bp
5.10 Calculate the maximum number of all possible stereoisomers of this compound.		
$2^{10}$ or 1024		1 bp
5.11 Natural amino acids exist as L-amino acids. Determine whether the amino acid highlighted in grey is a natural amino acid by drawing the amino acid in the Fischer projection and assigning it the corresponding stereo descriptor D/L.		
$\begin{array}{c} \text{COOH} \\   \\ \text{H}_2\text{N}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_3 \end{array} \quad \text{oder} \quad \begin{array}{c} \text{COO}^- \\   \\ ^+\text{H}_3\text{N}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_3 \end{array}$ , L-amino acid, natural		2 bp
5.12 Circle all non-natural amino acids in the peptide above.		
see above		2 bp

## B. Kinetics of somatostatin decomposition

The peptide hormone somatostatin is secreted in the pancreas during digestion in vertebrates and inhibits the formation of the growth hormone somatotropin. It was first isolated in 1972/73 by Roger Guillemin from the hypothalami of 490 000 sheep.

Somatostatin is indicated for the treatment of various disorders of the pancreas, small intestine and oesophagus. However, the peptide hormone decomposes very rapidly in vivo (in the range of minutes).

The decomposition of somatostatin was studied under different storage conditions (temperature, pH, ionic strength,...). The decomposition was measured in the presence of a phosphate buffer (pH 7.4) at room temperature and an initial concentration of  $0.01 \text{ mol L}^{-1}$ . After 10 days 24% of the somatostatin had decomposed, and after 42 days 65%.

5.13 Fill in the table below and determine mathematically OR graphically the reaction order of decomposition.

time	0 days	10 days	42 days
fraction of somatostatin decomposed	0%	24%	65%
$c(t)$	0.01	0.0076	0.0035
$\ln c(t)$	-4.605	-4.879	-5.655
$1/c(t)$	100	132	286

First order – linear is only  $\ln c(t)$  vs.  $t$

3 bp

5.14 Determine the rate constant of this reaction (with unit).

$$k = 0.025 \text{ d}^{-1}$$

1 bp

5.15 Determine the half-life at the beginning of the reaction.

$$28 \text{ d}$$

1 bp

In addition, the following values for rate constants of the reaction were determined at 23°C and 60°C (units not given, but identical for both!).

$$k(23^\circ\text{C}) = 0.004; k(60^\circ\text{C}) = 0.275$$

5.16 Calculate the activation energy of somatostatin decomposition under these conditions (in  $\text{kJ mol}^{-1}$ ).

$$E_A = \ln \frac{k_{T_2}}{k_{T_1}} \times R \times \left( \frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} = \ln \frac{0.275}{0.004} \times R \times \left( \frac{1}{296.15} - \frac{1}{333.15} \right)^{-1} = 93.8 \text{ kJ/mol} \quad 2 \text{ bp}$$

