

# 47. Austrian Chemistry Olympiad Substitute Competition Level II

June, 24<sup>th</sup> 2021

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**Notes – as a reminder**

You have already received the instructions in advance of the competition, here are just a few key words to remind you:

- You are solely responsible for ensuring that we can match and read your answers.
- Show calculation methods if required.
- Do not forget units.
- Use all digits of molar masses and constants!
- In organic reaction schemes, use the abbreviations (e.g.: MsCl, tBu...) that are also used in the statement.

## Iron

## A. Bornite

Bornite, ( $\text{Cu}_5\text{FeS}_4$ ,  $M = 501.88 \text{ g mol}^{-1}$ ), named after the Austrian Mineralogist Ignaz von Born, is an abundant mineral. Pretty crystals, however are rare. Like all sulfide ores, Bornite can be roasted, *i.e.* heated under oxygen supply leading to the with the formation of copper(II)oxide, iron(III)oxide, and sulfur(IV)oxide.

1.1 Write a balanced equation for roasting with integer coefficients.

When looking at the structure of bornite, one quickly encounters complicated relationships. Above 228 °C, a high-temperature modification ("high bornite") is stable. The sulfide ions form a cubic close packing, where Cu and Fe occupy the tetrahedral holes (TL).

1.2 To which Bravais lattice does a cubic closed packing correspond and along which line (edge, face diagonal, space diagonal) do the atoms touch each other?

1.3 Specify the number of TL in a unit cell.

1.4 Find the fractions of TL in the unit cell that are occupied by Cu and Fe ions. Write fractions, not decimals.

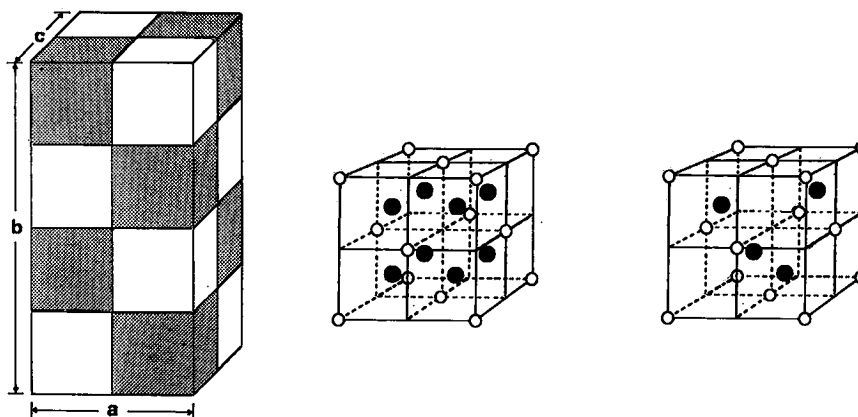
The lattice constant of high bornite is  $a = 5.50 \text{ \AA}$ .

1.5 Calculate the density of high bornite in  $\text{g cm}^{-3}$

On cooling the high bornite transforms into a low-temperature modification (low bornite). The metal ions seem to keep their arrangement, but the symmetry is lost, and so low bornite can be attributed to the orthorhombic system. The density increases slightly to  $5.09 \text{ g cm}^{-3}$ .

The following structure has been proposed. The repetitive unit is a "supercell" of two cubic cells A and B

:



from left to right: Supercell, cell type A, cell type B  
(modified, from Canadian Mineralogist Vol 16 (1978), pp. 397-404)

In cell type A all TL are occupied, in cell type B half of the TL are occupied with Cu-ions.

**1.6** Give the number of bornite formulae units in the above shown supercell.

**1.7** Find the fractions of the TL in A-type cells that have to be occupied by Cu- and Fe-ions so that the correct formulae of bornite results. Write fractions, not decimals.

In fact symmetry is distorted, the aspect ratios of the supercell are  $a:b:c = 0.501:1:0.501$ .

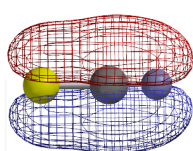
**1.8** Calculate the lattice constants  $a$ ,  $b$ ,  $c$  for low bornite.

**B. Iron complexes**

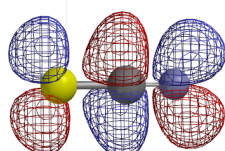
Numerous iron complexes are known. You certainly are familiar with the detection of iron by  $\text{SCN}^-$ .

1.9 Draw two Lewis structures for the thiocyanate ion, showing that this ion can coordinate with both the N and the S atom.

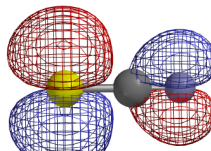
Below you can see four calculated molecular orbitals of the thiocyanate ion, with the S atom being on the left in each case.



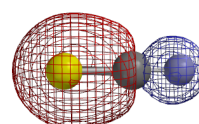
(A)



(B)



(C)



(D)

1.10 Answer the following questions by writing the letter(s) of the correct orbital image(s) to the question number..

- 1) Anti-bonding between C and N is ...
- 2) The orbital with the highest energy is ...
- 3) The MO containing a stand-alone p-orbital of the S-atom ...
- 4) The MO with  $\pi$  - bonding over all atoms is ...
- 5) A  $\sigma$ -bond is represented by ....

1.11 Sketch the two configurational isomers for  $[\text{Fe}(\text{OH}_2)_3(\text{SCN})_3]$  and assign the correct stereo-descriptors.

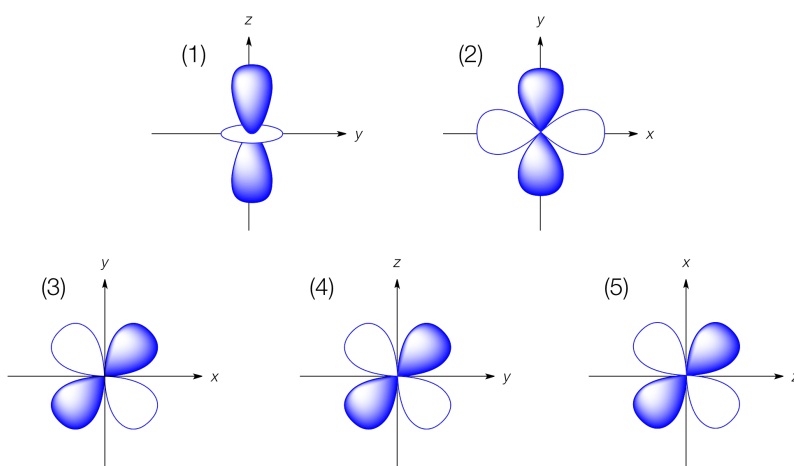
1.12 Name the complex  $[\text{Fe}(\text{OH}_2)_3(\text{SCN})_3]$

A salt containing hexacyanidoferrate(II) as anion consists of 43.75% N, 9.990% O, 6.308% H as well as carbon.

