

# 48<sup>th</sup> Austrian Chemistry Olympiad

## Federal competition

Theoretical part  
May 26, 2022

.....  
Name

|   | $r_{p_{\max}}$ |
|---|----------------|
| 1 Molecules with multiple bonds             | 8.5            |
| 2 Organic chemistry with the ancient Romans | 17.5           |
| 3 Thermodynamics in the Solvay process      | 6              |
| 4 Stereochemistry of lysergic acid          | 5              |
| 5 Cs & Co                                   | 8              |
| 6 Formation and decay of hydrogen iodide    | 4.5            |
| 7 Equilibria of mercury                     | 10.5           |
|   | 60             |

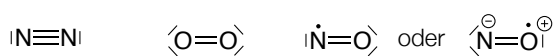
## Molecules with multiple bonds

## A. Three small molecules

From the example of three diatomic molecules assembled from O and N atoms, one can learn a lot about bonding models and model building in general.

Probably the simplest way to explain bonds with the help of electrons are valence formulas according to Lewis. Unfortunately, the simplest way is not always the correct one. Because the Lewis formulas predict an unpaired electron only for one of the three molecules, and even there only because there is no other way.

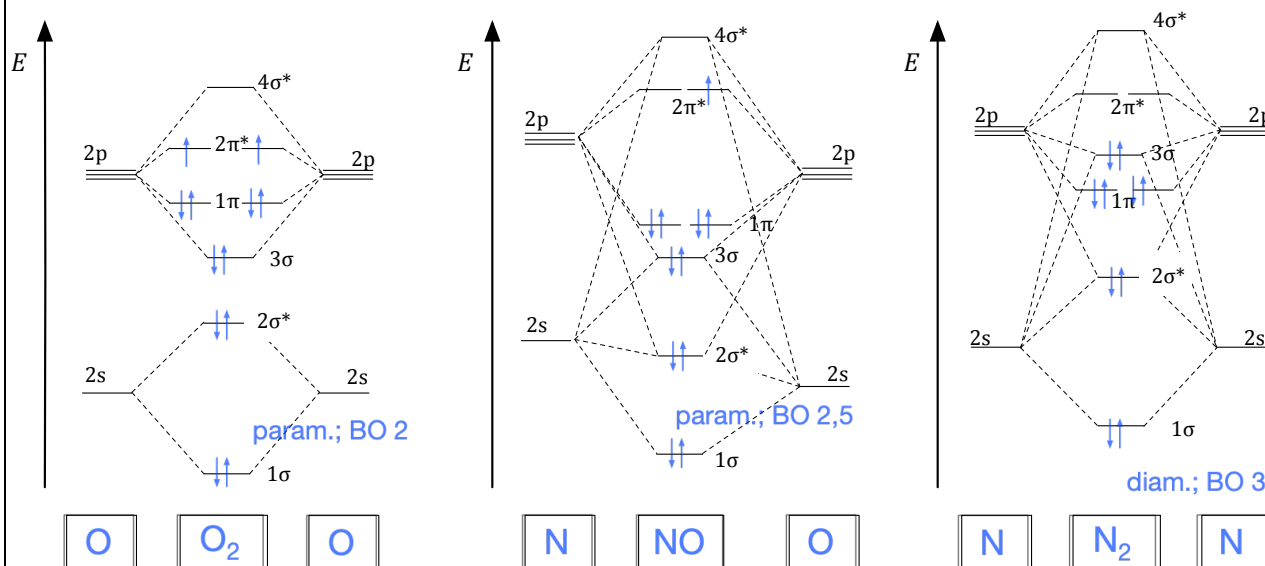
1.1 Draw complete Lewis formulas for  $N_2$ ,  $O_2$ , and  $NO$  showing that only one of the molecules should have an unpaired electron.



1.5 bp

The number of paired or unpaired electrons determines whether a molecule is diamagnetic or paramagnetic. Since the experiment shows that two of the molecules mentioned are paramagnetic, one must take another step forward and consider molecular orbitals.

1.2 The following graph shows empty MO schemes. Label them, fill the MO levels with electrons, indicate the bond order for each molecule, and determine whether it should be dia- or paramagnetic.



correct labeling - 0.5bp;

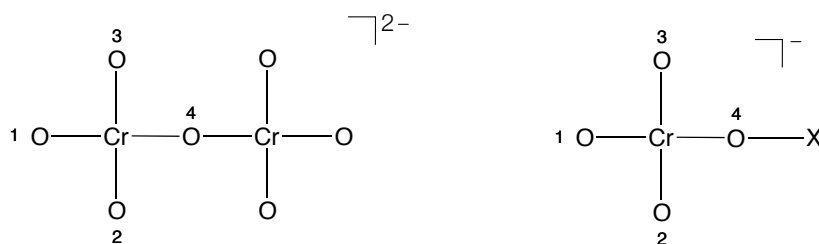
correct electron configuration - 1.5 bp

correct bond order each 0.5bp ; correct dia/paramagnetic each 0.5 bp

5 bp

## B. A medium-sized molecular ion

The dichromate anion  $\text{Cr}_2\text{O}_7^{2-}$  is well known from analytical chemistry. The covalent framework is symmetrical, which is why we will only consider the left part (with a negative charge) in the following and abbreviate the right part with X.



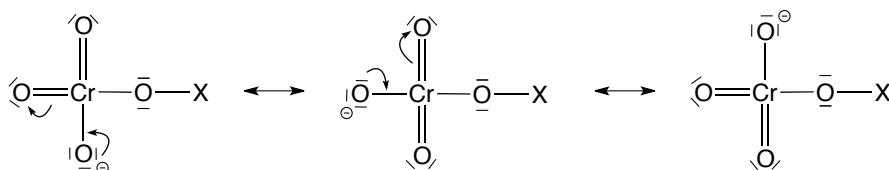
1.3 Indicate which molecular geometry you expect according to VSEPR for (a) the Cr atom (b) the O atom number 4.

(a) tetrahedral

(b) bended

1 bp

1.4 Draw three mesomeric (resonance) Lewis formulas of the left part showing that three of the Cr-O bonds are equivalent. Use the abbreviation X. Draw the "flipping" of the electron pairs using appropriate arrows.



1.5 bp

1.5 In the dichromate two different Cr-O bond distances are measured: 179 pm and 163 pm. Which of the bond distances do you expect for (a) the bond  $\text{Cr-O}^4$ , and (b) the bond  $\text{Cr-O}^3$ ?

$\text{Cr-O}^4$  : 179pm,  $\text{Cr-O}^3$  : 163 pm

1 bp

1.6 Give the complete electron configuration for (a) chromium (6 unpaired spins) (b) chromium(III).

a)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

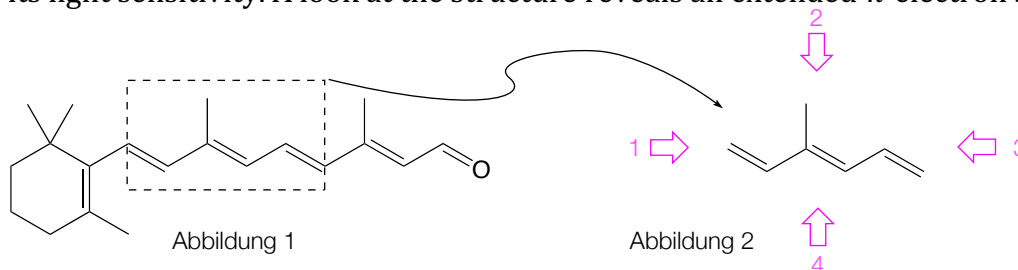
0.5 bp

b)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

0.5 bp

### C. An even larger molecule

**Retinal** is the chromophore in light-sensitive proteins, especially in rhodopsin, which also gives our retina its light sensitivity. A look at the structure reveals an extended  $\pi$ -electron system.



Let us first look at the molecule (derived from the middle section of retinal) drawn in Fig. 2 (Abbildung 2, right).

1.7 Name the molecule (Fig. 2) according to IUPAC including all required stereodescriptors.

*(E)*-3-methylhexa-1,3,5-triene

1 bp

Below you can see 6 calculated molecular orbitals of this molecule. The molecule is always in the same position as drawn above.

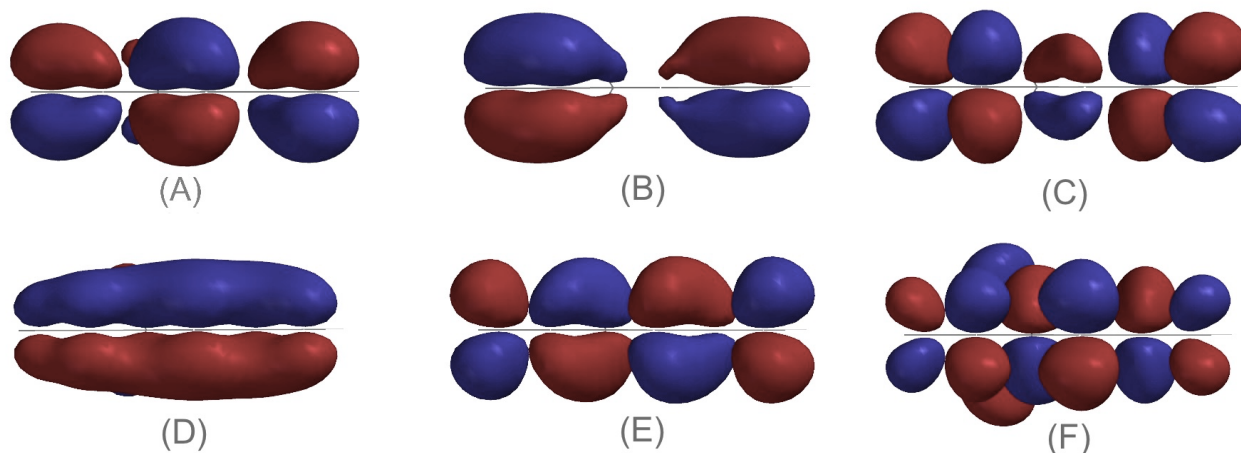


Figure 3 - Molecular orbitals

1.8 From which of the four directions drawn in Figure 2 is the molecule viewed? Indicate the number.

(4)

0.5 bp

1.9 Order molecular orbitals from Figure 3 by increasing energy.

(D) < (B) < (A) < (E) < (C) < (F)

1.5 bp

1.10 Indicate for (A) and for (F) whether they are  $\sigma$ - or  $\pi$ -molecular orbitals.

(A):  $\pi$ , (F):  $\pi$

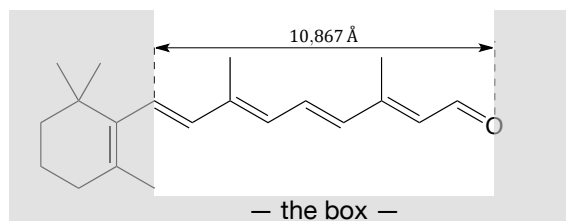
1 bp

1.11 One of the MOs shown is the HOMO, one is the LUMO. Indicate the corresponding letters.

HOMO: (A), LUMO (E)

