

46. Austrian Chemistry Olympiad National Competition Substitute competition II

27. June 2020

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Notes - as a reminder

You have already received the information in the run-up to the competition, here are just a few keywords to remember:

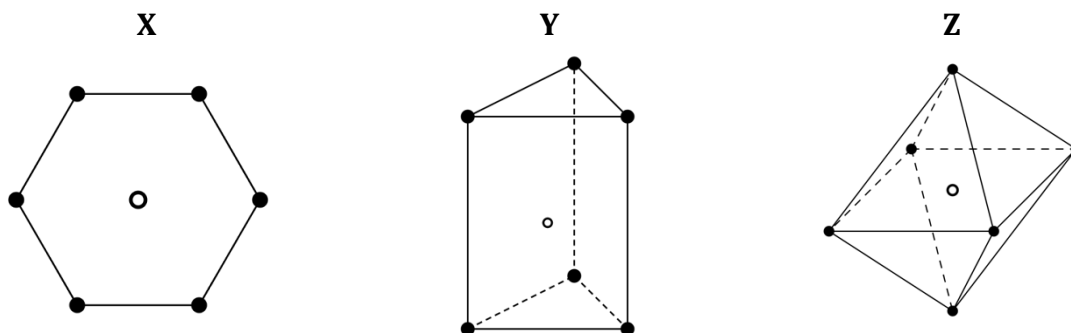
- You are solely responsible for ensuring that we can match and read your answers.
- Show calculation methods when required.
- Do not forget the units.
- Use all digits of the molar masses and constants!
- For organic reaction schemes use the abbreviations (e.g., MsCl, tBu, ...) which are also used in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

Problem 1 (N. Langer)

6 points

Isomer counting by Alfred Werner and complexes of cobalt

Alfred Werner used the technique of isomer counting to deduce the structure of metal complexes with coordination number of six. Three of the shapes he considered are shown below.



In each structure, the empty circle shows the location of the central metal atom and the filled circles show the location of the ligands. Structure **X** is hexagonal planar, structure **Y** is trigonal prismatic and structure **Z** is octahedral.

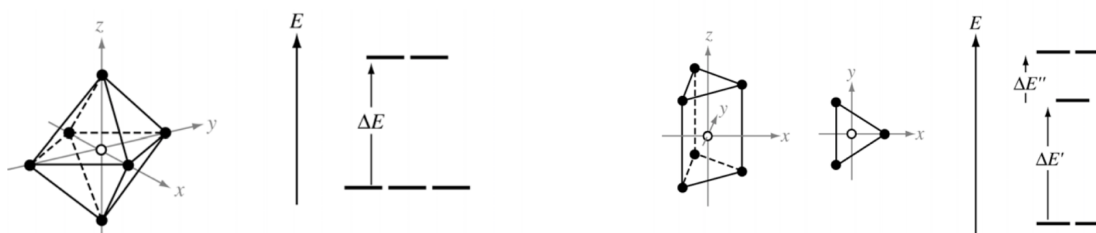
For each of the three shapes, there is just one structure when all of the ligands are the same, i.e. when the complex has the general formula MA_6 where A is the ligand. However, when achiral ligands A are substituted by one or more achiral ligands, it may be possible for each structure to form geometrical isomers. It might also be possible for one or more of the geometrical isomers to be optically active and exist as pairs of enantiomers.

The monodentate ligands A are substituted by monodentate ligands B or by symmetrical bidentate ligands, denoted C-C. Bidentate ligand C-C can only link between two atoms on adjacent positions, i.e. those positions connected by a line in the structures **X**, **Y**, and **Z**.

*1.1 In the answer sheet, create the table below. Indicate how many geometric isomers exist for each of the three structures X, Y, and Z. Write the number of possible geometric isomers in each box. If one of the isomers occurs as a pair of enantiomers, add an asterisk * to the number.*

	number of predicted geometric isomers		
	hexagonal planar X	trigonal prismatic Y	oktahedral Z
MA_6	1	1	1
MA_4B_2			
$MA_4(C-C)$			
$MA_2(C-C)_2$			

There are no known complexes that adopt the hexagonal planar geometry **X**, but structures are known for both the trigonal prismatic geometry **Y** and the octahedral geometry **Z**. In these complexes, the orbitals derived from the metal d-orbitals have different energies depending on the geometry of the complex. The splitting patterns for the trigonal prismatic geometry and for the octahedral geometry are shown below.