1.13 Calculate C-content in mass percent rounded to two decimals.

1.14 Determine the complete formulae of the salt by calculation. Hint: Start with the iron in the anion. .

Many complexes of iron are octahedral. As it is well known, the ligands cause the splitting of the d-orbitals. In the octahedral ligand field, a distinction is made between the energetically elevated  $e_g$  orbitals (1) and (2) and the lowered  $t_{2g}$  orbitals (3) - (5), which are shown here:



1.15 Assign the standard labels to the d-orbitals (1) to (5).

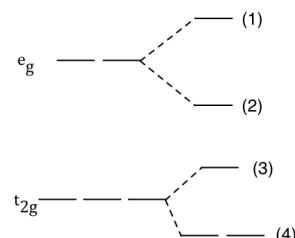
The hexacyanidoferrate(II)-ion is a diamagnetic, low-spin, octahedral complex with  $\Delta_0 = 32800 \text{ cm}^{-1}$  and  $P = 210 \text{ kJ/mol}$ .

1.16 Write the complete (!) electron configuration for the central atom.

1.17 Express  $\Delta_0$  in units of eV.

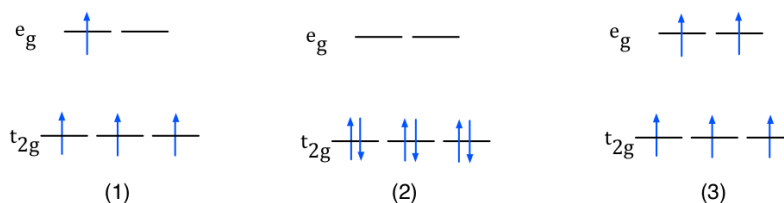
1.18 Calculate the ligand field stabilisation energy (LFSE) for the complex in eV.

Some complexes show the so-called Jahn-Teller effect: the regular octahedron is distorted into a square bipyramid by moving the atoms on the  $z$ -axis further from the centre. The energy levels become split even further. However, the effect only occurs, if a further enlargement of the LFSE can be achieved.



1.19 Which of the d-orbitals is being raised or lowered? Assign the standard labels (e.g.  $dz^2$ ) to each d-orbital from (1) to (4)

Three different electron configurations for (undistorted) octahedral complexes are shown.



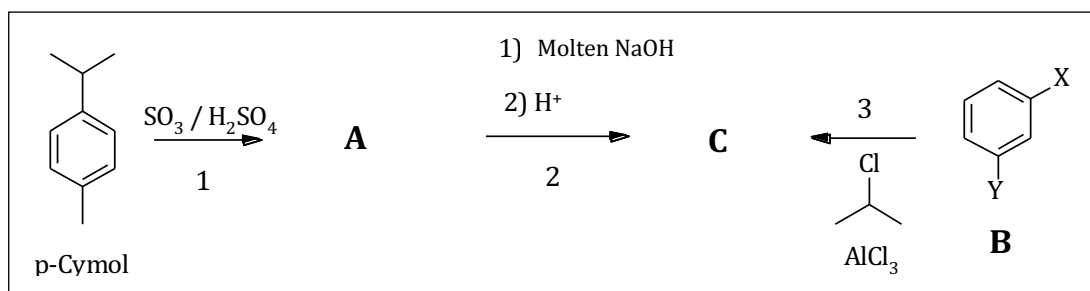
1.20 Assign „yes“ or „no“ to the configurations (1), (2), (3) depending on whether or not you expect a distortion by the Jahn-Teller-effect.

### Cooking with chef Scherl

Chemistry was not neglected when cooking online with Chef Scherl and his assistants. A lasagne was prepared as a delicious dish.

#### A. Typical Italian flair – synthesis of oregano

The flavouring substance in oregano (C) is a monoterpene that must not be missing in any lasagne.



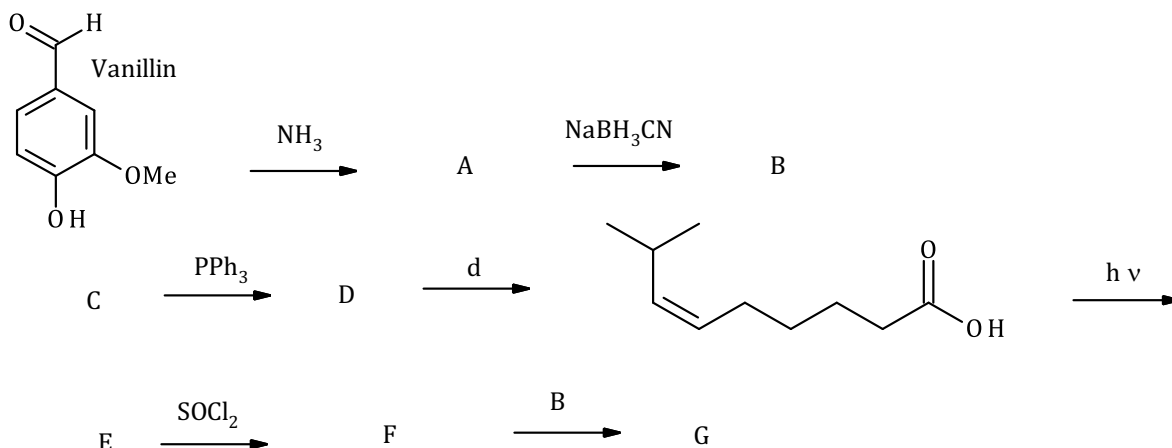
2.1 Draw structural formulae of **A**, **B** and **C**.