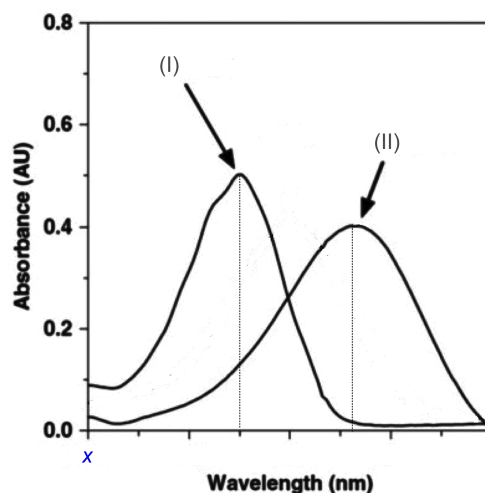
1 bp

In the usual representation of the all-*trans*-retinal in textbooks, one could fall for the idea to consider almost all  $\pi$ -electrons as particles in the (potential) box. A molecular model program kindly provides also the length of the potential box.



|  |        |
|--|--------|
| <i>1.12 Indicate the number of <math>\pi</math>-electrons in this box.</i>   |        |
| 10   | 1 bp   |
| <i>1.13 Calculate the wavelength of the HOMO-LUMO transition in the model of the particle in the box in nm.</i>  |        |
| <p>HOMO = <math>E_5</math> ; LUMO = <math>E_6</math> (1 bp)</p> $E_n = \frac{h^2 n^2}{8mL^2} \Rightarrow$ $E_6 - E_5 = \frac{h^2}{8mL^2} (6^2 - 5^2) = \frac{(6.6261 \cdot 10^{-34} \text{ Js})^2}{8 \cdot (9.1094 \cdot 10^{-31} \text{ kg}) \cdot (10.867 \cdot 10^{-10} \text{ m})^2} (11) = 5.6119 \cdot 10^{-19} \text{ J}$ $\lambda = \frac{hc}{E} = \frac{(6.6262 \cdot 10^{-34} \text{ Js})(2.9979 \cdot 10^8 \text{ ms}^{-1})}{5.6119 \cdot 10^{-19} \text{ J}} = 354 \text{ nm}$ |        |
| <i>1.14 Indeed, all-<i>trans</i>-retinal dissolved in hexane shows an extinction maximum at 380 nm. One might think that the potential box considered here is (a) too short or (b) too long. Indicate the correct letter.</i>  |        |
| (a)  | 0.5 bp |

All-*trans*-retinol is obtained by reduction of the carbonyl group, which leads to a change in the  $\pi$ -electron system. Its absorption maximum is shifted by about 55 nm in one direction compared to that of all-*trans*-retinal ( $\lambda_{\text{max}} = 380 \text{ nm}$ ). One of the curves shown on the right belongs to retinal, the other to retinol.



|  |        |
|--|--------|
| <i>1.15 Indicate the number of curve (I) or (II) belonging to the all-<i>trans</i> retinol.</i>  |        |
| (I)  | 0.5 bp |
| <i>1.16 What wavelength corresponds to the distance between two adjacent bars on the abscissa (x-axis)? (a) 5 nm (b) 10 nm (c) 15 nm (d) 20 nm (e) 25 nm. Indicate the correct letter.</i> |        |
| (e) 25 nm  | 0.5 bp |
| <i>1.17 Which values should be written at x and y? Give them in nm.</i>  |        |
| x: 250nm; y: 450 nm  | 1 bp   |

The molar decadic absorption coefficient of all-*trans*-retinol at the absorption maximum was determined to be  $\epsilon = 52700 \text{ Lmol}^{-1}\text{cm}^{-1}$ .

1.18 Calculate the concentration of a sample whose absorbance in a 1 cm cell is  $A = 0.445$ .

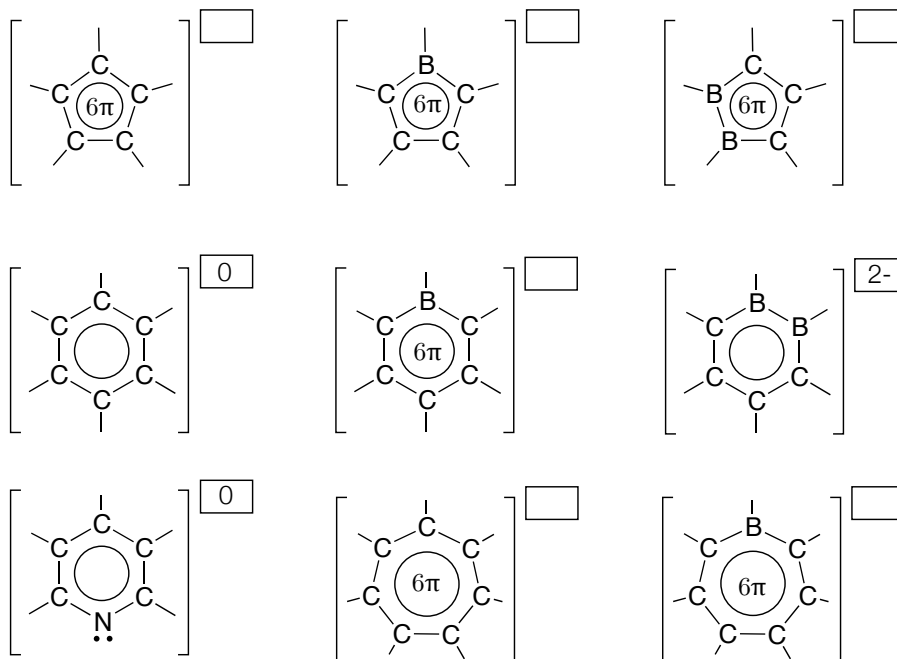
$$c = \frac{A}{\epsilon d} = \frac{0.445}{52700} = 8.44 \cdot 10^{-6} \text{ mol L}^{-1}$$

0.5 bp

#### D. Aromatic?!

Benzene is known to obey the Hückel rule, according to which the number of  $\pi$ -electrons should be 2, 6, 10, ... Other ring-shaped molecule(s) can also exhibit aromatic stability according to this rule. Nine aromatic structures are shown, with either the number of  $\pi$ -electrons or the charge indicated for each.

1.19 Complete the formulas by writing the number of  $\pi$ -electrons in an empty circle or the charge in an empty box. Also write 0 (zero) explicitly.

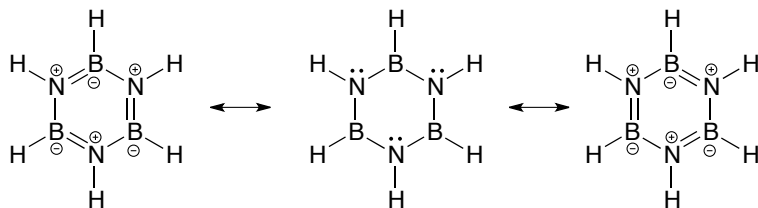


f.l.t.r.: 1st row: -1, -2, -3, second row: 6 $\pi$ , -1, 6 $\pi$ , third row: 6 $\pi$ , +1, 0  
each error -0.5bp, min 0bp

3.5 bp

Borazine  $B_3N_3H_6$  has sometimes been nicknamed "inorganic benzene", since it also has a very nice hexagonal shape (but only with a triple axis of rotation).

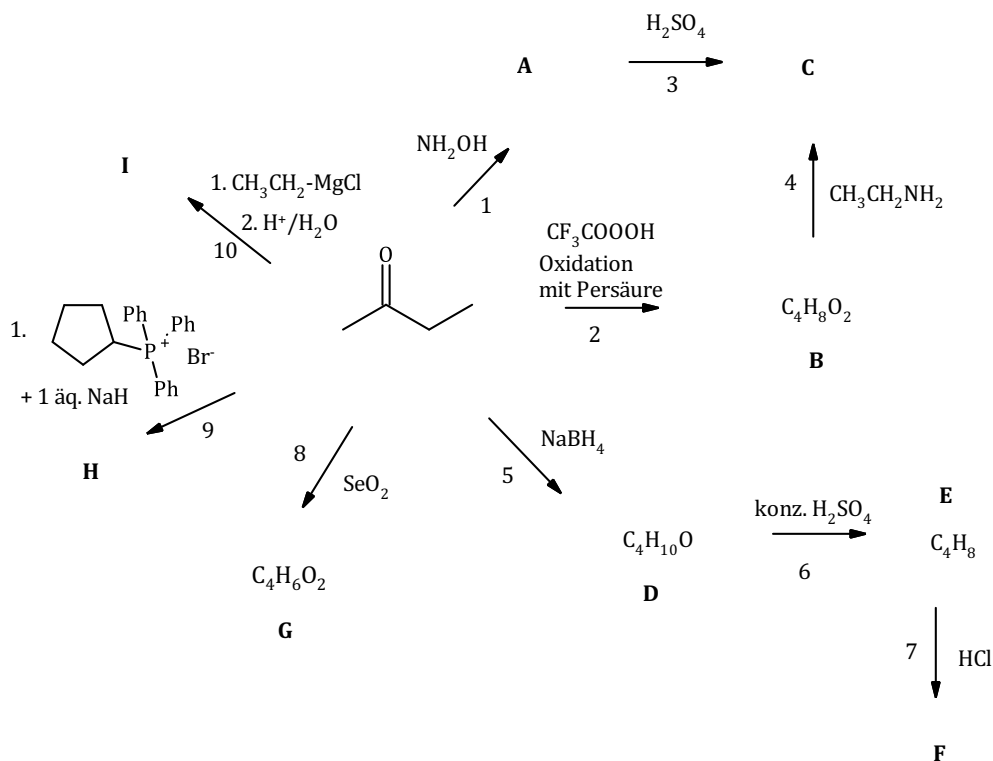
1.20 Draw three mesomeric (resonance) formulas of borazine (with formal charges and lone pairs) showing that the B-N bonds are equal. One of the boundary formulas doesn't contain any multiple bonds.



2 bp

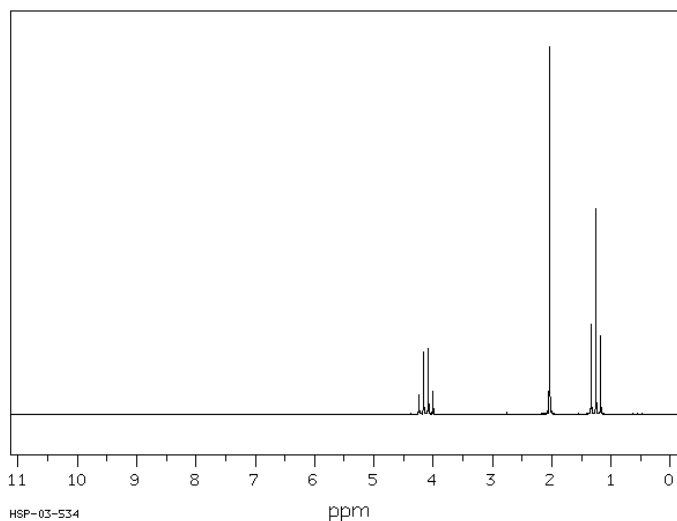
## Organic chemistry with the ancient Romans

## A. Some reactions from organic chemistry (13.5 bp)



## Notes:

- For **B**, **I**, **G** the  $^1\text{H}$  NMR data (measured in  $\text{CDCl}_3$ ) are given below.
- Reaction 1 produces water as a by-product.
- Substance **E** is an *E*-isomer
- $^1\text{H}$  NMR spectrum of substance **B**:



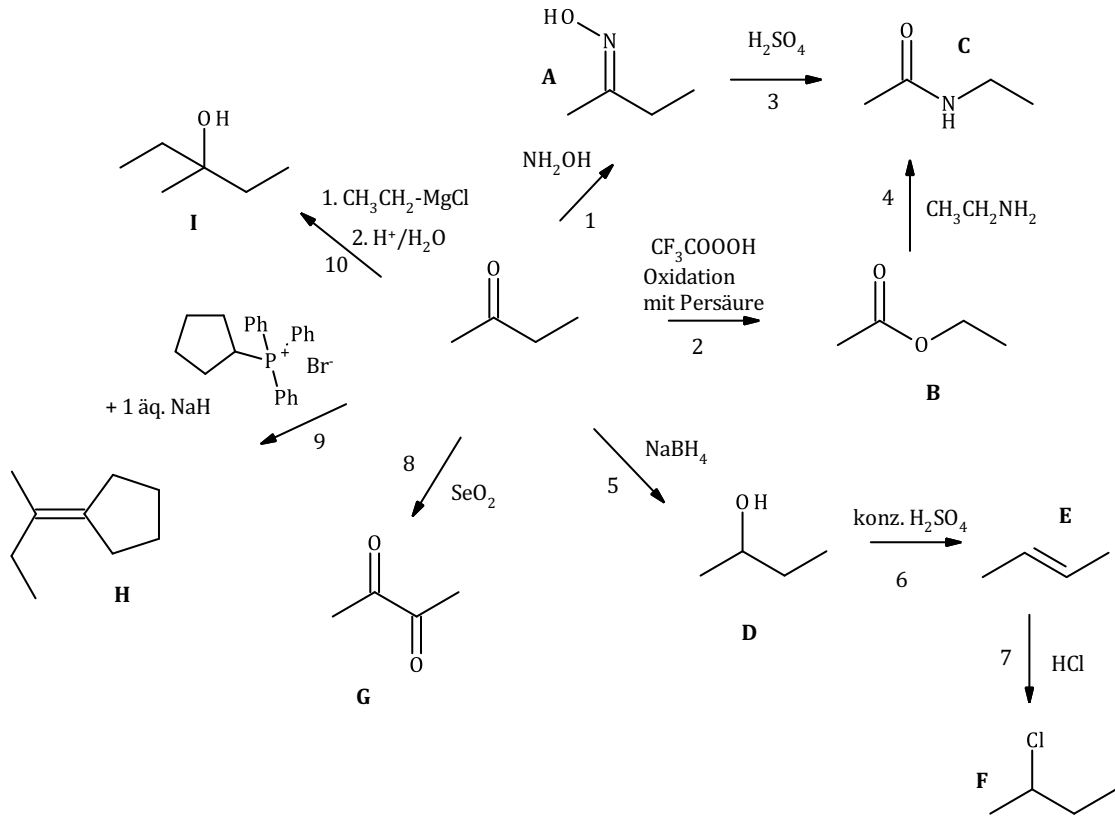
- $^1\text{H}$  NMR data of substance **I**: 1.53 ppm (s, broad, 1H); 1.49 ppm (m, 4H); 1.13 ppm (s, 3H); 0.90 ppm (t, 6H).
- The  $^1\text{H}$  NMR spectrum of substance **G** shows only a singlet with integral 6 at 2.34 ppm.

2.1 Write down the IUPAC name of the reactant.

Butan-2-one

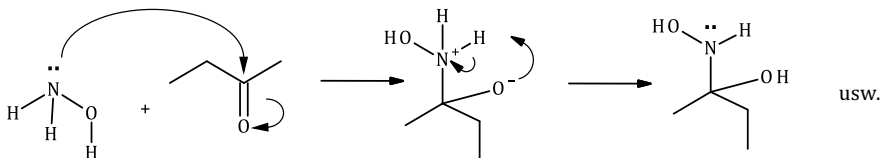
0.5 bp

2.2 Draw the constitutional formulas of substances **A**, **B**, **C**, **D**, **F**, **G**, **H**, and **I** and the configurational formula of **E**.



A: 1 bp, B: 1.5 bp, C: 1 bp, D: 1 bp, E: 1 bp, F: 1 bp, G: 1 bp, H: 1.5 bp, I: 1.5 bp

2.3 For reaction 1, write down the first two steps of the mechanism (without any catalysis). Use arrows showing "the migration" of electron pairs. Write in the structures any free pairs of electrons that are present. Name the reaction mechanism.



2 bp

nucleophilic addition:  $A_N$  (subsequently elimination of  $H_2O$ )

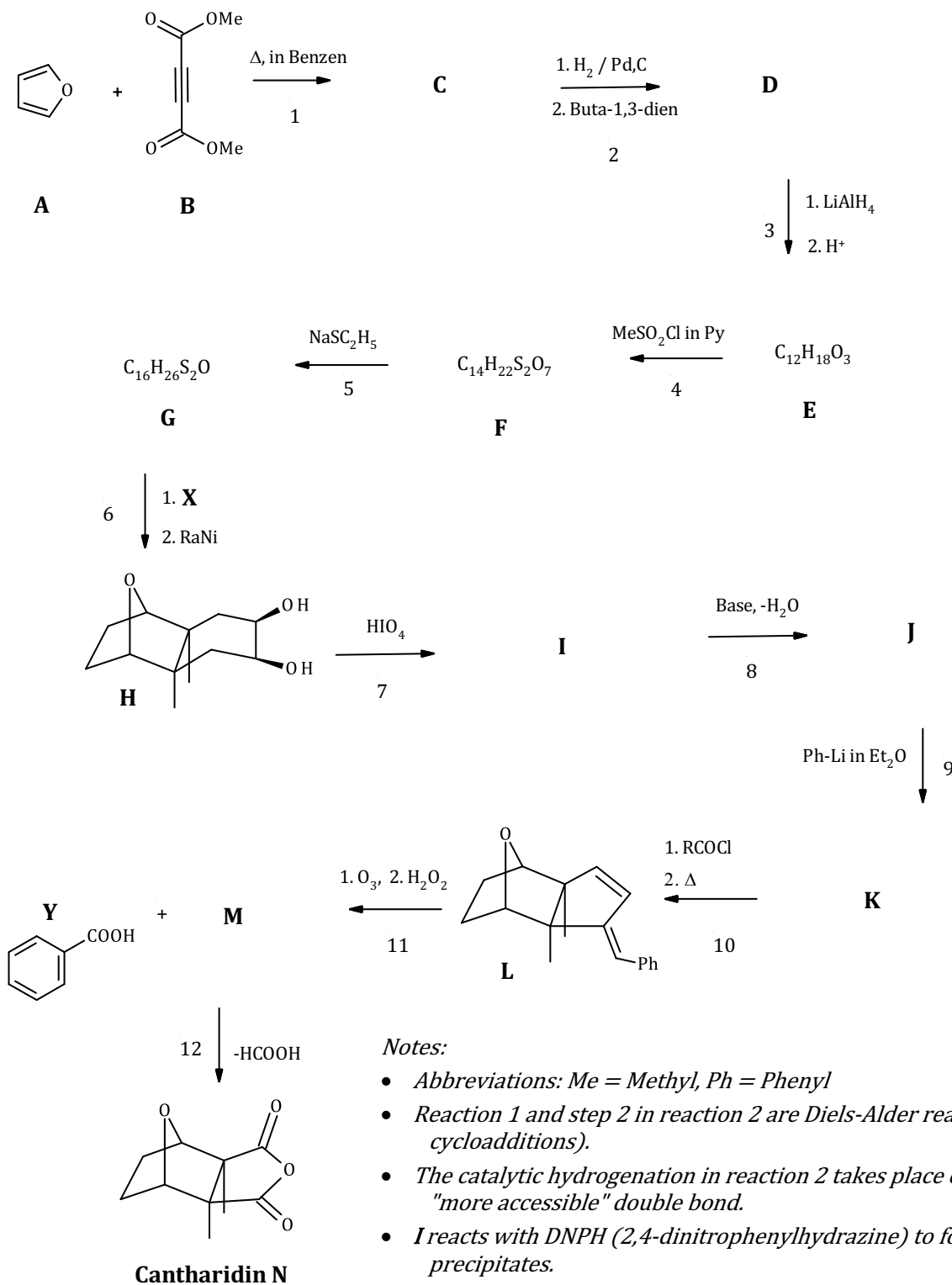
0.5 bp



## B. Synthesis of cantharidin (26.5 bp).

Stork, G.; van Tamelen, E. E.; Friedman, L. J.; Burgstahler, A. W. *J. Am. Chem. Soc.* 1951, 73, 4501.

Cantharidin is a terpenoid that beetles secrete as a defensive secretion or sex pheromone, depending on the species. Today it is known that it is a strong poison, although it is said to have an effect as an aphrodisiac. According to war reports, this has already been the undoing of Napoleon's troops in Egypt. The soldiers fed on frogs, which in turn ate beetles, which could have led to a bioaccumulation of the poison in the food chain. In the following, the synthesis of cantharidin published by the Belgian J. Stork in 1951 is considered in more detail.



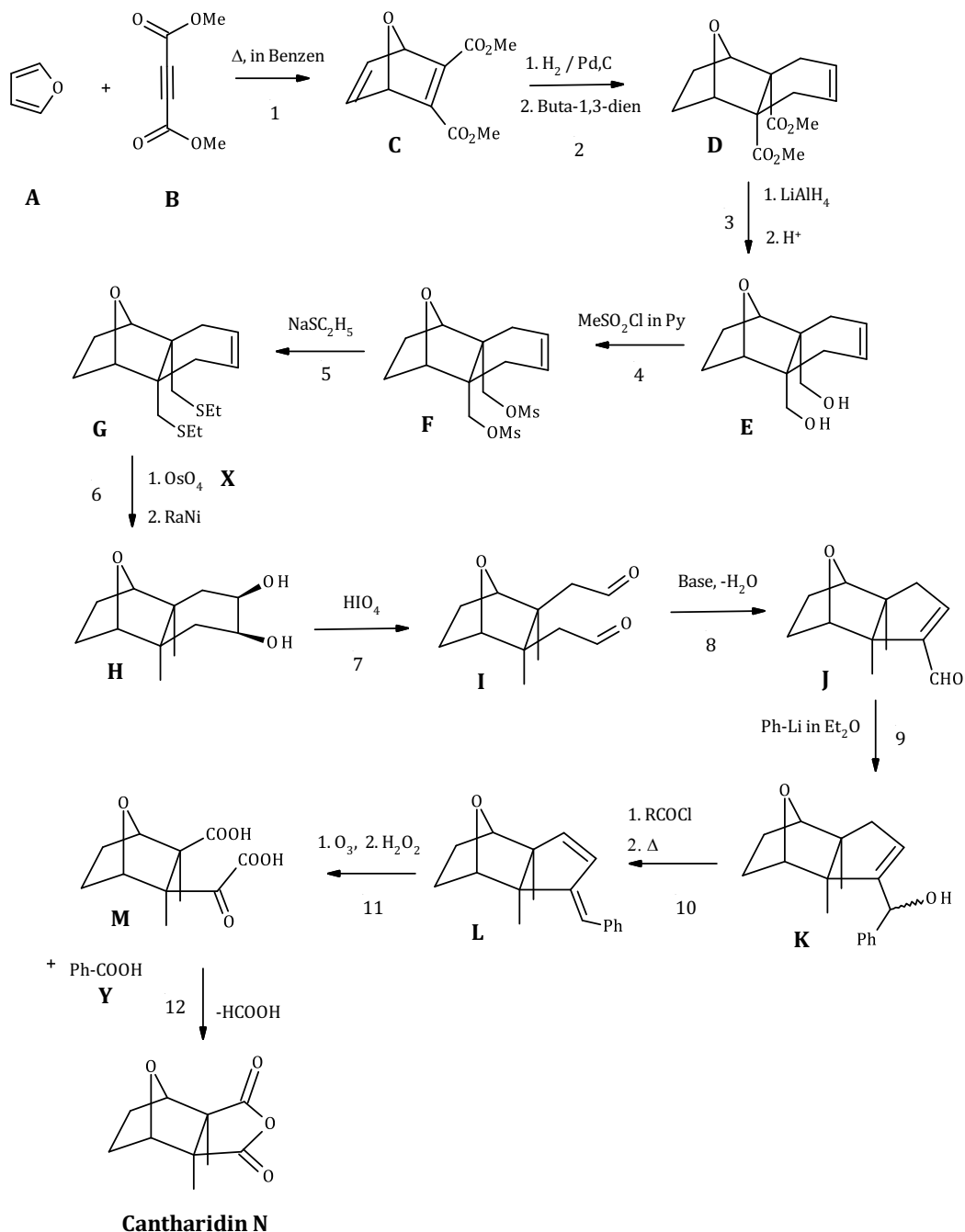
2.5 Give the names of the functional groups in the following structures:

of reactant **B**: **carboxylic acid ester**

of product **N**, which is formed in step 12: **carboxylic acid anhydride**

**1 bp**

2.6 Draw the configurational formulas of substances **C, D, E, F, G, X, I, J, K, and M**. Do not draw the rings planar, but use the structural representations given in the reaction diagram as a guide.