## Problem 6 (J. Novacek)

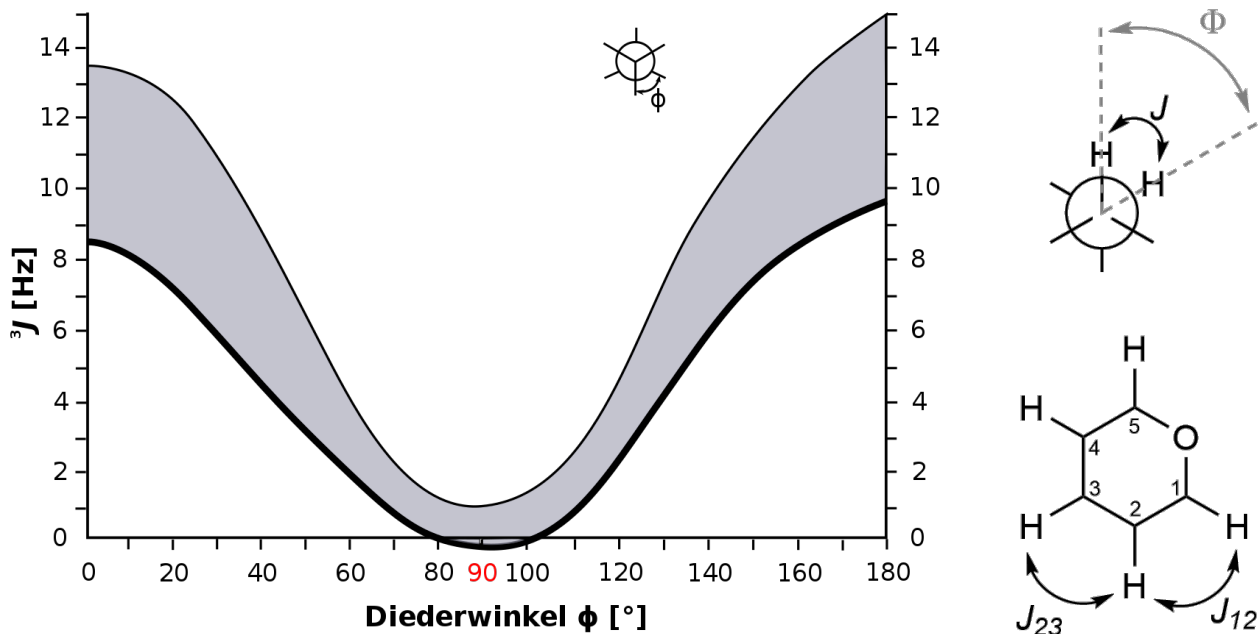
7 bp = 2.5 Points

## About the structure of uronic acids

A. Absolute configuration of  $\alpha$ -L-iduronic acid

NMR spectroscopy is a very powerful method in structure elucidation. From the number of signals, their chemical shifts and their coupling patterns, a lot of information can already be gained about the structure of a compound. Another important contribution to structure elucidation - especially for "more rigid" structural elements such as double bonds or ring structures - is provided by the magnitude of the coupling constant.

The coupling constant of vicinal coupling  ${}^3J$  correlates with the dihedral angle  $\Phi$  according to the Karplus curve shown in the diagram below (named after its discoverer, the Vienna-born US Nobel laureate Martin Karplus).

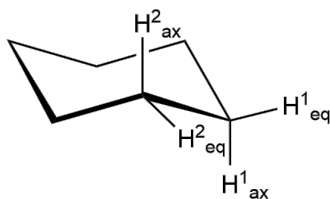


The coupling constants were measured and averaged for several  $\alpha$ -O-substituted *L*-iduronic acids. It was found that these compounds exist in three different conformations that are in equilibrium with each other. Two of these conformations (named  ${}^1C_4$  and  ${}^4C_1$ ) are chair conformations, while the third conformation ( ${}^2S_0$ ) is a twist boat conformation.

For the  ${}^4C_1$  conformation the following coupling constants have been measured:

$$J_{12} = 8.0 \text{ Hz}; J_{23} = 9.7 \text{ Hz}, J_{34} = 9.0 \text{ Hz}, J_{45} = 4.8 \text{ Hz}$$

## 6.1 Determine the dihedral angles below.



$$\Phi(H^1_{eq}, H^2_{eq}) = 60^\circ$$

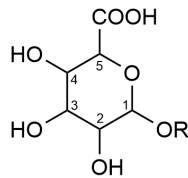
$$\Phi(H^1_{eq}, H^2_{ax}) = 60^\circ$$

$$\Phi(H^1_{ax}, H^2_{eq}) = 60^\circ$$

$$\Phi(H^1_{ax}, H^2_{ax}) = 180^\circ$$

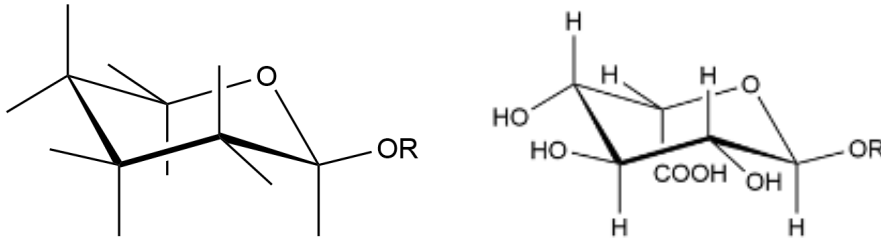
1 bp





An  $\alpha$ -O-substituted *L*-iduronic acid:

6.2 Complete the structure of the  ${}^4C_1$  conformation of  $\alpha$ -O-substituted *L* iduronic acid.

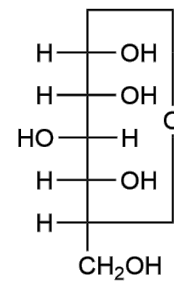


2 bp

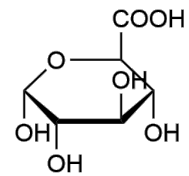
### B. Uronic acids

Uronic acids are formed by oxidation of the primary hydroxyl group of monosaccharides.

The uronic acid derived from *D*-glucose is called *D*-glucuronic acid. Just like saccharides, uronic acids can be open-chain or ring-shaped.

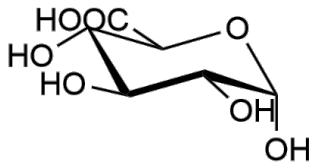


D-Glucose



Uronsäure 3

6.3 Draw the *D*-glucose derived *D*-glucuronic acid in the chair configuration.



2 bp

6.4 Compare each compound with uronic acid 3 and tick the correct answers:

*D*-glucuronic acid and uronic acid 3 are:

conformers

anomers

enantiomers

diastereomers

structural isomers

$\alpha$ -*L*-iduronic acid (R = H) and uronic acid 3 are:

conformers

anomers

enantiomers

diastereomers

structural isomers

enantiomers; diastereomers

2 bp

## Problem 7 (M. Scherl)

36.5 bp = 11 Points

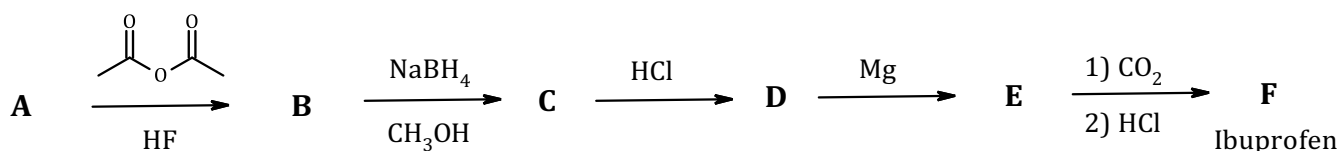
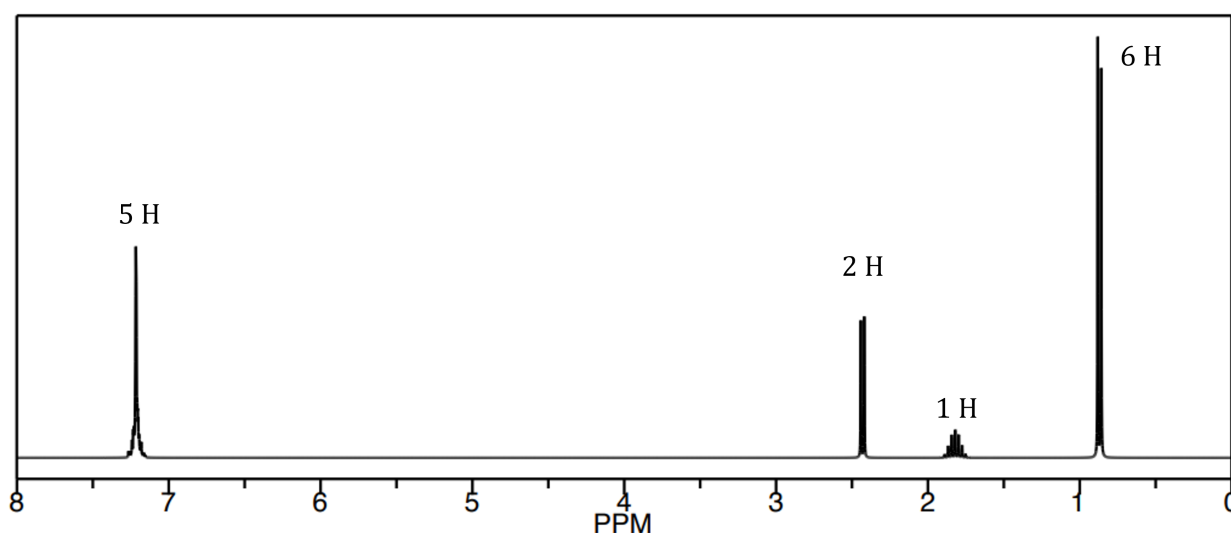
## Analgesic to comatose

## A. Ibuprofen

In July 2022 media reported: "Pharmacies in Germany are currently struggling with supply shortages of medicines for children. There is a shortage above all of fever-control juices containing the active ingredients ibuprofen and paracetamol." This might give you the idea of using proven synthesis knowledge to start your own preparative work. In this assignment, you will deal with the synthesis of ibuprofen ( $C_{13}H_{18}O_2$ ) – at least on paper.

300 mg of the organic compounds **A** with  $M < 150 \text{ g mol}^{-1}$  are combusted at 800 K and 101200 Pa and 281.90 mg water vapor and 1.467 L carbon dioxide are obtained.

Given is a  $^1\text{H-NMR}$  spectrum of **A** in  $\text{CDCl}_3$ .



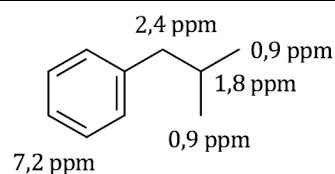
The conversion from **A** to **B** can also be achieved with  $\text{CH}_3\text{COCl}/\text{AlCl}_3$ .

7.1 Write down the sum formula of **A**.

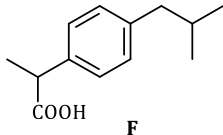
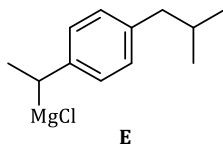
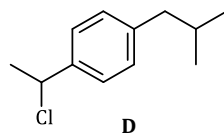
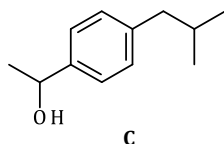
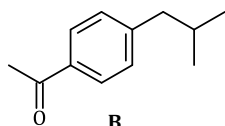
$C_{10}H_{14}$

1.5 bp

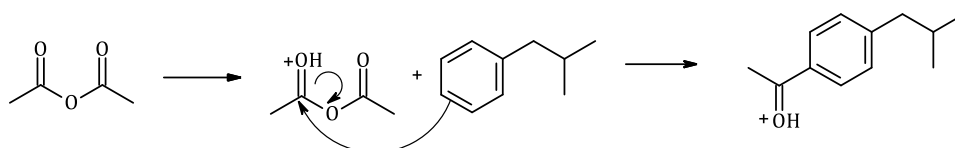
7.2 Draw the constitutional formula of **A** and assign the protons to the signals in the NMR-spectrum by writing the chemical shifts "... ppm" next to the protons in the structure.