2.2 Indicate the reaction mechanisms for reactions 1, 2, and 3 in the above scheme.

2.3 In one sentence, state the reason why aluminium chloride is used as catalyst for reaction 3.

**B. Really spicy – from vanillin sugar to chili**

Chili is essential for a viable lasagna recipe. Chilies contain a substance responsible for "spiciness". Strangely enough, a reactant for its synthesis is vanillin.

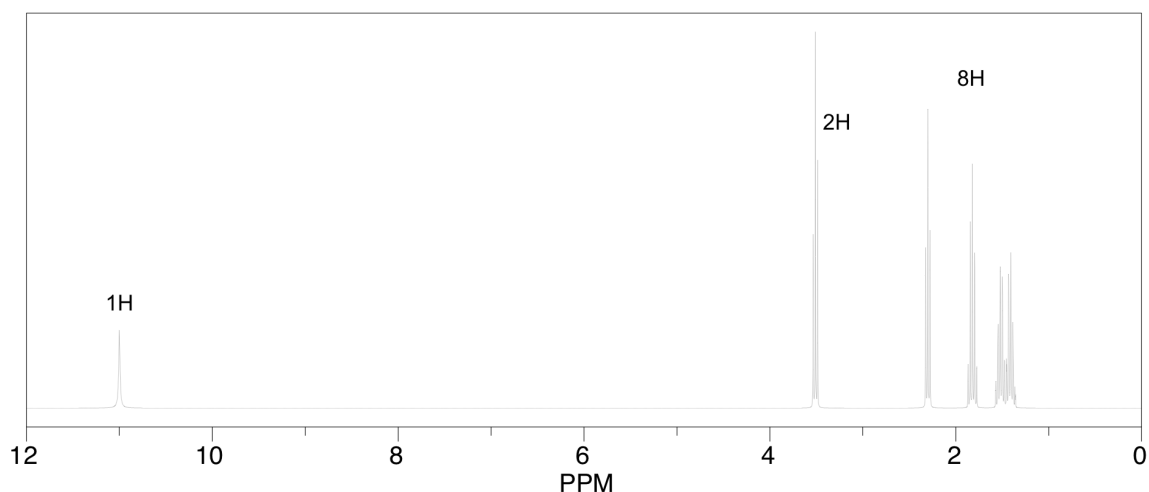


Hints:

- For substance **C** ( $\text{C}_6\text{H}_{11}\text{BrO}_2$ ) see the  $^1\text{H-NMR}$ -spectrum below.
- In the spectrum of **E** there are two signals (range  $\delta = 6$  to  $7$  ppm) with a coupling constant  $J = 15.8$  Hz.

2.4 Draw the structural formulae of substances <b>A - G</b> .
2.5 Write down the two reagents for <b>d</b> .
2.6 Determine the stereo descriptor for the product of reaction <b>D</b> with <b>d</b> and state the type of isomerism.
2.7 Give the IUPAC name of vanillin.

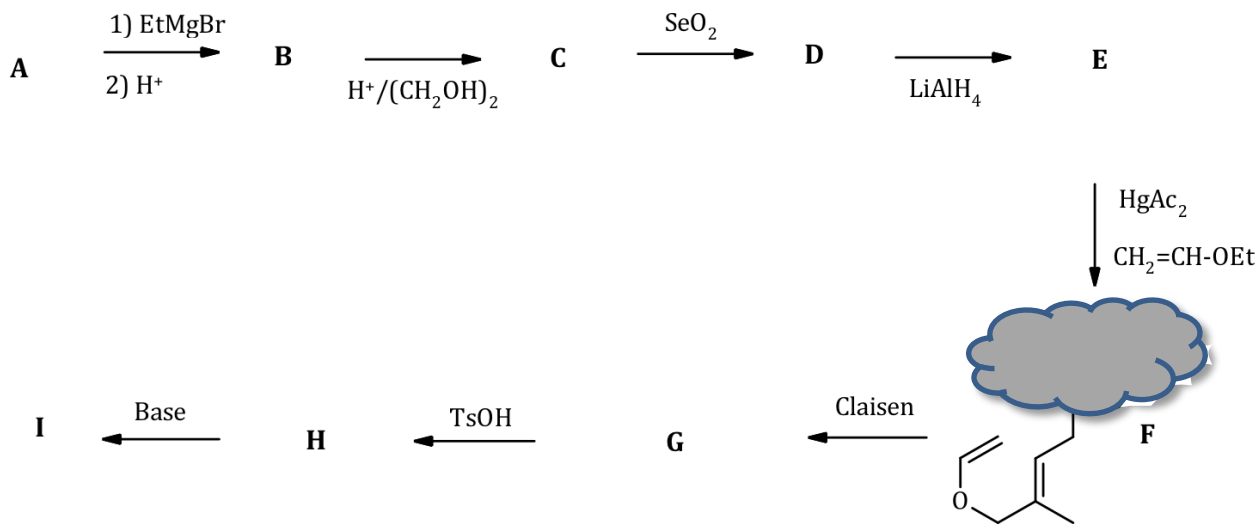
$^1\text{H-NMR}$  of substance **C**





## C. Fit by coleslaw - synthesis of caraway

Fresh coleslaw is rich in vitamin C and of course caraway must not be missing. Synthesis of its main ingredient is shown below, whereby, unfortunately, a cloud has also been placed over the scheme.