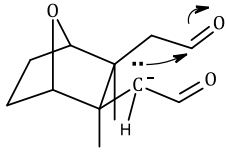


**C: 2.5 bp, D: 2.5 bp, E: 2 bp, F: 1.5 bp, G: 2 bp, X: 1 bp, I: 2 bp, J: 2.5 bp, K: 2 bp, M: 2bp**

2.7 Give the abbreviations (e.g.,  $S_R$ ,  $A_E$ , ...) for the reaction types of reactions 4, 8, and 9.

**4:  $S_N$  8:  $A_N$  9:  $A_N$**

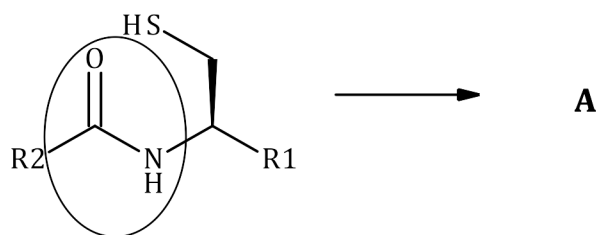
**1.5 bp**

|   |      |
|---|------|
| 2.8 Indicate whether the species "NaSC <sub>2</sub> H <sub>5</sub> " in reaction 5 is a nucleophile, radical or electrophile and label the reactive site as accurately as possible.             |      |
| Nucleophile NaSC <sub>2</sub> H <sub>5</sub>  | 1 bp |
| 2.9 Rank the possible leaving groups CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup> , OH <sup>-</sup> , and CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup> starting with the worst to the best one. |      |
| OH <sup>-</sup> < CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup> < CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>   | 1 bp |
| 2.10 Draw the first reactive species arising from I in reaction 8. Draw arrows in this structure indicating the further course of the mechanism.  |      |
|  <p>I</p>  | 2 bp |

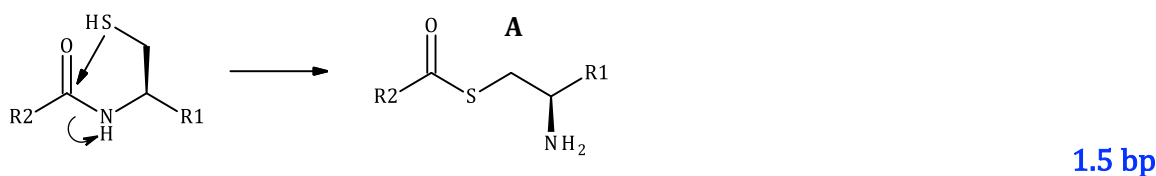
### C. Self-splicing of proteins (2 bp).

Do we owe our existence to the protein-rich beans that were mainly responsible for our ancestors not starving in Europe? The importance of beans for the ancient Romans is shown by the fact that four of the most important Roman families are named after legumes (so-called *Fabaceae*): Fabius (after the fava bean), Lentulus (after the lentil), Piso (after the pea), and Cicero (after the chickpea). Unfortunately, with the fall of the Roman Empire, the knowledge about the importance of these legumes disappeared. Only later the bean regained its important place in nutrition.

Protein "self-splicing" was first discovered in 1990. Thioester intermediate **A** is formed in the process. Nowadays, it is also used in peptide synthesis.



2.11 Write down the structure of **A**. Draw arrows in the structure of the reactant to indicate the course of the mechanism.



2.12 Name the functional group circled in the structure above.

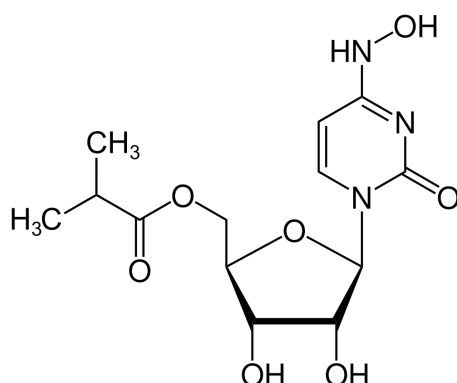
Carboxamide 0.5 bp

## D. Molnupiravir (1 bp)

**Molnupiravir** is an antiviral drug for the oral, outpatient treatment of mild to moderate courses of COVID-19. As of Nov. 4, 2021, this has been conditionally approved in the United Kingdom in individuals with risk factors as well as the elderly. Molnupiravir does not have approval in the EU (as of April 2022). The EMA already supports its use in emergencies, i.e. COVID-19 patients not requiring ventilation and carrying an increased risk for severe disease.

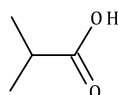
[www.gov.uk/government/news/first-oral-antiviral-for-covid-19-lagevrio-molnupiravir-approved-by-mhra](https://www.gov.uk/government/news/first-oral-antiviral-for-covid-19-lagevrio-molnupiravir-approved-by-mhra); November 4, 2021, accessed 4/30/2022.

European Medicines Agency EMA: [www.ema.europa.eu/en/news/ema-issues-advice-use-lagevrio-molnupiravir-treatment-covid-19](https://www.ema.europa.eu/en/news/ema-issues-advice-use-lagevrio-molnupiravir-treatment-covid-19); November 19, 2021, accessed 4/30/2022.



2.13 Give the constitutional formula and IUPAC name of the acid from which this drug could be synthesized via esterification.

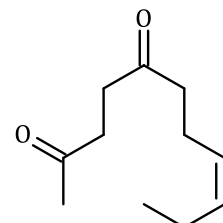
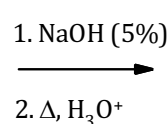
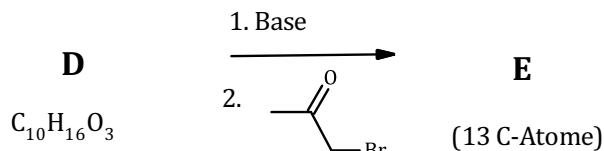
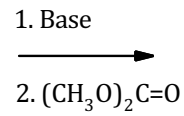
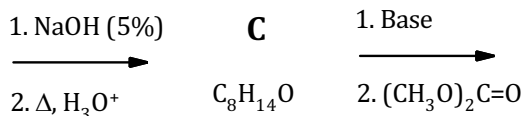
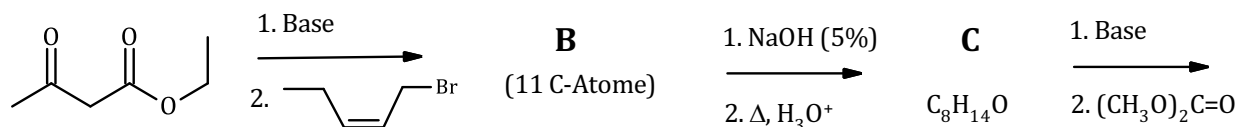
2-methylpropanoic acid



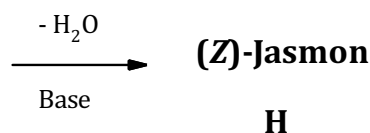
1 bp

### E. Synthesis of (*Z*)-jasmon (11.5 bp)

From a chemical point of view, jasmon belongs to the class of cyclopentenones. As a fragrance in jasmine flowers, the Romans already used the scent for perfume production.



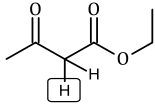
**G** Zwischenprodukt vor Ringbildung



#### Notes:

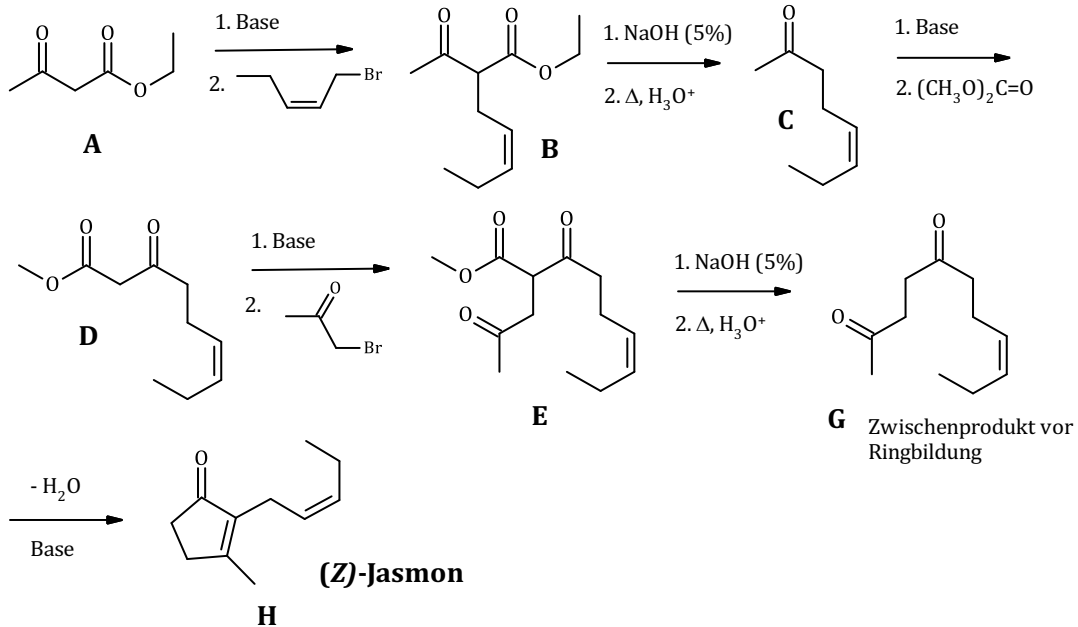
- Remember that  $\beta$ -carbonyl carboxylic acids decarboxylate readily under basic and acidic conditions.
- In the step **C**  $\rightarrow$  **D**, deprotonation occurs at the primary carbon.
- In the last step of the synthesis scheme, an aldol addition takes place to form a cyclopentenone ring. The  $^1\text{H-NMR}$  of **H** exhibits numerous signals, but only two with an integration of 3, more specifically a singlet (2.2 ppm) and a triplet (1.1 ppm).