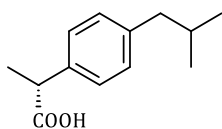
2 bp

7.3 Draw the constitutional formulas of **B - F**.

7.5 bp

7.4 Write down the reaction mechanism for the conversion **A** → **B**.

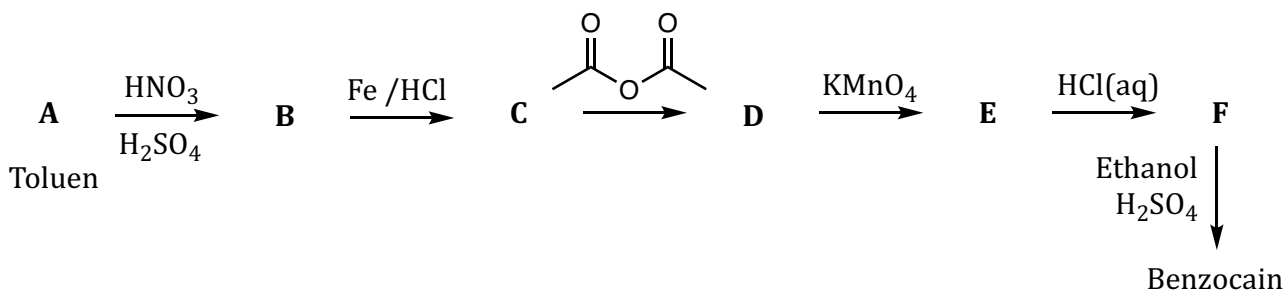
2.5 bp

7.5 *Ibuprofen is used as a racemate. Only the (*S*)-isomer is pharmacologically active. The (*R*)-isomer is converted to the active form in the body by an isomerase. Draw the configuration of the pharmacologically active form.*

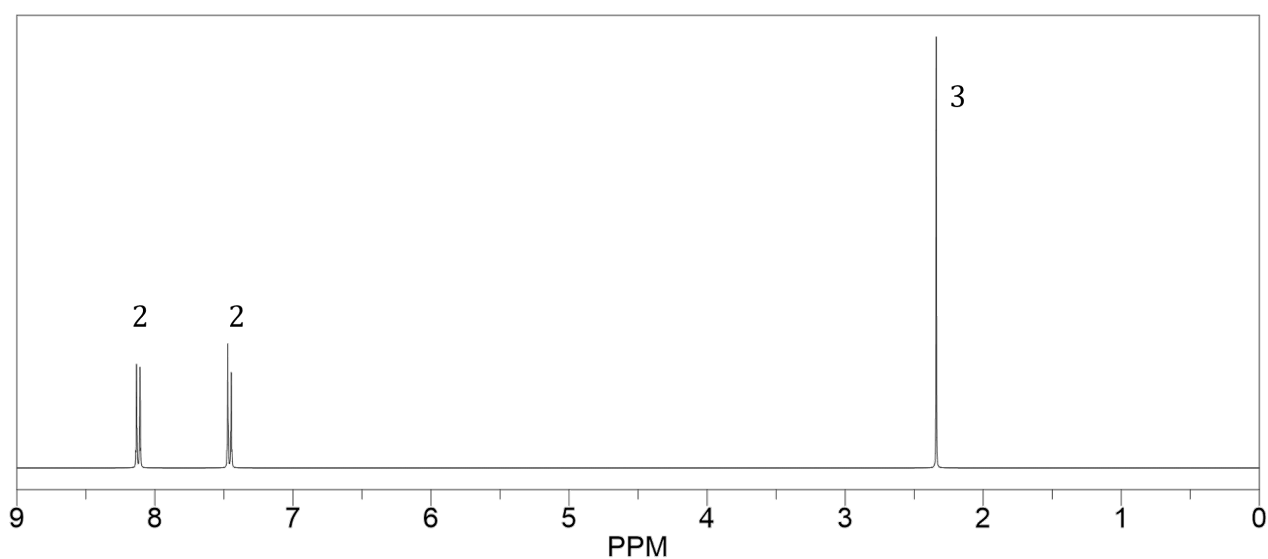
1 bp

**B. Benzocaine**

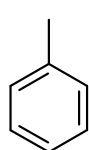
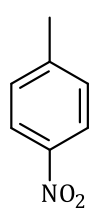
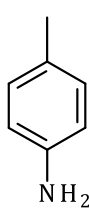
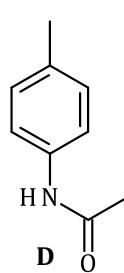
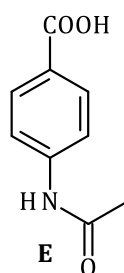
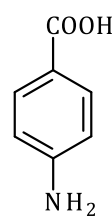
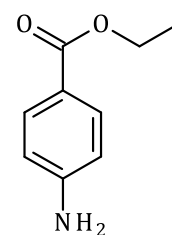
Benzocaine belongs to the group of active ingredients known as local anaesthetics. It is used in numerous over-the-counter (OTC) drugs to relieve painful complaints in the mouth and throat. A synthetic route starting from toluene (methylbenzene) is shown below:



$^1\text{H-NMR}$ -Spectrum of B

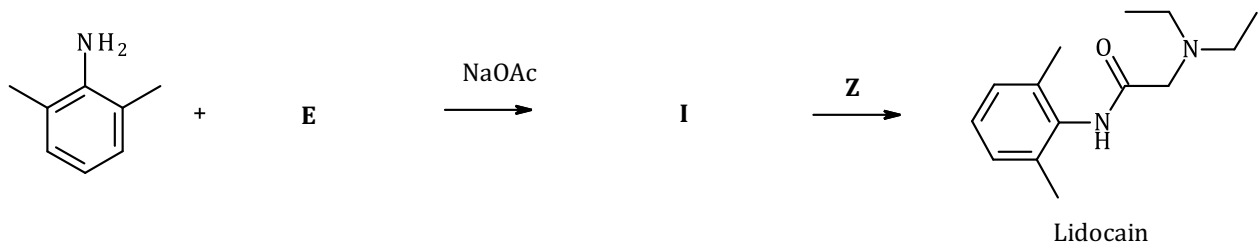


7.6 Draw the constitutional formulas of A – F as well as Benzocaine.

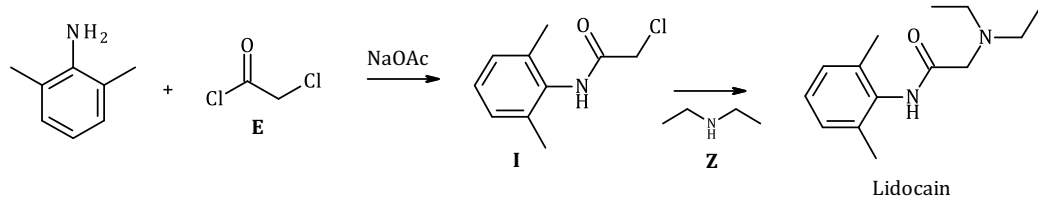
**A****B****C****D****E****F****Benzocaine****8 bp**

### C. Lidocaine

Lidocaine also belongs to the group of active ingredients known as local anaesthetics. It has local anaesthetic, analgesic, antiarrhythmic and antipruritic effects. The effects are based on the inhibition of the influx of sodium ions into the neurons via voltage-dependent sodium channels.



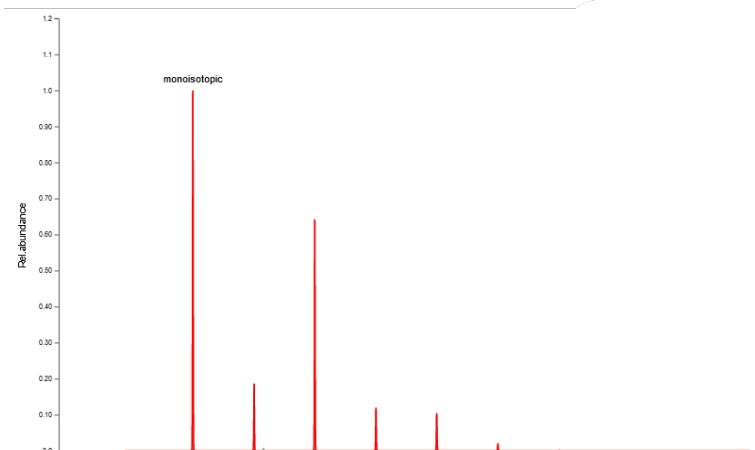
7.7 Draw the constitutional formulas of reactant **E**, intermediate **I** and reagent **Z**.



4 bp

### D. Sertraline

The antidepressant sertraline is a halogenated organic compound. The halogen content in the compound is 23.15%. Furthermore, it is known that only one type of halogen is present in the compound. The isotopic distribution of the compound is also given (the distance between two signal peaks is 1).



7.8 Which halogen is contained in sertraline?

chlorine

1 bp

7.9 Calculate the molar mass of the compound.

The ratio of the isotopes shows that there are 2 chlorine atoms in the compound.

$M(2\text{Cl}) = 70.9 \text{ g/mol}$ ,

$M(\text{sertraline}_2) = M(2\text{Cl})/23.15\% = 306 \text{ g/mol}$

2 bp

While metabolic pathways of drugs-of-abuse are frequently studied, pharmacokinetics is much less explored. However, since it is certainly of importance how these drugs are transported in the body, and especially how they thereby influence the transport of other substances (be they

endogenous substances or drugs), the transport of various drugs-of-abuse by means of P-glycoprotein (a membrane protein) has been studied. Sertraline is considered a model substance (and reference) for this transport. The induced activity of the ATPase follows Michaelis-Menten kinetics.

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

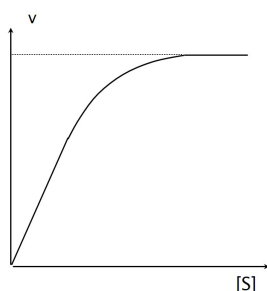
For  $[S] = 2 \mu\text{mol L}^{-1}$  a velocity of  $0.001075 \text{ mol L}^{-1} \text{ min}^{-1}$  was measured, the maximum velocity was determined to be  $0.0043 \text{ mol L}^{-1} \text{ min}^{-1}$ .