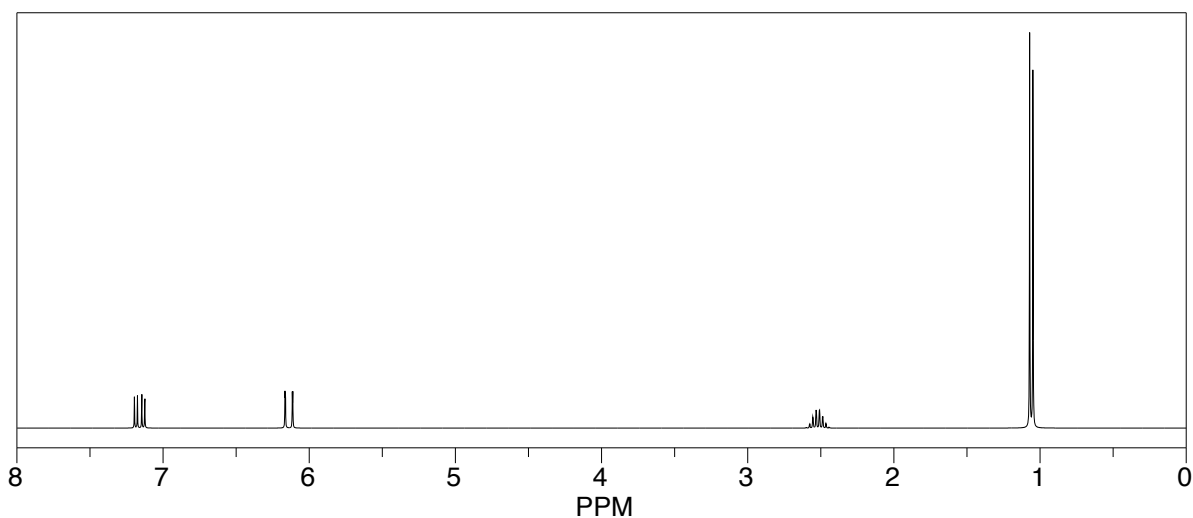


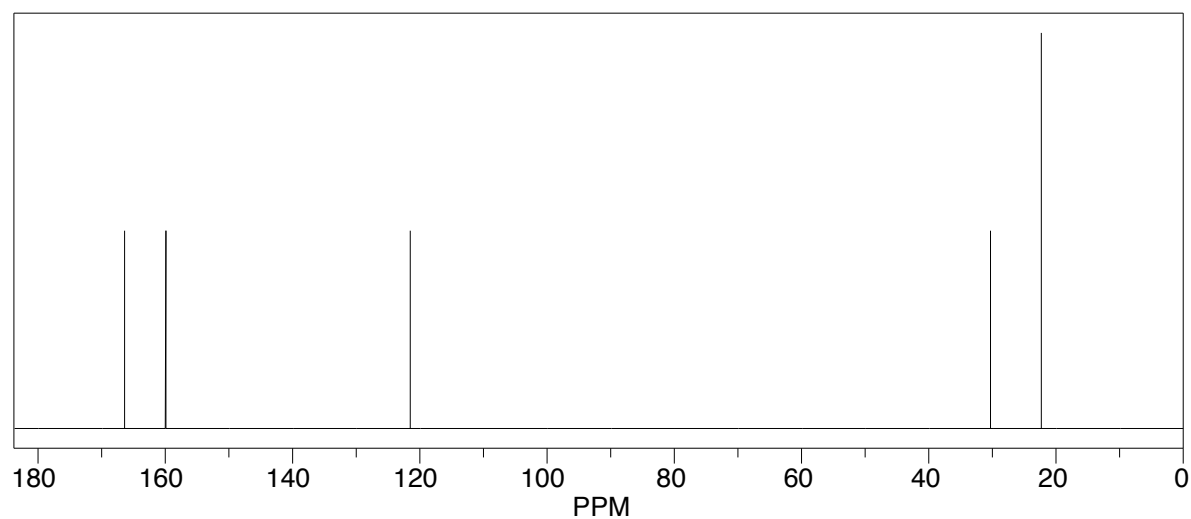
Hints:

**A** shows two molecular peaks in the mass spectrum in the ratio 75:25 = 132u:134u. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of **A** are given. The two H nuclei (δ = 6.14 ppm and 7.18 ppm) have a coupling constant J = 16 Hz. **A** is particularly unstable to hydrolysis.

**C** has only one proton in the range of 6-7 ppm and cannot form E/Z isomers. **D** has a proton at 9.8 ppm in the <sup>1</sup>H-NMR spectrum. When forming **F** from **E**, the group hindered by the cloud remains unchanged. **I** has a molecular formulae of C<sub>10</sub>H<sub>14</sub>O.

### <sup>1</sup>H-NMR-Spektrum von A



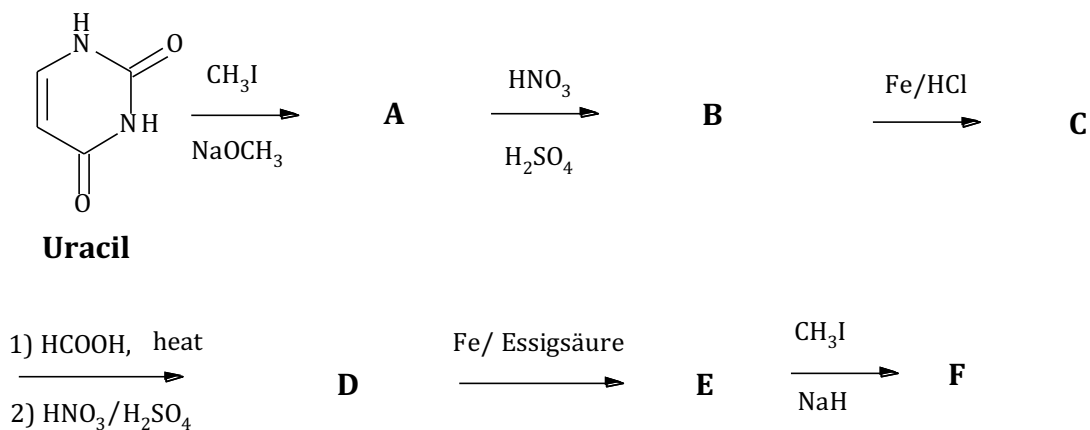
<sup>13</sup>C-NMR-spectrum of **A**

*2.8 Draw structural formulae of A - I. Draw the R-enantiomer of I.*

*2.9 In the structure of H label the most acidic H-atoms.*

**D. Cheerful again – synthesis of coffee**

An ingredient of coffee can be synthesised as shown below.



Hints:

**A** contains 6 C-atoms.

During the conversion from **D** to **E** a further heterocycle is formed via a ring closure.