2.14 Draw reactant **A** and circle the proton with the smallest  $pK_A$  value.



0.5 bp

2.15 Draw the constitutional formulas of substances **B**, **C**, **D**, **E**, and **H** ((*Z*)-jasmon). Note the stereochemistry whenever this is necessary and possible.



**B:** 2 bp, **C:** 2 bp **D:** 2.5 bp **E:** 1.5 bp **H:** 3 bp

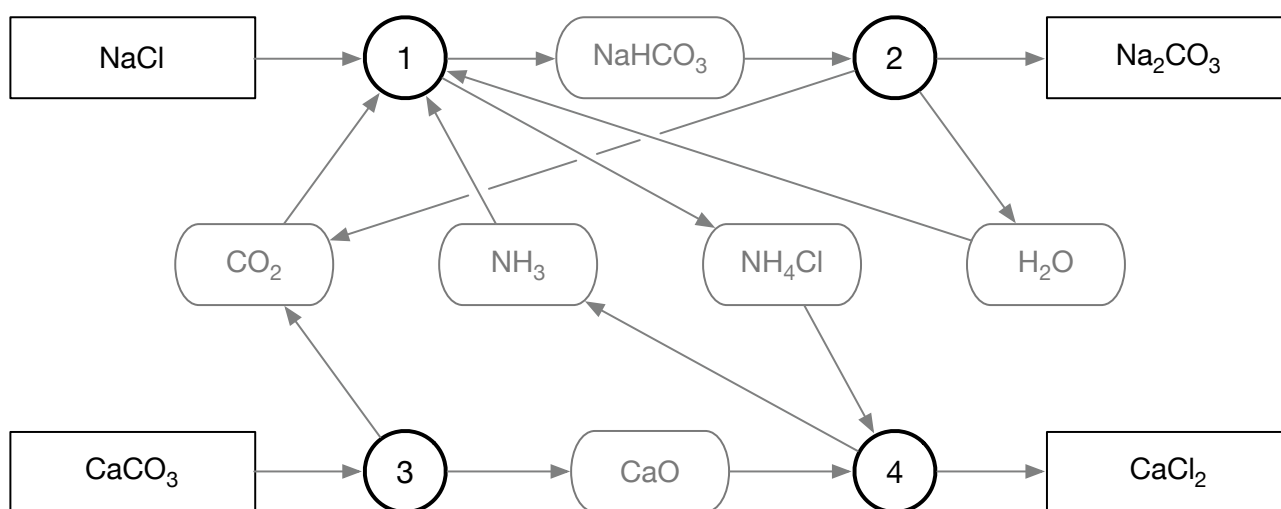
## Thermodynamics in the Solvay process

### A. Solvay process

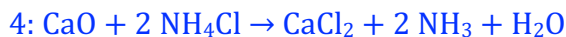
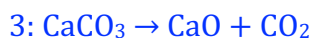
Starting materials for the synthesis of soda ash (sodium carbonate) are sodium chloride and calcium carbonate. Unfortunately, the reaction in aqueous solution takes place just in the wrong direction, namely like this:



A way out is provided by a multi-stage implementation shown in the following scheme. It was developed by Earnest SOLVAY. The circles represent reactions, the substances are represented by their formulas in boxes.



3.1 Write down coordinated equations for reactions 1, 2, 3 and 4 and show by appropriate addition of these that the overall reaction of the Solvay process corresponds to the desired reaction (reverse reaction of R1).



2.5 bp

3.2 You might have noticed that one arrow is missing in the above diagram. From where to where should it be drawn? ("From... to ...")

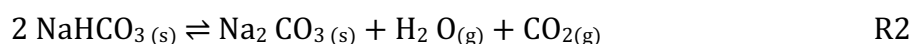
From reaction 4 to H<sub>2</sub>O

0.5 bp

|                                    | $\Delta_f H^\circ/\text{kJmol}^{-1}$ | $\Delta_f G^\circ/\text{kJmol}^{-1}$ | $S^\circ/\text{Jmol}^{-1}\text{K}^{-1}$ | $C_p/\text{Jmol}^{-1}\text{K}^{-1}$ |
|------------------------------------|--------------------------------------|--------------------------------------|---|-------------------------------------|
| $\text{H}_2(\text{g})$             | 0,0                                  |                                      | 130,7                                   | 28,80                               |
| $\text{H}_2\text{O}(\text{g})$     | -241,8                               | (A)                                  | 188,8                                   | 33,60                               |
| $\text{O}_2(\text{g})$             | 0,0                                  |                                      | 205,2                                   | 29,40                               |
| $\text{CHNaO}_3(\text{s})$         | -950,8                               | (B)                                  | 101,7                                   | 87,60                               |
| $\text{CNa}_2\text{O}_3(\text{s})$ | -1131                                | -1045                                | 138,9                                   | 112,3                               |
| $\text{CO}_2(\text{g})$            | -393,5                               | -394,4                               | 213,8                                   | 37,10                               |

Thermodynamic data from the CRC Handbook

A crucial step in the process is the thermal decomposition of the sodium hydrogen carbonate:



At 298 K the value for the equilibrium constant for this reaction (R2) is  $K_p = 1.016 \cdot 10^{-6}$ .

|  |
|--|
| <b>3.3</b> Give the expression for the equilibrium constant $K_p$ .  |
| $K_p = \frac{p_{\text{H}_2\text{O}}}{p^\ominus} \cdot \frac{p_{\text{CO}_2}}{p^\ominus}$ <span style="float: right;"><b>0.5 bp</b></span>  |
| <b>3.3</b> Calculate $\Delta_R G^\circ_{298}$ .  |
| $\Delta_R G^\circ = -RT \ln K = (-8.3145 \text{ JK}^{-1}\text{mol}^{-1})(298 \text{ K}) \ln 1.016 \cdot 10^{-6} = 34.19 \text{ kJmol}^{-1}$ <span style="float: right;"><b>1.5 bp</b></span>   |
| <b>3.5</b> Calculate the two missing quantities (A) and (B) in the table.  |
| $\begin{aligned} \Delta_f G^\circ(\text{H}_2\text{O}(\text{g})) &= \Delta_f H^\circ - T\Delta_f S^\circ = -241.8 - 0.298 \cdot \left(188.8 - 130.7 - \frac{1}{2}205.2\right) \\ &= -228.5 \text{ kJmol}^{-1} \\ \Delta_f G^\circ(\text{NaHCO}_3(\text{s})) &= \frac{1}{2}(-1045 - 228.5 - 394.4 - 34.19) = -851.0 \text{ kJmol}^{-1} \end{aligned}$ <span style="float: right;"><b>3 bp</b></span> |



In the industrial process, the reaction is carried out at 180°C (453 K). At this temperature, the saturation vapor pressure of water is already 1001.9 kPa, which means that condensation begins as soon as the partial pressure of water exceeds this pressure.

3.4 Calculate  $K_p$  at 453 K, assume  $\Delta_R H^\circ$  to be constant.

$$\Delta_R H_{298} = -1131 - 393.5 - 241.8 + 2 \cdot 950.8 = 135.3 \text{ kJmol}^{-1}$$

$$\ln K_{453} = \ln K_{298} - \frac{\Delta_R H^\circ}{R} \left( \frac{1}{453} - \frac{1}{298} \right) = 4.885 \Rightarrow K_{p_{453}} = 132$$

2 bp

3.5 Calculate the equilibrium partial pressure  $p_{CO_2}$  above the just dry reaction mixture at this temperature, i. e. when the water vapor has reached its saturation pressure.

$$p_{CO_2} = \frac{K_p}{p_{H_2O}} = \frac{132.0}{10.019} = 13.2 \text{ bar}$$

2.5 bp

Let's turn our attention to future ventures of mankind on other planets. How about a Solvay plant on Venus for example? The working conditions would be exciting: The atmosphere contains only 20 ppm H<sub>2</sub>O but 96.5% (V/V) CO<sub>2</sub> and the whole thing at a total pressure of  $p_{\text{ges}} = 92$  bar. In addition, the average temperature is 737 K.

3.6 Calculate  $\Delta_R H^\circ$  and  $\Delta_R S^\circ$  of reaction R2 on Venus, consider  $C_p$  to be independent of temperature.

$$\Delta_R S_{298} = 138.9 + 188.8 + 213.8 - 2 \cdot 101.7 = 338.1 \text{ Jmol}^{-1}\text{K}^{-1}$$

$$\Delta_R C_p = 112.3 + 37.10 + 33.60 - 2 \cdot 87.60 = 7.8 \text{ Jmol}^{-1}\text{K}^{-1}$$

$$\Delta_R H_{737} = \Delta_R H_{298} + \Delta_R C_p (737 - 298) = 135.3 + 0.0078 \cdot 439 = 138.7 \text{ kJmol}^{-1}$$

$$\Delta_R S_{737} = \Delta_R S_{298} + \Delta_R C_p \ln \frac{737}{298} = 338.1 + 7.8 \cdot 0.905 = 345.2 \text{ Jmol}^{-1}\text{K}^{-1}$$

4 bp

3.7 Determine by calculation whether NaHCO<sub>3</sub> decomposes spontaneously on Venus according to equation R2.

$$\Delta_R G^\circ = 138700 - 737 \cdot 345.2 = -115700 \text{ Jmol}^{-1}$$

$$K_p = e^{-\frac{\Delta_R G^\circ}{RT}} = 1.59 \cdot 10^8$$

Partial pressures in the atmosphere of Venus:

$$p_{CO_2} = 92 \cdot 0.965 = 88.78 \text{ bar};$$

$$p_{H_2O} = 92 \cdot 20 \cdot 10^{-6} = 0.00184 \text{ bar}$$

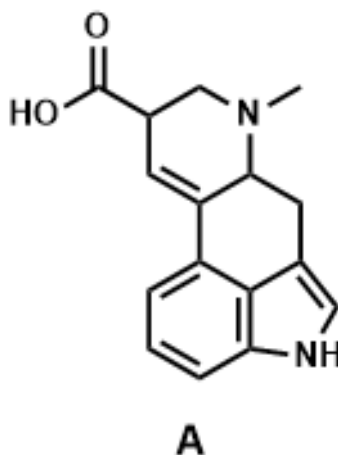
Reaction quotient  $Q = p_{CO_2} \cdot p_{H_2O} = 0.163 \ll K_p \Rightarrow \text{NaHCO}_3$  decomposes spontaneously

3 bp

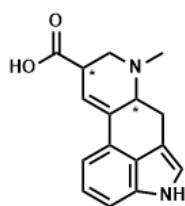
## Stereochemistry of lysergic acid

## A. Stereochemistry of lysergic acid

Lysergic acid **A** is the precursor of a large number of alkaloids and was used, among other things, to induce labor. Lysergic acid diethylamide, or LSD for short, is much better known in the general public.



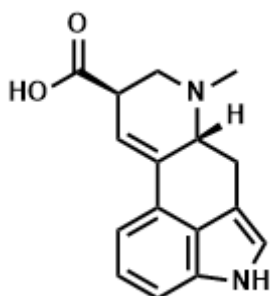
4.1 Mark all stereocenters of lysergic acid in the above formula with an asterisk (\*) and indicate how many different stereoisomers of lysergic acid exist.



2 stereocenters, 4 stereoisomers

2 bp

4.2 All stereocenters of lysergic acid have *R* configuration. Draw the structure of lysergic acid with the correct stereochemistry.