7.10 Write down the value of  $K_M$  with the corresponding units.

$$K_M = 6 \times 10^{-6} \text{ mol/L}$$

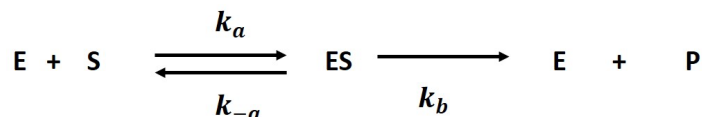
1 bp

7.11 Sketch a diagram in which you plot  $v$  against  $[S]$ . It is not necessary to scale the axes.



1 bp

The following mechanism can be assumed for an enzymatic reaction:



Thereby applies:

- For ES a steady-state-approximation can be assumed.
- The substrate is present in excess, the rate of reaction corresponds to the rate of formation of the product.
- The total amount of enzyme  $[E]_0$  consists of free enzyme and the enzyme in the enzyme-substrate complex.

7.12 Write down the differential rate equations for  $[ES]$  and  $[P]$ .

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

$$\frac{d[P]}{dt} = k_b[ES]$$

2 bp

7.13 Specify the expression that is set to zero when assuming a steady-state-approximation.

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

3 bp

## Problem 8 (M. Scherl)

23 bp = 7 Points

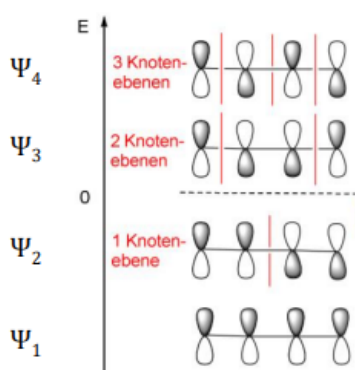
## Woodward and his frontier orbitals

Robert B. Woodward was one of the most important synthesis chemists. In the 1960s, for example, he developed the synthesis of vitamin B12 with A. Eschenmoser (ETH-Zurich). With R. Hoffmann, he applied electron theory to synthetic problems. Together they developed the "Woodward-Hoffmann rules", which allow statements about the course and products of pericyclic reactions, depending on whether they proceed thermally or photochemically.

A. Detailed investigation of a  $\pi$ -system

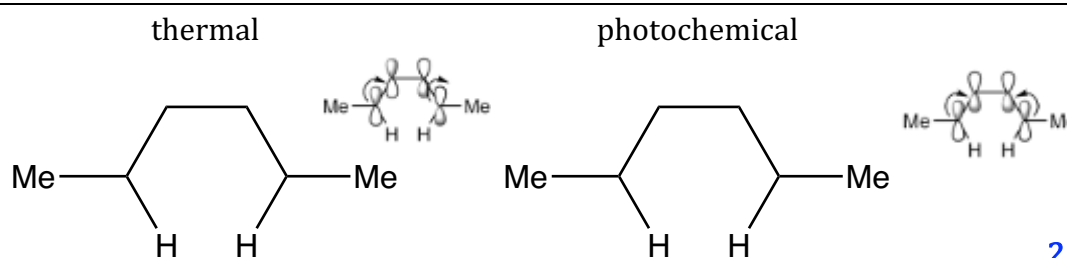
(*E,E*)-Hexa-2,4-diene forms different products depending on the reaction conditions which can be either photochemical or thermal.

8.1 Draw the  $\pi$ -orbitals of (*E,E*)-hexa-2,4-diene and sort them according to increasing energies (1 = lowest energy).



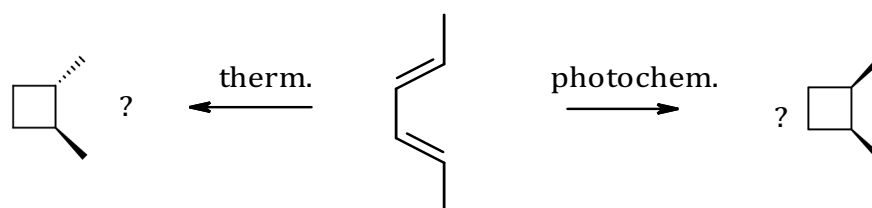
2 bp

8.2 In the representations of hexa-2,4-diene, draw the relevant  $\pi$ -orbitals for a photochemical or thermal reaction. In addition, draw arrows showing the rotation of the orbitals leading to a binding orbital overlap.