1.2 Draw the energy level diagram for both coordinations/shapes and label which d-orbitals are which.

The complexes $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Mn}(\text{CN})_6]^{2-}$ are both octahedral. One has a magnetic moment of $5,9 \mu_{\text{B}}$, the other has a magnetic moment of $3,9 \mu_{\text{B}}$.

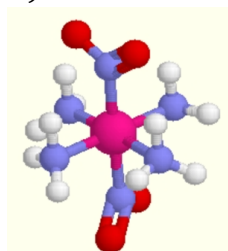
1.3 Draw an occupancy scheme for the d-orbitals for both complexes and write the appropriate magnetic moment.

Octahedral complexes are far more common than trigonal prismatic. Werner isolated five compounds **C**, **D**, **E**, **F**, **G** containing Co(III), Cl, and NH_3 only, each of which contained one octahedral complex. Werner's five compounds had the molar conductivities shown below. The conductivities are extrapolated to infinite dilution and are expressed in arbitrary units. Compound **G** does not react with aqueous AgNO_3 ; compounds **C**, **D**, and **E** react with different stoichiometric ratios of aqueous AgNO_3 ; **E** and **F** react with the same stoichiometric ratio of aqueous AgNO_3 .

	C	D	E	F	G
Molar conductivity in $\text{S cm}^2 \text{ mol}^{-1}$	510	372	249	249	~ 0

1.4 Draw all possible structures of compounds **C**, **D**, **E**, **F**, **G**.

Here is a three-dimensional model of another octahedral complex of cobalt with different ligands (N is purple, H is white, O is red).



1.5 Enter the IUPAC name, including the stereo descriptor of the cobalt(III) complex.

Many complexes exist as isomers, with a distinction being made between stereo and structural isomers.

1.6 Give the formula for an ionization isomer of $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{SO}_4$.

Cobalt(III) complexes are octahedral and intensely colored. Three complex compounds with ligand field splitting are listed in the table. The possible colors are yellow, orange-yellow, blue, and dark green.

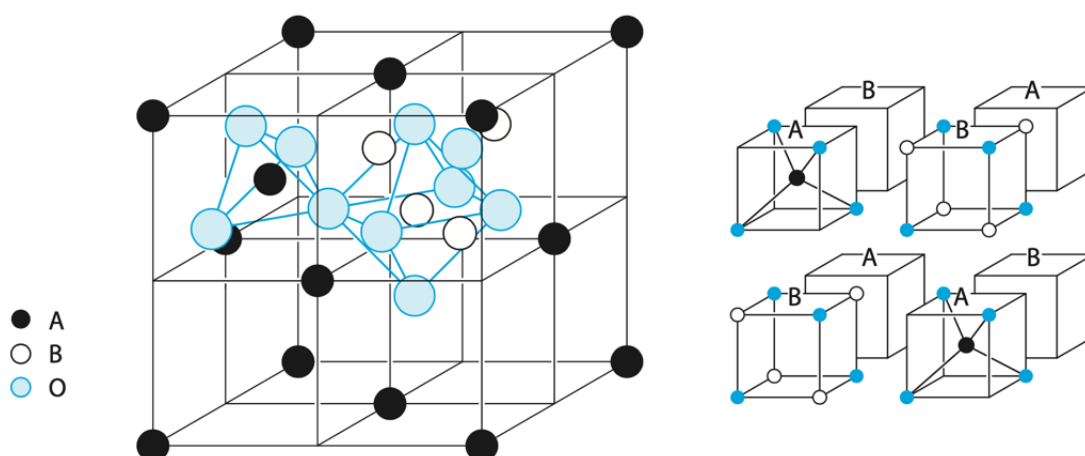
	Complex	Ligand field splitting in cm^{-1}
(i)	$[\text{Co}(\text{C}_2\text{O}_4)_6]^{3-}$	18000
(ii)	$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	18200
(iii)	$[\text{Co}(\text{NH}_3)_6]^{3+}$	22900
(iv)	$[\text{Co}(\text{en})_3]^{3+}$	33500

1.7 Assign the correct color to each complex (e.g., write (vii) green).

Cobalt does not form only complex compounds. The olive green cobalt(II) oxide is formed from the elements at 1100°C . The ionic radius of Co^{2+} is $0,82 \text{ \AA}$ and that of the oxide ion is 140 pm .