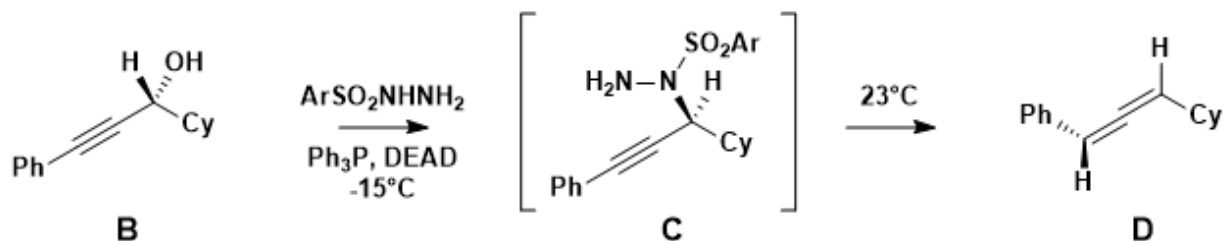
3 bp

## B. Synthesis of lysergic acid

The first total synthesis of (racemic) lysergic acid was achieved by *Woodward* as early as in 1956. In 2011, *Fujii* and *Ohno* published an enantioselective synthesis with a palladium-catalyzed domino cyclization as the key step. The starting material of this key step is the chiral allene **G**.

Allene **G** can be prepared from propargylic alcohol **E** using a method developed by *Myers* in 1996. Here you can see the principle of this method.

Myers Method:



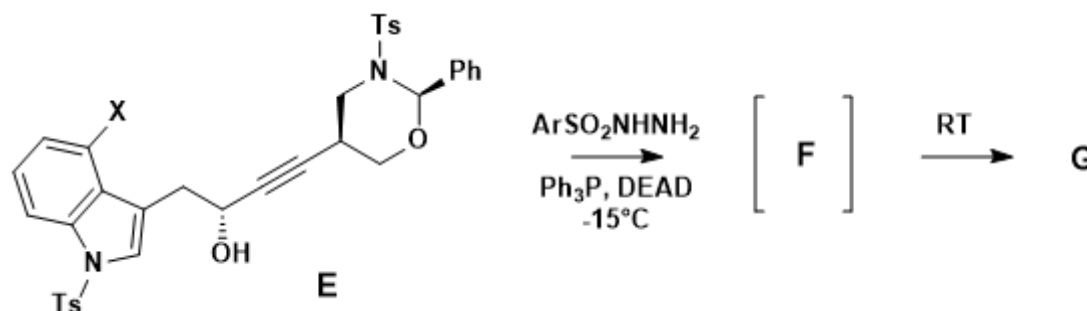
4.3 Write down the stereo descriptor of **D**.

aR

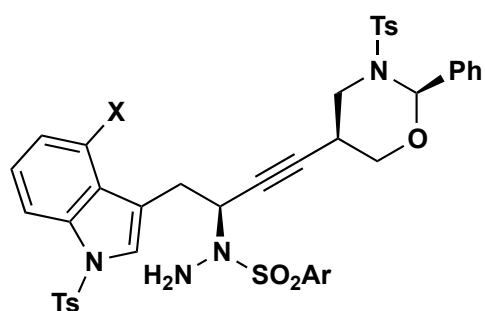
2 bp

### Synthesis of the chiral allene **G**

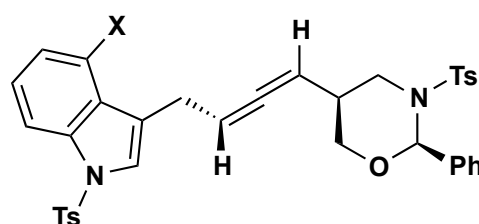
(X = halogen, TsOH = Me-Ph-SO<sub>3</sub>H, DEAD diethyl azodicarboxylate (EtOCO)<sub>2</sub>N<sub>2</sub>):



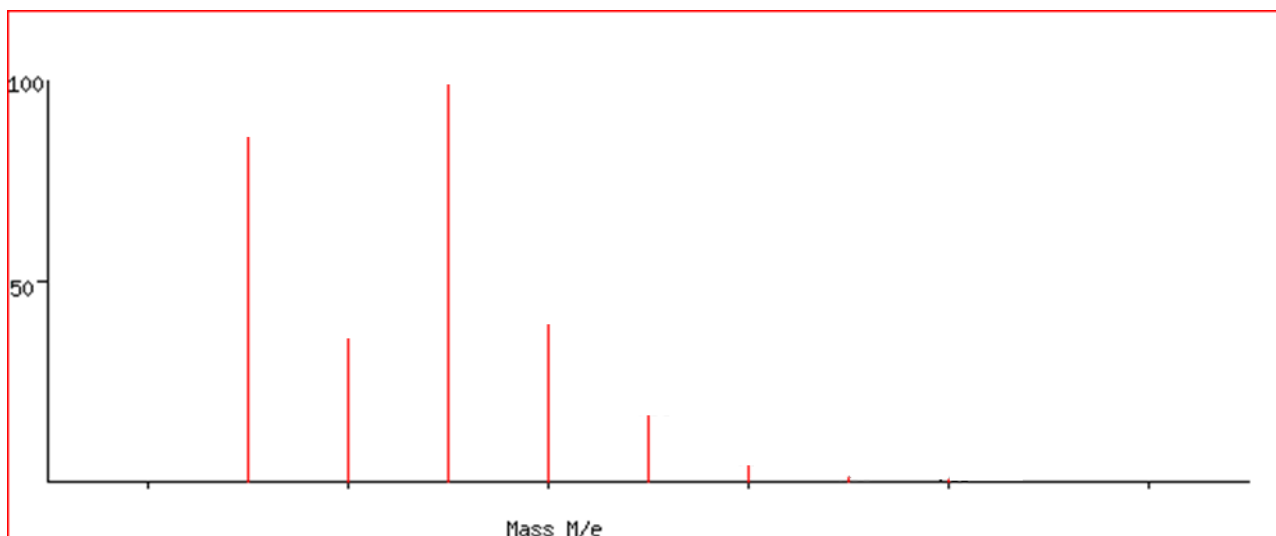
4.4 Draw the intermediate **F** with the correct stereochemistry.



4.5 Draw the chiral allene **G** with the correct stereochemistry.



The following mass spectrum shows the isotope distribution of propargylic alcohol **E**. The distance between each signal is 1.



4.6 Determine - based on the isotopic distribution only - which halogen *X* is present in **E** and give its name.

Bromine

2 bp

*Cs & Co***A. Cesium chloride**

The reaction of cesium with chlorine gas is strongly exothermic. The standard enthalpy of formation of cesium chloride is -443 kJ/mol. Below more physical data around cesium and chlorine are given:

|  |       |                              |
|--|-------|------------------------------|
| Sublimation enthalpy of Cs:              | +78.0 | kJ/mol                       |
| 1. ionization energy of Cs:              | 3.89  | eV                           |
| 2. ionization energy of Cs:              | 23.16 | eV                           |
| Dissociation energy of Cl <sub>2</sub> : | 243   | kJ/mol                       |
| Electron affinity of Cl:                 | 3.62  | eV (Attention "stupid sign") |

5.1 Calculate the lattice energy of CsCl.  
(Hint: Draw the Born-Haber cycle).

Calculation:

$$\Delta_f H^\circ = \Delta_{Sub} H^\circ + \Delta_{1.Ion} H^\circ + \frac{1}{2} \cdot \Delta_{Diss} H^\circ + (-\Delta_{EAff} H^\circ) + \Delta_{Gitt} H^\circ$$

$$\Delta_{Gitt} H^\circ = -443 - 78,0 - 375 - \frac{1}{2} \cdot 243 + 349 = -669 \text{ kJ/mol} \quad \mathbf{2.5 \text{ bp}}$$

5.2 By which factor do you have to multiply the lattice energy of CsCl to get an estimate for the lattice energy of BaO?

4

**1 bp**

Among other things, cesium chloride is used in atomic absorption spectrometry (AAS) as an ionization buffer to counteract the ionization of easily ionizable metals. Cesium chloride shows a better performance in this task than potassium chloride.

5.3 Which of the following statements here are **not true**? Indicate the numbers.

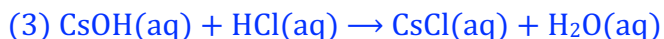
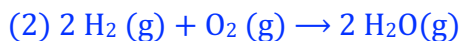
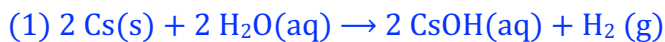
- The ionic radius of K<sup>+</sup> is smaller than that of Cs<sup>+</sup>.
- The radius of the hydrated Cs<sup>+</sup> is smaller than that of the hydrated K<sup>+</sup> ion.
- Cs<sup>+</sup> Ions increase the pH of an aqueous solution.
- Due to the covalent nature of the bond between the Cs<sup>+</sup> and Cl<sup>-</sup> ions, CsCl is more suitable as an ionization buffer for AAS than potassium chloride.

iii, iv

(4x0.5 bp) **2 bp**

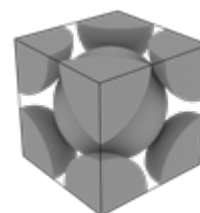
The student L. takes great pleasure in strongly exothermic reactions. To produce cesium chloride, he throws a small amount of elemental cesium into a beaker of water (1) complying with all safety precautions. A small explosion occurs (2). He then neutralizes the resulting solution with a suitable acid (3).

5.4 Formulate chemical equations with indices (*s, l, g, aq*) for reactions (1), (2), and (3) that occur in this rather questionable experiment.



0.5 each = 1.5 bp

When the solution is evaporated, the resulting solid crystallizes in a cubic structure with a  $\text{Cl}^-$  at each corner and a  $\text{Cs}^+$  in the center of the unit cell. (Ionic radii:  $r_+ = 169 \text{ pm}$ ;  $r_- = 181 \text{ pm}$ ).



5.5 To which Bravais lattice does this unit cell belong? Mark with a cross correctly.

primitive cubic

body centered cubic

face centered cubic

cubic primitive (CsCl type!!)

0.5 bp

5.6 Calculate the lattice constant *a*.

$$d_r = 2r_- + 2r_+ = 700 \text{ pm} \quad a = \frac{d_r}{\sqrt{3}} = 404 \text{ pm}$$

1 bp

Using X-rays of wavelength 71.0 pm, the glancing angle  $2\theta$  of the (100) reflection was measured to be  $10.00^\circ$  in X-ray diffraction on a cesium chloride single crystal.

5.7 Check your previous calculation of the lattice constant by calculating it again using Bragg's law.

$$\sin \theta = \frac{\lambda}{2a} \sqrt{h^2 + k^2 + l^2}$$

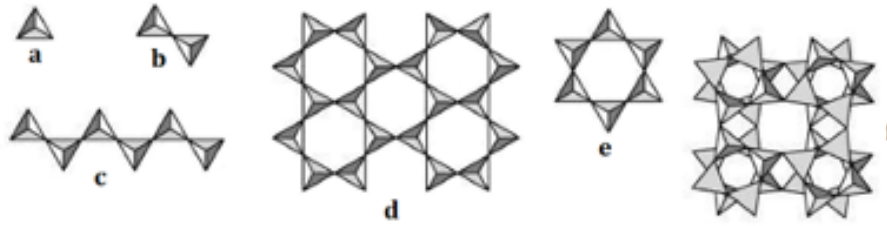
$$a = \frac{\lambda}{2 \cdot \sin \theta} \cdot \sqrt{h^2 + k^2 + l^2} = \frac{71}{2 \cdot \sin 5} \cdot \sqrt{1 + 0 + 0} = 407 \text{ pm}$$

1.5 bp

The Tanco Mine is a cesium-lithium-tantalum mine located in the Canadian province of Manitoba on the shores of Bernic Lake. The ore deposit consists of a granitic pegmatite ore body. Mined are spodumene, a lithium ore, wodginite, a tantalum ore and since 1992 mainly pollucite, a cesium ore.