<i>2.10 Draw structural formulae of <b>A - F</b>.</i>
<i>2.11 Name the mechanisms for 1) the reaction <b>Uracil</b> → <b>A</b> and 2) the reaction <b>D</b> → <b>E</b> in the above given scheme.</i>
<i>2.12 Draw a mesomeric structure of <b>A</b>, that clearly shows the reactive position of that molecule.</i>
<i>2.13 Describe the role of <b>NaOCH<sub>3</sub></b> and <b>NaH</b> respectively for the reactions <b>Uracil</b> → <b>A</b> and <b>E</b> → <b>F</b></i>

## Thermodynamic

### A. Calcium chloride

Calcium chloride is a well-known desiccant due to the high hygroscopicity of anhydrous  $\text{CaCl}_2$ . It can be made by dissolving lime in hydrochloric acid:

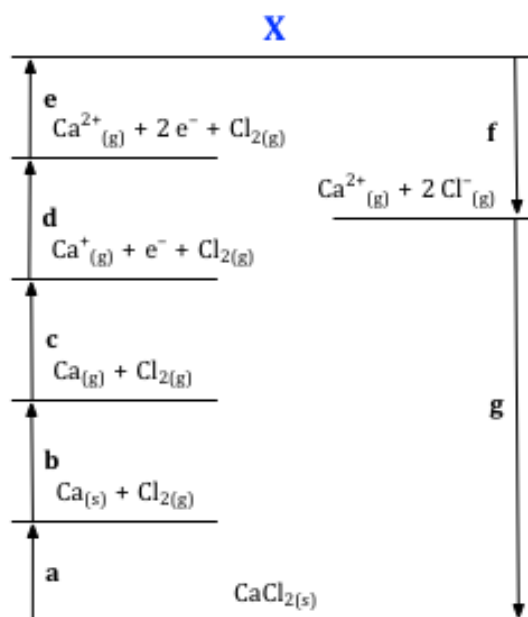
$\text{CaCO}_{3(s)} + 2 \text{HCl}_{(aq)} \rightarrow \text{CaCl}_{2(aq)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)}$ . Per 50 g of  $\text{CaCO}_3$ , 7.3 kJ of energy are released. First, a hexahydrate is obtained from the solution. Then it is dried at standard pressure by heating to almost 300° C to the anhydrous form. That requires 362 kJ of energy per mole of  $\text{CaCl}_2$ .

The table shows some enthalpies:

	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}_{(s)}$	$\text{H}_2\text{O}_{(l)}$	$\text{H}_2\text{O}_{(g)}$	$\text{CO}_2_{(g)}$	$\text{HCl}_{(g)}$	$\text{HCl}_{(aq)}$
$\Delta_f H^\circ / \text{kJmol}^{-1}$	-2608	-285.8	-241.8	-393.5	-92.31	-167.2

*3.1 Calculate the enthalpy of formation for  $\text{CaCl}_2$  with 1 decimal place.*

Of course anhydrous  $\text{CaCl}_2$  can also be produced from the elements according to the Born-Haber cycle given below:



Here is a list of enthalpies most of which are given:

		$\Delta H^\circ$ -values in kJ/mol
(1)	First ionisation energy of Ca	590.0
(2)	Second ionisation energy of Ca	1145.0
(3)	Bond dissociation enthalpy of $\text{Cl}_2$	242.6
(4)	Lattice energy of $\text{CaCl}_2$	?
(5)	Negative enthalpy of formation of $\text{CaCl}_2$	?
(6)	Sublimation enthalpy of calcium	177.8
(7)	double electron affinity of Cl (as $\Delta_{\text{Ea}}H$ )	-698.0

If you did not get a value at 3.1 use  $\Delta_f H^\circ(\text{CaCl}_2) = -1000$  kJ/mol.

3.2	Indicate the species present at the step designated X. Do not forget indices and electric charges.
3.3	Assign the numbers of the energies (1) to (9) to the letters in the Born-Haber cycle a to h.
3.4	Calculate the lattice energy of $\text{CaCl}_2$ .

**B. Fritzi, entropy and humidity**

The change in entropy of an ideal gas during isothermal expansion or compression can be expressed as

$$\Delta S = nR \ln \frac{V_2}{V_1} = -nR \ln \frac{p_2}{p_1}$$

*3.5 Prove the equivalence of the two expressions (with  $V$  and  $p$  respectively) for an ideal gas.*

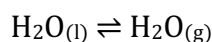
The value for the molar standard evaporation entropy ( $\Delta_{\text{vap}}S^\circ$  109.1 J K<sup>-1</sup> mol<sup>-1</sup>) at 1 bar (100000 Pa) is less known than the boiling point of water (373.15 K) at 1 atm (101325 Pa). In the following, let us treat water vapour as an ideal gas.

*3.6 Calculate the molar entropy change when water vapour is brought from standard pressure (1bar) to 1 atm. Give the answer with 5 significant figures.*

*3.7 Calculate the molar entropy of evaporation of water at 1 atm and 100 °C. Give the answer with 5 significant figures.*

*3.8 Calculate the enthalpy of evaporation of water  $\Delta_{\text{vap}}H_{373.15}$ . Give the answer with 5 significant figures.*

The process of evaporation can be described like a chemical reaction:



From the standard enthalpies of formation at 298 K one can calculate a “standard enthalpy of reaction” - the standard enthalpy of evaporation  $\Delta_{\text{vap}}H^\circ_{298}$

The  $\Delta_f H^\circ$  values for water are taken from the previous section.  $C_p(\text{H}_2\text{O}_{(l)}) = 75.30 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $C_p(\text{H}_2\text{O}_{(g)}) = 33.60 \text{ J K}^{-1} \text{ mol}^{-1}$

*3.9 Calculate the standard enthalpy of evaporation of water  $\Delta_{\text{vap}}H^\circ_{298}$  and the enthalpy of evaporation  $\Delta_{\text{vap}}H_{373}$ . Using Kirchhoff's law.*

Little Fritzi always has problems with the respiratory tract. Frightened, his parents realize that in his bedroom (48.6 m<sup>3</sup> air volume) at 22 ° C, there is a relative humidity of only 38%. The saturation vapor pressure at this temperature is 2646 Pa.

*3.10 Calculate the partial pressure of the water vapor in the bedroom in Pa.*

The parents wet a tea towel (40×50 cm), the cloth absorbs 70.0 g of water, and they hang it in Fritzi's room. After 6 hours, the cloth is dry. The pressure in the room is 1 atm. Assume that the water from the tea towel is wholly turned into humidity.