2.5 bp

8.3 Write down the configurational formulas for thermal and photochemical cyclization of above hexadiene and assign the terms disrotatory and conrotatory.



disrotatory

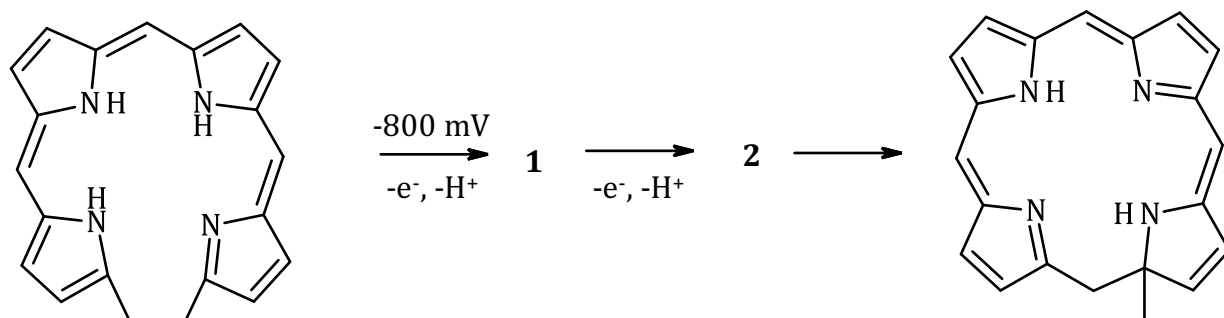
conrotatory

2 bp

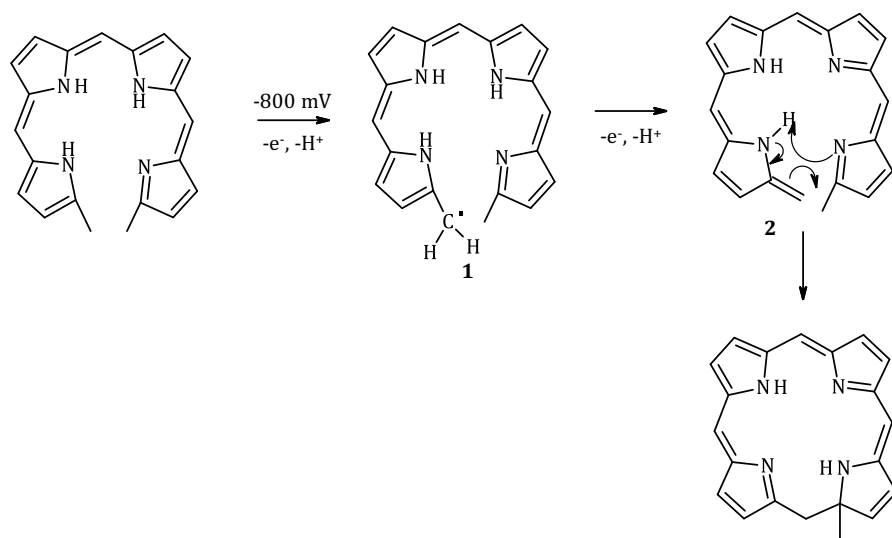
**B. Porphyrins**

Porphyrins (from the ancient Greek πορφύρα, porphyra, purple dye) are dyes consisting of four pyrrole rings linked by four methine groups to form a cycle. Prominent representatives are chlorophylls and heme (in enzymes and haemoglobin).

In 1993, Smith proposed a mechanism for an electrochemical synthesis of porphyrins.



**8.4** Draw the constitutional formulas of **1** and **2**. Draw arrows in the structure of **2** showing those electron pair movements that lead to the formation of the product.