Pollucite is a mineral from the mineral class of aluminosilicates. It crystallizes in the cubic crystal system with the composition  $(\text{Cs,Na})_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot \text{H}_2\text{O}$ .

The structures of the known silicate families are shown in the following figure.



5.8 Give the Si-O ratio and the name for each of the silicate families a to f.

- a) Si:O = 1:4 (orthosilicate)
- b) Si:O = 2:7 (pyrosilicate)
- c) Si:O = 1:3 (metasilicate)
- d) Si:O = 2:5 (phyllosilicate)
- e) Si:O = 1:3 (cyclic metasilicate)
- f) Si:O = 1:2 (tectosilicate).

each Si:O ratio 0.25 bp, each name 0.25bp  
3 bp

5.9 To which of the silicate families does pollucite belong?

tectosilicate

0.5 bp

Lepidolite is another rare cesium-bearing aluminosilicate with the general formula  $\text{KCs}_{0...6}\text{Al}_{0...2}[\text{F}_2(\text{Si},\text{Al})_4\text{O}_{10}]$ . It develops predominantly white, grayish-purple to pink mineral aggregates. The pink color is caused by  $\text{Mn}^{2+}$  present in low amounts.

5.10 To which of the silicate families mentioned does lepidolite belong?

Si:O = 2:5 (phyllosilicate)

0.5 bp

5.11 List all theoretically possible compositions of lepidolites with the following conditions: There must be at least three Si and at least one Cs in the formula.

- $\text{KCs}_2\text{Al}[\text{F}_2(\text{Si}_4\text{O}_{10})]$
- $\text{KCs}_5[\text{F}_2(\text{Si}_4\text{O}_{10})]$
- $\text{KCs}_3\text{Al}[\text{F}_2(\text{Si}_3\text{AlO}_{10})]$
- $\text{KCs}_6[\text{F}_2(\text{Si}_3\text{AlO}_{10})]$

0.5 each = 2 bp



Silicate 1



Silicate 2

5.12 Assign these two photos to the two minerals pollucite and lepidolite.

Silicate 1: Pollucite

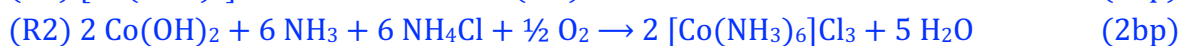
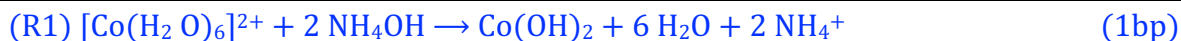
Silicate 2: Lepidolite

1 bp

## B. Complexes of cobalt

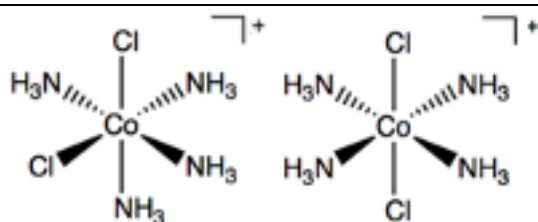
From a solution of hexaaquacobalt(II) chloride, a precipitate of cobalt(II) hydroxide initially precipitates on addition of ammonia solution (R1), which dissolves in the excess of ammonia and ammonium chloride and the presence of atmospheric oxygen as oxidizing agent to form various aminocobalt(III) complexes. In particular, the orange-yellow hexaammincobalt(III) chloride (R2) but also tetraamminedichloridocobalt(III) chloride are formed.

5.13 Give coordinated (ion) equations for reactions (R1) and (R2).



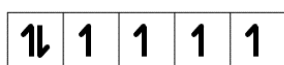
3 bp

5.14 Draw 2 diastereomers of tetraamminedichloridocobalt(III).



1 bp

5.15 For tetraamminedichloridocobalt(III), write the scheme according to Pauling and indicate which hybridization of the Co-central ion is present.



3d

$sp^3 d^2$



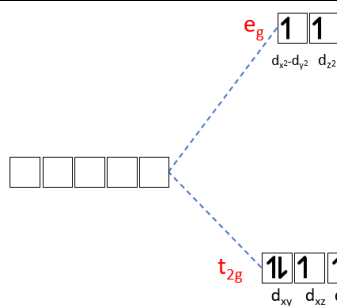
4s

4p

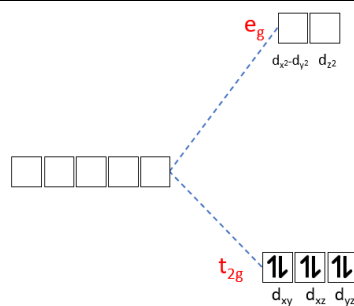
4d

(two valid solutions for the scheme) 1.5 bp

5.16 Now also draw two d-orbital schemes according to ligand field theory including occupation for the high-spin and the low-spin complex.



high spin



low spin

2 bp



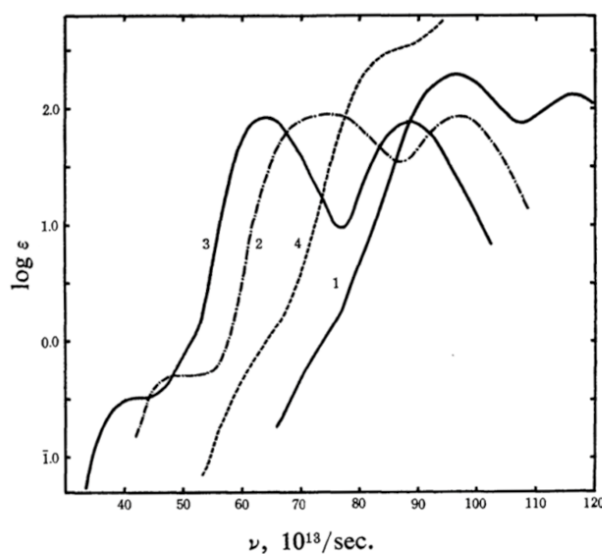
5.17 Calculate the magnetic moments (spin-only) in Bohr magnetons for the high spin and low spin tetraammine dichloridocobalt(III) complex.

high spin:  $\mu_{\text{ber}} = \sqrt{n(n+2)} \cdot \mu_{\text{B}} = \sqrt{4(4+2)} \cdot \mu_{\text{B}} = 4,90 \mu_{\text{B}}$  (1 bp)

low spin:  $\mu_{\text{ber}} = 0 \mu_{\text{B}}$  (0.5 bp)

1.5 bp

Junnosuke FUJITA and Yoichi SHIMURA published absorption spectra of *cis*-[Co(CN)<sub>2</sub>en<sub>2</sub>]<sup>+</sup> (A), [Co(CN)<sub>6</sub>]<sup>3-</sup> (B), [Coen<sub>3</sub>]<sup>3+</sup> (C), and [Co(CN)<sub>5</sub>SO<sub>3</sub>]<sup>4-</sup> (D) in 1963.



(Abb.: The Absorption Spectra of Cobalt(III) Complexes. III. The Spin-forbidden Bands; Fujita Junnosuke and Shimura Yoichi; Bulletin of the Chemical Society of Japan 1963 36:10, 1281-1285)

5.18 Assign the four complexes A-D to the four spectra 1-4.

Spectrum 1: B

Spectrum 2: A

Spectrum 3: C

Spectrum 4: D

(0.5 bp each)

2 bp

### Formation and decay of hydrogen iodide

*Bodenstein* carried out kinetics measurements on hydrogen iodide at the end of the 19<sup>th</sup> century. He concluded that both formation and decay represent a bimolecular reaction and was also able to determine the activation energies for the formation and decay of hydrogen iodide.



$$E_{A,\text{formation}} = 167 \text{ kJ}\cdot\text{mol}^{-1}, E_{A,\text{decay}} = 184 \text{ kJ}\cdot\text{mol}^{-1}$$

6.1 The decay of hydrogen iodide corresponds to a reaction of: (Tick correctly!)

 0<sup>th</sup> order

 1<sup>st</sup> order

 2<sup>nd</sup> order

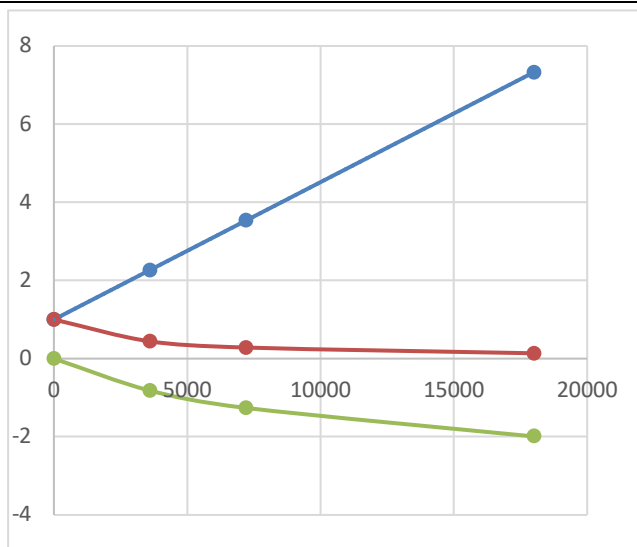
 2<sup>nd</sup> order

1 bp

The following measurement values were obtained at 556 K:

|                               |       |        |        |        |
|-------------------------------|-------|--------|--------|--------|
| $t / \text{h}$                | 0     | 1      | 2      | 5      |
| $[\text{HI}] / \text{mol/mL}$ | 1,000 | 0,441  | 0,283  | 0,136  |
| $\ln[\text{HI}]$              | 0,000 | -0,817 | -1,261 | -1,991 |
| $1/[\text{HI}]$               | 1,000 | 2,265  | 3,531  | 7,328  |

6.2 Using a graph, show that the assumption of a bimolecular reaction does not contradict the given measured values. Make sure that the axes are labeled correctly.



only  $1/[A]$  (blue) is linear, therefore 2<sup>nd</sup> order

2 bp

6.3 Indicate (with sign) by what percentage the initial concentration must be changed to achieve a doubling of the reaction rate.

+41%

1 bp

6.4 Determine the reaction rate constant (with 3 significant digits) and write it down with the corresponding unit.

 $k = 1.27 \text{ mL}/(\text{mol}\cdot\text{h})$  or  $k = 3.52 \cdot 10^{-7} \text{ L}/(\text{mol}\cdot\text{s})$ 

2 bp

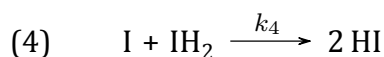
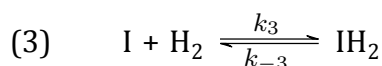
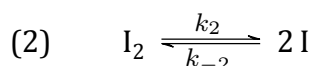
6.5 Calculate the rate constant for the decay at 720 K.

$$\ln \frac{k_{720}}{k_{556}} = -\frac{E_A}{R} \left( \frac{1}{720} - \frac{1}{556} \right) = -\frac{184000}{8,3145} (-4,097 \cdot 10^{-4}) = 9,066$$

$$k_{720} = 1.10 \cdot 10^4 \text{ mL}/(\text{mol}\cdot\text{h}) \text{ or } k = 3.06 \cdot 10^{-3} \text{ L}/(\text{mol}\cdot\text{s})$$

2 bp

Later investigations have shown that the formation of hydrogen iodide is not quite as simple as originally assumed. It could be shown that the following elementary reactions play a role in the formation of hydrogen iodide.