1.8 In which type (CsCl , NaCl , ZnS) does cobalt(II) oxide crystallize? Prove your claim with a calculation.

Another cobalt compound is Thénards Blau. That compound, also called cobalt blue ($M = 176.89 \text{ g/mol}$), has a spinel structure shown below:



A and B are two different metal ions with different oxidation numbers that coordinate tetrahedrally and octahedrally with O^{2-} ions. In fact, tetrahedrally coordinated sites are often called A sites, and octahedrally coordinated sites are called B sites. The figure on the left introduces the unit cell of spinel. The right one shows the inner workings of the 8 cube parts,

so to speak, and thus indicates exactly where which atoms are located. The four rear cubes are not filled in for clarity, but of course, they are occupied as well as the front ones.

1.9 Determine the formula of the unit cell and the empirical formula for compounds with spinel structure.

1.10 Determine the molecular formula of Thénards Blue.

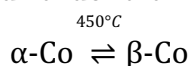
Cobalt compounds are used in medicine to treat cyanide poisoning. The person poisoned with cyanide receives an infusion with a solution of a chelate complex consisting of cobalt(II) and the hexavalent ligand (EDTA)⁴⁻. In a ligand exchange reaction, the cyanide ions present in the blood form very stable hexacyanidocobalt(II) complex, which is easily soluble in water and excretable.

1.11 Give a coordinated ion equation of the ligand exchange reaction.

Another medical application is the nuclide cobalt-60 as a powerful gamma radiation source for irradiating malignant tumors when other forms of therapy fail. Cobalt-60 is exclusively obtained artificially by neutron activation from the only stable cobalt-59 nuclide and shows β^- decay.

1.12 Write down the two nuclear reaction equations for the formation and decay of cobalt-60.

Elemental cobalt is steel grey, shiny, and harder than iron. It crystallizes in the modifications:



While α -Co has a hexagonal-dense crystal structure, the structure of β -Co is face-centered cubic (fcc). The metal radius of cobalt is 1,25 Å.

1.13 Calculate the density of β -Co in g/cm³.

Problem 2 (W. Faber)

6 points

Chlorine in the pool and equilibrium

Inexpensive frame pools are being sold more and more frequently in Austria. Such a frame pool was purchased to offer the teachers a balance to their hard work. This pool has a capacity of 17,00 m³. It was completely filled up with tap water and now has a temperature of 25°C. For further calculations, it can be assumed that the tap water initially contained no dissolved salts.

Then 50,00 kg of NaCl were added to the water in the pool and dissolved. A so-called "salt plant" is responsible for the disinfection of the pool water. Here the pool water is subjected to electrolysis, using a current of 3,79 A. Chlorine gas is produced at the anode and hydrogen at the cathode.

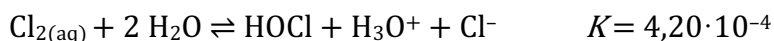
2.1 Calculate the concentration of chloride ions in the pool water before the electrolysis.

2.2 Write the reaction equations for the cathodic and anodic processes.

2.3 Calculate the mass of chlorine gas produced per hour, assuming a complete electric yield.

2.4 Calculate the pH value of the pool if electrolysis was conducted for 10 hours and assuming that only the hydroxide ions formed at the cathode influence this pH value.

For further calculations, assume that in the pool mentioned above with a volume of 17,00 m³ after the addition of 50,00 kg of NaCl and several days of electrolysis, a total of 60,0 g of chlorine gas has dissolved in the water of the pool and that the pool contents has a stable pH of 9,50 and that none of the reactions taking place have a significant influence on the concentration of dissolved chloride ions or the pH value. The chlorine gas reacts with water according to the following equation:



As is common practice with reaction constants, the concentration of water is set to 1 for this constant. The hypochlorous acid HOCl formed is a weak acid with a pK_a value of 7,54.

2.5 To determine which chlorine-containing oxidant plays the most significant role in preventing contamination of the pool, calculate the concentrations of dissolved chlorine gas, hypochlorous acid, and hypochlorite anion in equilibrium under the given conditions.

In the previous example, it was assumed that the pH value does not change during the reactions taking place. The actual change should now be determined. For simplification, we now assume that the entire 60,0 g chlorine gas is first converted into hypochlorous acid. The pH value before the introduction of the chlorine gas is again 9,50.

2.6 Calculate the pH value in the pool by taking into account the H_3O^+ ions formed during the hydrolysis of the chlorine gas. Neglect the acid effect of the (weak) hypochlorous acid.

Problem 3 (C. Hurban)

3 points

Electrochemistry of some chlorine compounds

Various chlorine compounds are still used as disinfectants.

Incomplete Latimer diagrams for chlorine are given at pH = 0 and pH = 14. All potentials are given in Volts.