*3.11 Calculate the humidity after the tea towel drying.*

### C. Bart and Henry

Fritzi's elder brother Bart is keen on medium-dangerous experiments. He came up with the idea of making soda water and got himself dry ice ( $\text{CO}_2(\text{s})$ ). According to the Austrian Food Book, water must contain at least 4g/L carbon dioxide to be called soda water. To be on the safe side, Bart takes 20 g (0.500 mol) of dry ice. His room has 20°C (293 K) and air pressure of 1.013 bar. He finds a screw-on glass jug (1.00 L content), inserts the dry ice, and quickly screws the lid. Then he wants to get water and leaves. Luckily he is not in the room when the glass explodes after the sublimation of half of the dry ice.

*3.12 Calculate the pressure in the glass immediately before the explosion in bar with two decimals.*

Such mishaps do not shake Bart. To a second similar glass jug, he first adds 0.500 L of water ( $\rho = 1.00 \text{ g cm}^{-3}$ ) and then again, the same amount (0.500 mol) of dry ice and closes it immediately. According to Henry's law (for  $\text{CO}_2$  at this temperature, the Henry constant  $K_{\text{H}(\text{x})} = 1.418 \text{ bar}$ ), some of the  $\text{CO}_2$  now dissolves in water, thus, saving Bart from a second explosion. In the following, neglect any protolysis reactions of  $\text{CO}_2$  in the water, the change in the amount of liquid by the dissolved  $\text{CO}_2$ , the air dissolved in water, and the volume of solid  $\text{CO}_2$ .

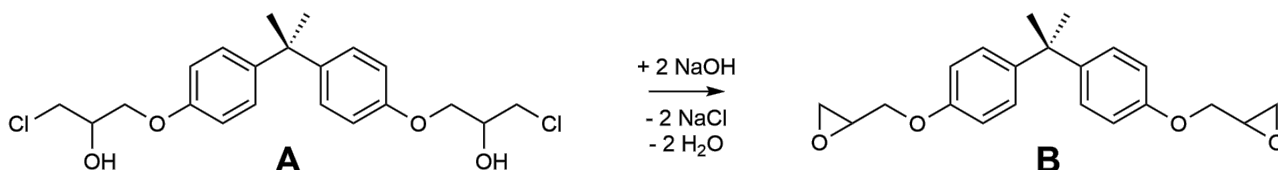
*3.13 Calculate the amount of substance of air in the sealed vessel.*

*3.14 Calculate the pressure (in bar) in the vessel after complete sublimation and adjustment of the solubility equilibrium at 293 K.*

## Kinetics of Epoxides

## A. Dehydrochlorination of Bisphenol A-Chlorohydrinethers

In the synthesis of epoxy resins, bisphenol A is converted with epichlorohydrin to (A). At the end of synthesis, excess epichlorohydrin is distilled off and still contained in (A) chlorine is separated by dehydrochlorination so as not to exceed a chlorine content of 0.1% in the product. Dehydrochlorination is carried out in two stages with sodium hydroxide.



The following values were recorded when determining the reaction rate:

$t / \text{min}$	0	1	5	10	20	40	60
$[A] / \text{mol/L}$	1.000	0.3400	0.0940	0.0490	0.0252	0.0128	0.0086
$\ln[A]$	0.000	-1.079	-2.364	-3.016	-3.681	-4.358	-4.756
$1/[A]$	1.000	2.941	10.64	20.41	39.68	78.13	116.3

4.1 Draw a diagram that shows the decrease of  $[A]$  versus time (in min).  
Use: 1 min ... 0.25 cm, 1 mol/L ... 10 cm

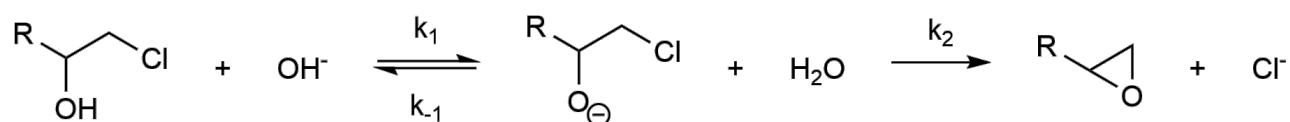
4.2 Determine the reaction order of this reaction. You can do this graphically or mathematically, but you have to show your approach. If you proceed mathematically show the correspondence to the rate law for at least three data points.

4.3 Write the differential rate law and report the value of rate constant  $k$  (to one decimal place) with appropriate units.

4.4 From 4.3 derive an expression for half-half life  $\tau$ .



Dehydrochlorination takes place according to the following mechanism:



The apparent rate constant can be expressed as:

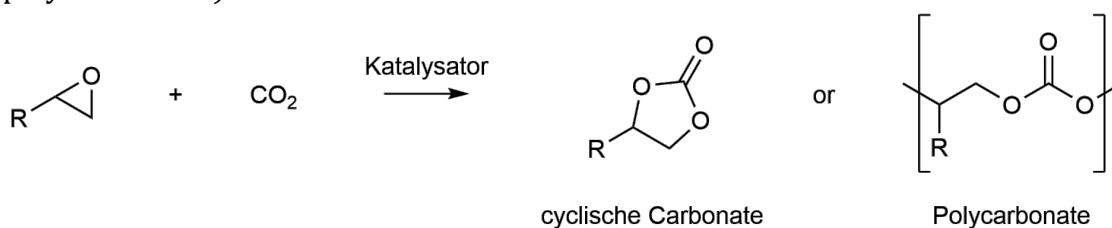
$$k_{app} = \frac{k_1 \cdot k_2}{k_{-1} \cdot [\text{H}_2\text{O}] + k_2}$$

4.5 Indicate whether the following statements are true (W) or false (F) by writing the number of the question on your answer sheet and then (W) or (F)