6.6 Establish the differential velocity laws for  $[\text{HI}]$  and  $[\text{IH}_2]$ .

$$\frac{d[\text{HI}]}{dt} = 2 k_4 \cdot [\text{I}] \cdot [\text{IH}_2]$$

$$\frac{d[\text{IH}_2]}{dt} = k_3 \cdot [\text{I}] \cdot [\text{H}_2] - k_{-3} \cdot [\text{IH}_2] - k_4 \cdot [\text{I}] \cdot [\text{IH}_2]$$

3 bp

Reactions (2) and (3) are very fast upstream equilibria, that is,  $k_4 \ll k_{-2}$ ,  $k_{-3}$  and the concentrations occurring in the equilibria can be determined using the corresponding equilibrium constants.

6.7 Express  $[\text{IH}_2]$  using the equilibrium constants  $K_2$  and  $K_3$  and the concentrations of  $[\text{H}_2]$  and  $[\text{I}_2]$ .

$$[\text{IH}_2] = K_2^{(1/2)} \cdot K_3 \cdot [\text{H}_2] \cdot [\text{I}_2]^{(1/2)}$$

2 bp

Under the condition of upstream equilibria, the reaction rate for the formation of hydrogen iodide (1) can be described as follows:

$$v = \frac{1}{2} \frac{d[\text{HI}]}{dt} = k_{tot} \cdot [\text{H}_2]^a \cdot [\text{I}_2]^b$$

6.8 Determine the reaction orders  $a$  and  $b$  and give the relationship between  $k_{tot}$  and the rate constants of the partial steps.

$$a = 1 \quad b = 1 \quad (1\text{bp})$$

$$k_{ges} = k_4 \frac{k_2}{k_{-2}} \cdot \frac{k_3}{k_{-3}} \quad (1\text{bp}) \text{ or } k_{ges} = k_4 K_2 K_3 \quad (0.5\text{bp})$$

2 bp

## Equilibria of mercury

Assume that 0.0500 g of mercury(II) oxide dissolves completely in 1.00 liter of water.

7.1 Write the equation for the reaction of mercury(II) oxide with water and calculate the pH of the resulting solution.



$$M(\text{HgO}) = 216,59 \text{ g/mol}$$

$$c_{\text{HgO}} = \frac{c^*}{M} = \frac{0,05}{216,59} = 0,000231 \text{ mol/L}$$

$$c_{\text{OH}^-} = 2 \cdot c_{\text{HgO}} = 0,000462 \text{ mol/L}$$

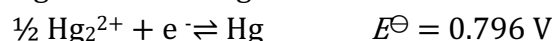
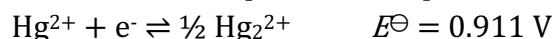
$$\text{pOH} = -\log(0,000462) = 3,34$$

$$\text{pH} = 10,66$$

3 bp

In compounds, mercury can occur divalent (as  $\text{Hg}^{2+}$  ion) and monovalent. The monovalent mercury is always present as a diatomic cluster; therefore, the ion is written in the form  $\text{Hg}_2^{2+}$ . The salts have corresponding formulas such as  $\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}_2\text{I}_2$ .

Given are the reduction potentials at pH = 0:



7.2 Calculate the reduction potential for the reaction  $\text{Hg}_2^{2+} + 2e^- \rightleftharpoons \text{Hg}$ .

$$E^\ominus = \frac{0,911 + 0,796}{2} = 0,8535 \text{ V}$$

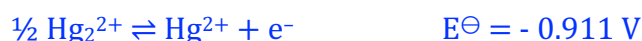
1 bp

The mercury(I) ion can also disproportionate:  $\text{Hg}_2^{2+} \rightleftharpoons \text{Hg}^{2+} + \text{Hg}$ .

7.3 Using the reduction potentials given, calculate the equilibrium constant for the disproportionation reaction.



$$\Delta G_1^\ominus = -z \cdot F \cdot E = -1 \cdot 96485 \cdot 0,796 = -76802,1 \text{ J/mol}$$



$$\Delta G_2^\ominus = -z \cdot F \cdot E = -1 \cdot 96485 \cdot (-0,911) = 87897,8 \text{ J/mol}$$



$$\Delta G^\ominus = \Delta G_1^\ominus + \Delta G_2^\ominus = 11095,8 \text{ J/mol}$$

$$K = e^{\frac{-\Delta G^\ominus}{R \cdot T}} = e^{\frac{-11095,8}{8,3145 \cdot 298,15}} = 0,011379$$

4 bp

A mercury(II) nitrate solution (0.0100 mol/L) reacts with an excess of elemental mercury.

7.4 Using the result from the previous example, calculate the concentrations of  $\text{Hg}^{2+}$  and  $\text{Hg}_2^{2+}$  in this solution. If you have not obtained a result for the equilibrium constant, use the value  $K = 0.012$ .

$$(1) \frac{[\text{Hg}^{2+}][\text{Hg}]}{[\text{Hg}_2^{2+}]} = \frac{[\text{Hg}^{2+}]}{[\text{Hg}_2^{2+}]} = 0.011379$$

$$(2) [\text{Hg}^{2+}] + [\text{Hg}_2^{2+}] = 0.01$$

$$(1) \text{ in } (2): \quad 0.011379 \cdot [\text{Hg}_2^{2+}] + [\text{Hg}_2^{2+}] = 0.01$$

$$[\text{Hg}_2^{2+}] = \frac{0.01}{1.011379} = 0.009887 \text{ mol/L}$$

$$[\text{Hg}^{2+}] = 0.01 - 0.009887 = 0.000113 \text{ mol/L}$$

5 bp

The solubility product of  $\text{Hg}_2\text{F}_2$  is  $3.10 \cdot 10^{-6}$ .

7.5 Calculate the standard potential for the reaction  $\text{Hg}_2\text{F}_2 + 2e^- \rightleftharpoons 2\text{Hg} + 2\text{F}^-$ .

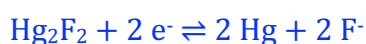


$$\Delta G_1^\ominus = -R \cdot T \cdot \ln K = 31443.5 \text{ J/mol}$$



$$E^\ominus = 0.796 \text{ V}$$

$$\Delta G_2^\ominus = -z \cdot F \cdot E = -153604 \text{ J/mol}$$



$$\Delta G^\ominus = \Delta G_1^\ominus + \Delta G_2^\ominus = -122161 \text{ J/mol}$$

$$E^\ominus = \frac{\Delta G^\ominus}{-z \cdot F} = \frac{-122161}{-2 \cdot 96485} = 0.633 \text{ V}$$

4 bp

To 1.00 liter of a mercury(II) nitrate solution (0.0100 mol/L), 1.00 g of solid NaOH is added. Two different complexes are formed, whose complex formation constants are given below:

$$[\text{Hg}(\text{OH})]^+ \quad \beta_1 = 2.00 \cdot 10^{10}$$

$$[\text{Hg}(\text{OH})_2] \quad \beta_2 = 5.01 \cdot 10^{21}$$

For the following calculations, assume that no precipitate forms and that there is no change in the oxidation state of mercury.

7.6 Calculate the pH of the resulting solution and the concentrations of all mercury species present in the solution. If simplifying assumptions have to be made, then these are to be checked with the results for their reasonableness.

$$(1) \quad 0.01 = [\text{Hg}^{2+}] + [[\text{Hg}(\text{OH})]^+] + [[\text{Hg}(\text{OH})_2]]$$

$$(2) \quad \frac{1}{40} = [\text{OH}^-] + [[\text{Hg}(\text{OH})]^+] + 2 \cdot [[\text{Hg}(\text{OH})_2]]$$

$$(3) \quad \frac{[[\text{Hg}(\text{OH})]^+]}{[\text{Hg}^{2+}] \cdot [\text{OH}^-]} = 2.00 \cdot 10^{10}$$

$$(4) \quad \frac{[[\text{Hg}(\text{OH})_2]]}{[\text{Hg}^{2+}] \cdot [\text{OH}^-]^2} = 5.01 \cdot 10^{21}$$

(3) and (4) combined with (1):

$$0.01 = [\text{Hg}^{2+}] + 2.00 \cdot 10^{10} \cdot [\text{Hg}^{2+}] \cdot [\text{OH}^-] + 5.01 \cdot 10^{21} \cdot [\text{Hg}^{2+}] \cdot [\text{OH}^-]^2$$

transformed to: 
$$\frac{0.01}{1 + 2.00 \cdot 10^{10} \cdot [\text{OH}^-] + 5.01 \cdot 10^{21} \cdot [\text{OH}^-]^2} = [\text{Hg}^{2+}]$$

Based on the high complexation constants, it can be assumed that almost all mercury will be present as a complex, and here preferentially as  $[\text{Hg}(\text{OH})_2]$ . For the hydroxide ion concentration this means that the hydroxide ion concentration decreases by  $0.01 \cdot 2 = 0.02$  mol, i.e. approx. 0.005 mol/L.

This means:

$$1 \ll 2.00 \cdot 10^{10} \cdot [\text{OH}^-] \ll 5.01 \cdot 10^{21} \cdot [\text{OH}^-]^2$$

So you can simplify to:

$$(5) \quad [\text{Hg}^{2+}] = \frac{0.01}{5.01 \cdot 10^{21} \cdot [\text{OH}^-]^2}$$

(3) and (4) combined with (2):

$$0.025 = [\text{OH}^-] + 2.00 \cdot 10^{10} \cdot [\text{Hg}^{2+}] \cdot [\text{OH}^-] + 2 \cdot 5.01 \cdot 10^{21} \cdot [\text{Hg}^{2+}] \cdot [\text{OH}^-]^2$$

combined with (5):

$$0.025 = [\text{OH}^-] + 2.00 \cdot 10^{10} \cdot \frac{0.01}{5.01 \cdot 10^{21} \cdot [\text{OH}^-]^2} \cdot [\text{OH}^-] + 2 \cdot 5.01 \cdot 10^{21} \cdot \frac{0.01}{5.01 \cdot 10^{21} \cdot [\text{OH}^-]^2} \cdot [\text{OH}^-]^2$$

$$0.025 = [\text{OH}^-] + \frac{1}{2.505 \cdot 10^{13} \cdot [\text{OH}^-]} + 0.02$$

results:

$$[\text{OH}^-] = 0.005 \text{ mol/L}$$

$$[\text{Hg}^{2+}] = \frac{0.01}{5.01 \cdot 10^{21} \cdot [\text{OH}^-]^2} = 7.98 \cdot 10^{-20} \text{ mol/L}$$

$$[[\text{Hg}(\text{OH})]^+] = 2.00 \cdot 10^{10} \cdot [\text{Hg}^{2+}] \cdot [\text{OH}^-] = 7.98 \cdot 10^{-12} \text{ mol/L}$$

$$[[\text{Hg}(\text{OH})_2] = 5.01 \cdot 10^{21} \cdot [\text{Hg}^{2+}] \cdot [\text{OH}^-]^2 = 0.01 \text{ mol/L}$$

The assumption was correct!

$$\text{pOH} = -\log(0.005) = 2.30$$

$$\text{pH} = 14 - \text{pOH} = 11.70$$

16 bp