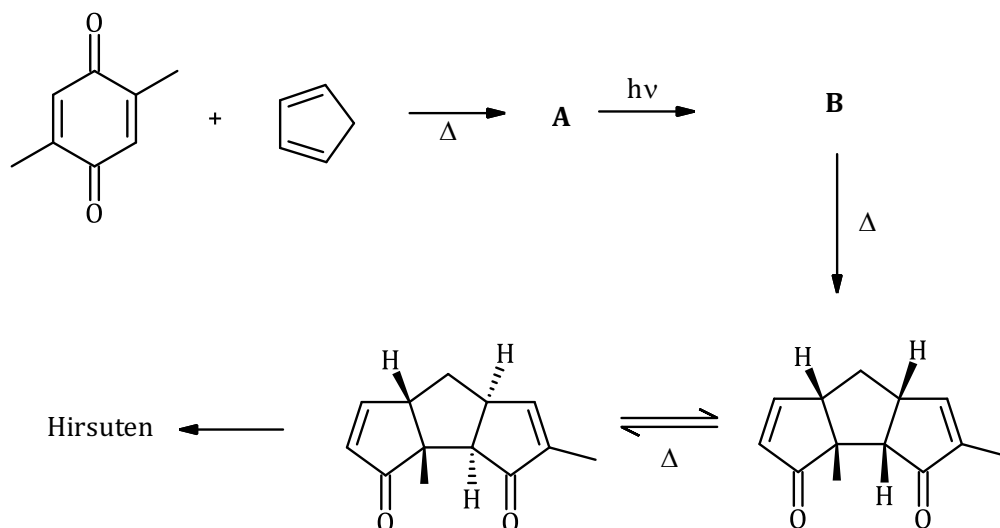
4.5 bp



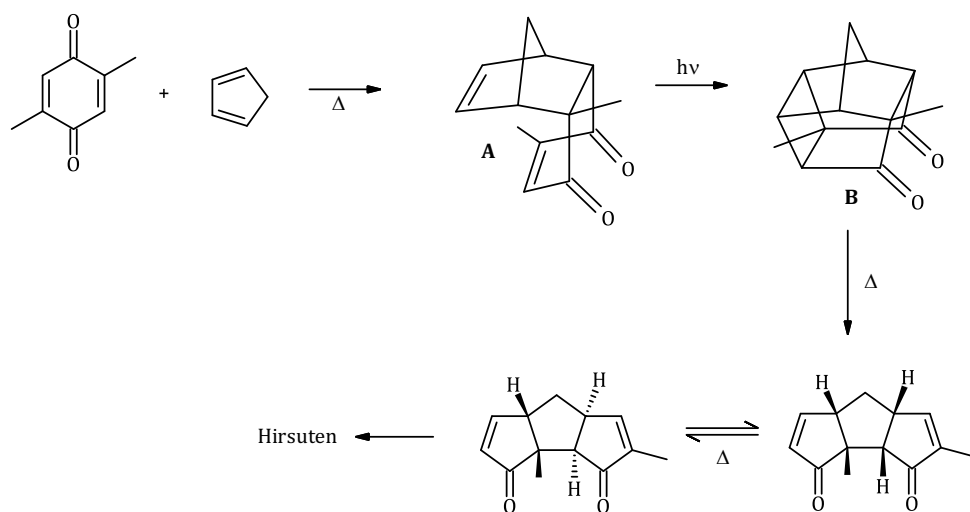
### C. Hirsuten as a model compound for cyclizations and pericyclic reactions

Although the sesquiterpene hirsuten is biologically inactive, it has served as a model for various syntheses (ring expansions, radical cyclizations, cycloadditions and some rearrangements). In 2002, Banwell et al. reported the preparation of hirsuten from the toluene-derived cyclohexadiene diol via a Diels-Alder reaction.

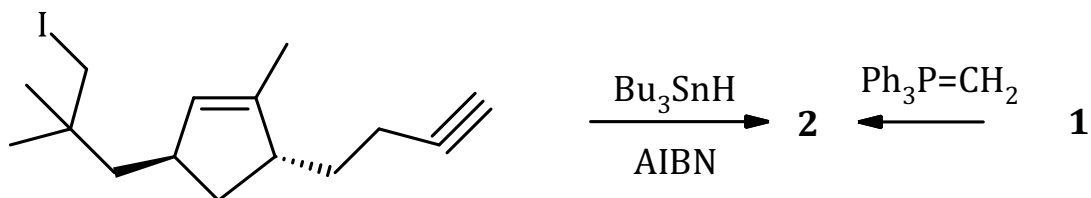
The synthesis shown below starts from an dioxo-compound:



8.5 Draw the structural formulas of **A** and **B** with the correct stereochemistry.

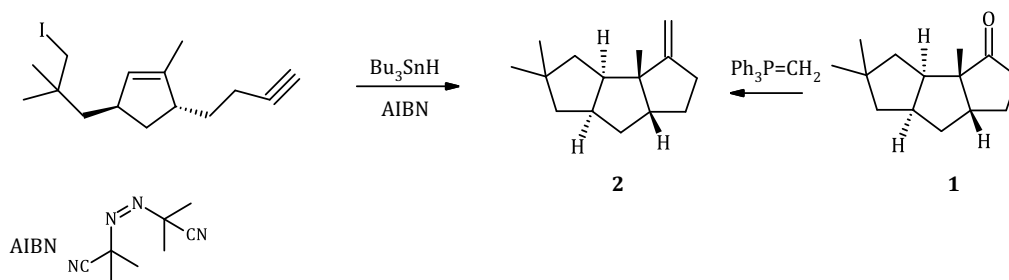


5bp



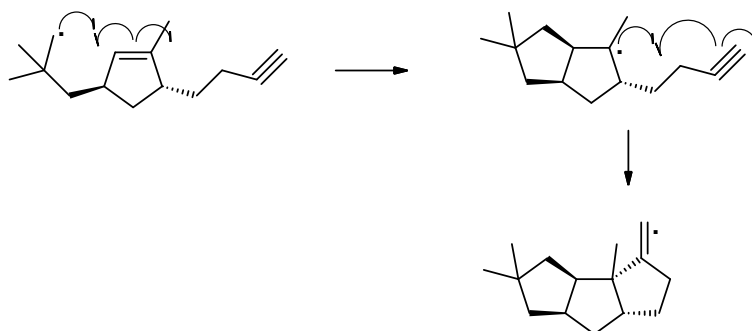
AIBN: Azobisisobutyronitrile ( $\text{NC}((\text{CH}_3)_2)\text{CN}=\text{NC}((\text{CH}_3)_2)\text{CN}$ ); like its precursor Hirsuten has three five-membered carbocycles.

8.6 Draw the structural formulas of **1** and **2** (hirsuten) with the correct stereochemistry. If you do not obtain a structure of **2**, show the reaction with  $\text{Ph}_3\text{P}=\text{CH}_2$  using general constitutional formulas.



4 bp

8.7 Draw the mechanism for the conversion of the iodinated enyne into **2** (hirsuten).



3 bp