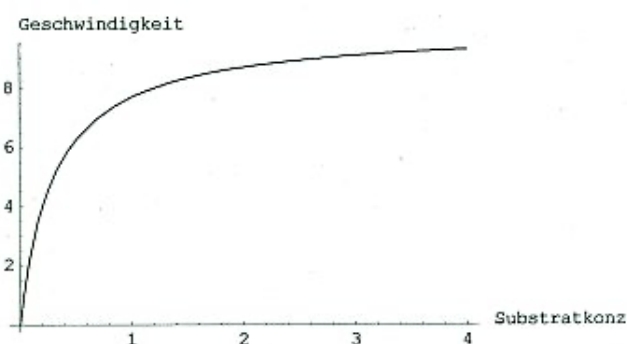
- 1) From the dependence of  $k_{app}$  on the water concentration one can deduce the ratio of the individual rate constants to one another
- 2) If  $k_2 \gg k_{-1}$ ,  $k_{app}$  can be approximated by  $k_2$ .
- 3) If the concentration of water is increased  $k_{app}$  can be approximated as  $\frac{k_1 \cdot k_2}{k_{-1}}$ .
- 4) If  $k_{app}$  is independent of the concentration of water,  $k_{app}$  can be approximated by  $k_1$ .
- 5) If  $k_{-1} \gg k_2$   $k_{app}$  decreases linearly with the concentration of water.

### B. Conversion of CO<sub>2</sub> into Cyclic Carbonates

One of the challenges in using CO<sub>2</sub> as a starting material for the synthesis of organic compounds is its fixation. One possibility for this is the reaction with epoxides to form cyclic carbonates (or polycarbonates).



With catalyst A, a dependence of the reaction rate on the substrate concentration is obtained, which is shown in the following diagram. A non-linear course can be seen. However, a linear approximation can be made at low substrate concentrations and at very high ones.



4.6 By reactions of which order can one approximate this curve at (a) low and (b) very high substrate concentrations.

(a)

4.7 Name the approximation model that is usually used to explain the above shown reaction kinetics.

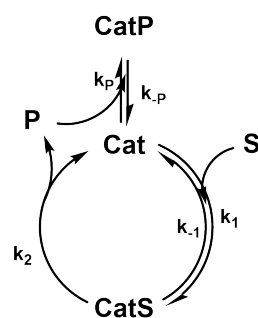
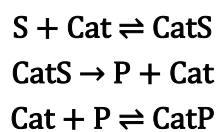
The rate constant  $k_{app}$  was measured at different temperatures:

$$k_{app.35^{\circ}\text{C}} = 2.83 \cdot 10^{-5} \text{ s}^{-1}$$

$$k_{app.65^{\circ}\text{C}} = 1.11 \cdot 10^{-4} \text{ s}^{-1}$$

4.8 Calculate the activation energy of the reaction in  $\text{kJ} \cdot \text{mol}^{-1}$ .

If the same reaction is carried out with catalyst B, then a kinetic model with product inhibition (see figure) must be assumed in order to be able to approximate the experimental values well.



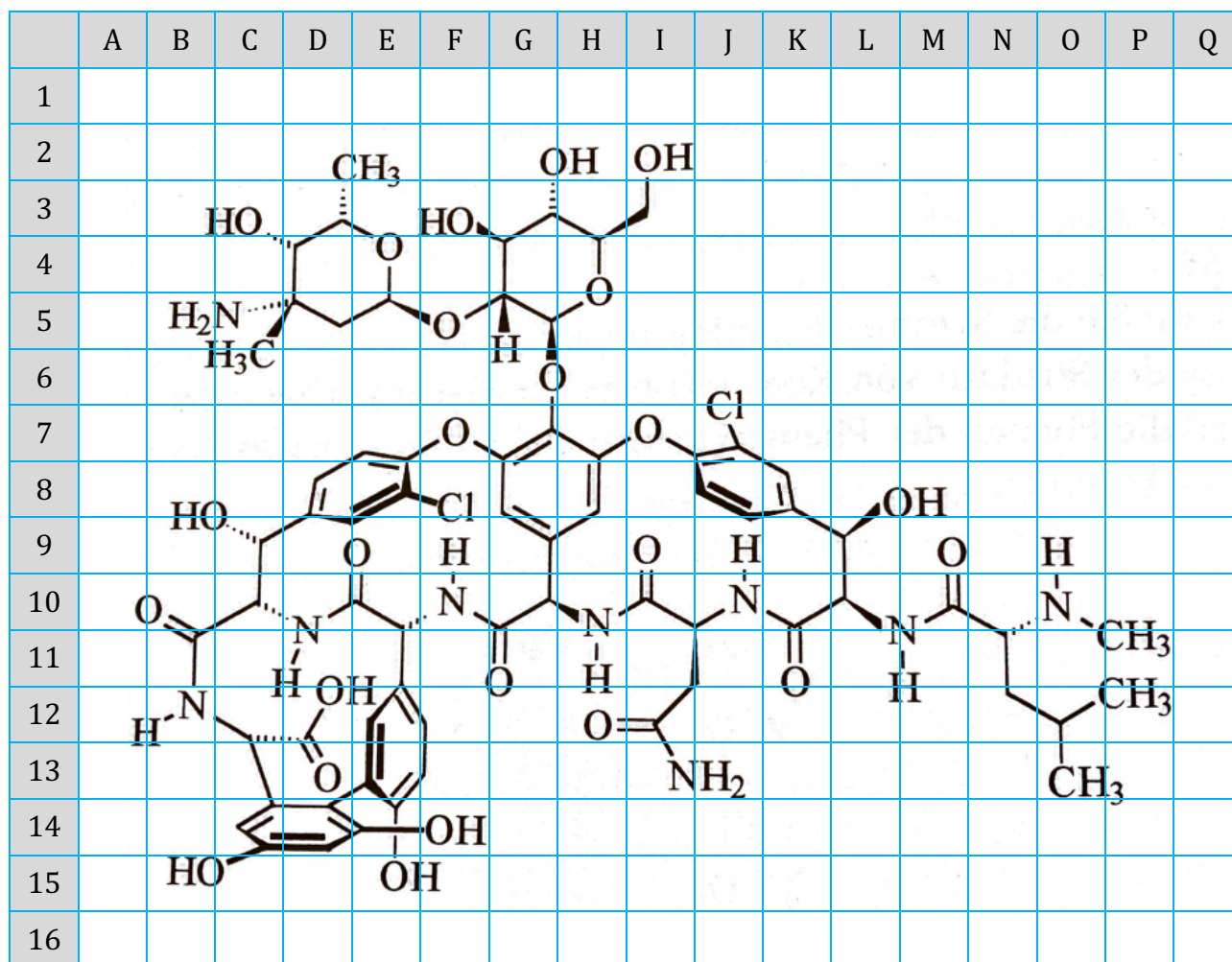
4.9 Write the differential rate laws for  $[S]$ ,  $[P]$ ,  $[Cat]$ ,  $[CatS]$ , and  $[CatP]$ .

## Task 5 (M. Scherl)

## Against Multiresistant Germs

## A. Vancomycin

Vancomycin is a reserve antibiotic of the glycopeptide antibiotic group and is used against multi-resistant hospital germs (e.g. staphylococci). You are now to find out which stereogenic units vancomycin contains and where they can be found. For this purpose, the formulae has been drawn here in a grid.



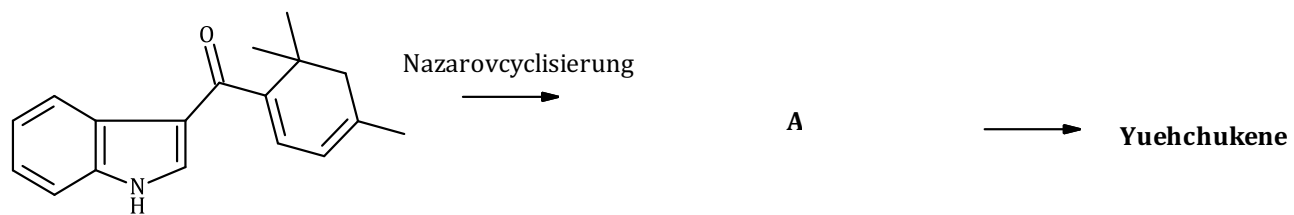
5.1 Write onto your answer sheet: "stereocenter", "axis of chirality", "plane of chirality"

To each of these write:

- "occurs" or "does not occur".
- the coordinates (grid) of ONE example of the respective stereogenic unit
- the correct stereodescriptor of this example

Example: "Chirality Something - occurs- N 15 - cis"

5.2 Give the coordinates of two C-atoms being part of amide-groups

**B. Synthesis of Yuehchukene**

Hint: The Nazarov cyclisation is thermal and therefore conrotatory.

5.3 Draw the structural formulae of **A** showing the correct stereochemistry.

### Hydrogen Cyanide HCN

Hydrogen cyanide (hydrocyanic acid, HCN) is produced via the Degussa-BMA process based on ammonia (NH<sub>3</sub>) and methane (CH<sub>4</sub>). As a by-product, elemental hydrogen is formed in this reaction.

6.1 Write a balanced equation for the hydrogen cyanide production.

6.2 Formulate the law of mass action for this reaction.

The reaction is carried out at 1250°C. In equilibrium the gaseous reaction mixture has a pressure of 1.00 bar and contains 71.8% hydrogen, 22.9% hydrogen cyanide, 2.5% ammonia, 1.7% methane and 1.1% nitrogen (all % V/V).

6.3 Calculate the equilibrium constant  $K_p$  for the reaction using the data given.

One can also calculate the equilibrium constant from thermodynamic data of the gaseous starting materials and end products of this reaction.

	$\Delta_f H^\ominus$ (kJ/mol)	$\Delta_f S^\ominus$ (J/K·mol)
Methane	-74.6	186.3
Ammonia	-45.9	192.8
Hydrogen cyanide	135.1	201.8
Hydrogen	0	130.7

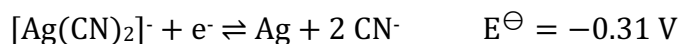
6.4 Calculate the standard Gibbs-energy of the reaction at 1250°C using these thermodynamical data.

6.5 Calculate the equilibrium constant from the calculated Gibbs-energy. State possible reasons for the difference to the result from 6.3.

Hydrogen cyanide or sodium cyanide play an important role in the extraction of silver and gold. For this process called "cyanide leaching", a solution of sodium cyanide is used.

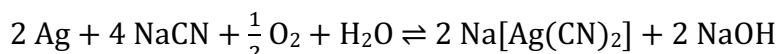
6.6 10.00 g NaCN are dissolved in 1.00 L of water. In the solution a concentration of  $2.251 \cdot 10^{-3}$  mol/L of hydrogen cyanide is measured. Calculate the pH of this solution and the  $pK_A$ -value of hydrogen cyanide. Neglect the self ionisation of water.

The following standard potentials are given:



6.7 Calculate the formation constant for the  $[\text{Ag}(\text{CN})_2]^-$  - complex at 298 K corresponding to the equation:  $\text{Ag}^+ + 2 \text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2]^-$ .

In cyanide leaching, the silver ore dissolves according to the following equation:



6.8 Calculate the equilibrium constant for this reaction.

The cyanide concentration in a solution was historically determined by an argentometric titration developed by Justus v. Liebig. The cyanide solution is titrated with a silver(I) nitrate solution. First the silver(I) ions form the complex  $[\text{Ag}(\text{CN})_2]^-$ . When all cyanide ions are bound in the complex, further addition of silver(I) ions leads to the formation of solid AgCN and thus to turbidity of the solution. The solubility product of silver(I) cyanide is  $5.97 \cdot 10^{-17}$ . If you have not received a result for the complex formation constant in 6.7, use  $K_f = 10^{20}$ .

6.9 10.00 g NaCN are dissolved in 1.00 litre of water. 10.00 mL of this solution are titrated with silver(I) nitrate solution ( $c = 0.100 \text{ mol/L}$ ). Calculate the required volume of silver nitrate solution up to the moment when the precipitation of AgCN starts. For now, assume that the formation of the complex is complete and irreversible. Assume further that acid-base-reactions of the cyanide ions can be neglected.

6.10 Now calculate the concentration of silver(I) ions in the titrated solution when the precipitation of AgCN starts. This time take the equilibrium of complex formation into account. Still assume that acid-base-reactions of cyanide can be neglected.