3.1 Calculate the standard potentials of the chlorate/chlorine redox pair at pH = 0 and pH = 14.

3.2 Write down the half equations for the redox pairs chlorate/chlorine and chlorine/chloride at pH = 0.

3.3 For both redox pairs from 3.2, enter mathematical expressions for the potential that make it clear why those two redox pairs behave differently at different pH values.

3.4 Draw a Frost diagram for the chlorine compounds at pH = 0 and pH = 14 in the same diagram.

3.5 Specify whether Cl₂ in acids (pH = 0) or bases (pH = 14) tends to disproportionate to ClO⁻ and Cl⁻. (yes/no) Justify your respective decision with the help of the frost diagram and/or data from the Latimer diagram.

3.6 Calculate the potential of the half cell chlorate/chlorine at T = 298 K, bringing the pH to 7.0 and not changing the other concentrations.

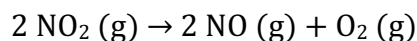
Problem 4 (C. Hurban)

5 points

Kinetics of air pollution

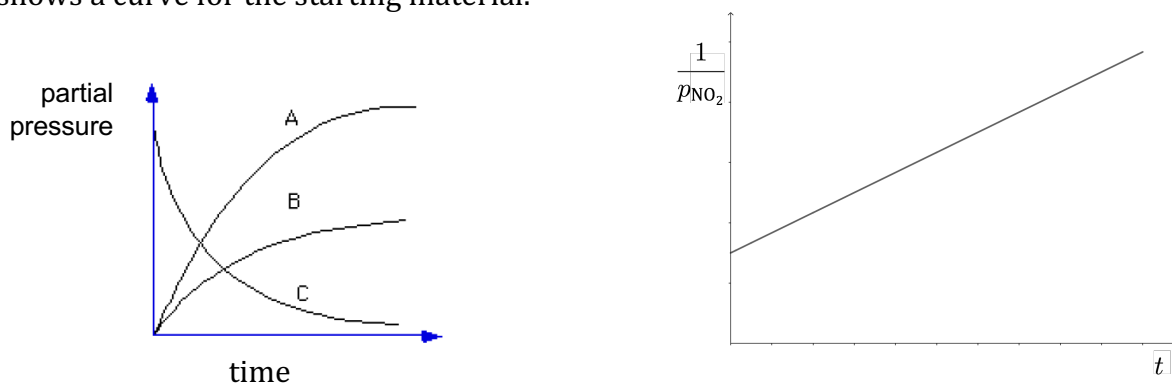
A. Formation of NO

The one-step reaction, according to the following equation, plays a major role in the field of air pollution:



4.1 Express the reaction rate with respect to partial pressures of all three species.

In the left figure, the partial pressures of three species are plotted against time; the right figure shows a curve for the starting material.



4.2 Which of the three curves on the left shows the temporal course of the oxygen partial pressure?

4.3 Specify the reaction order.

4.4 Specify the differential and integral rate law.

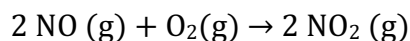
4.5 Derive an expression for the half-life τ from 4.4.

If NO₂ is filled into a container of 2,0 L with an initial pressure of 0,80 bar and 600°C, 50% of the NO₂ is converted after 3,0 minutes.

4.6 Calculate the rate constant of the reaction.

B. Formation of NO₂

The reaction in the other direction is more important at low temperatures:



The following rate law was found for them:

$$v = k \cdot c(\text{NO})^2 c(\text{O}_2)$$

4.7 Specify how the reaction rate changes when the following changes in concentration are made. (For example, write "(vi): v increases by a factor of 4")

- i) $c(\text{O}_2)$ is quadrupled,
- ii) $c(\text{NO})$ is quadrupled,
- iii) $c(\text{NO})$ is halved,
- iv) $c(\text{O}_2)$ is halved, and $c(\text{NO})$ is quadrupled,
- v) $c(\text{NO})$ is halved, and $c(\text{O}_2)$ is quadrupled.

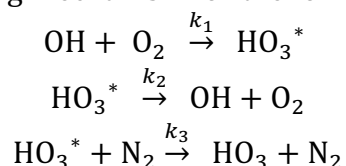
The initial velocity of the considered reaction remains constant if the temperature is increased from 460 °C to 600 °C, and all initial concentrations are bisected.

4.8 Calculate the activation energy.

C. Radicals

The radical OH plays a vital role in the chemistry of the atmosphere. It is very unstable and short-lived. Since it reacts with many air pollutants (such as methane and ozone) and often acts as the first step in their removal, it is sometimes referred to as the "cleaning agent of the troposphere".

It can also react with O₂, producing the radical HO₃. The reaction between O₂ and OH has been studied in detail, and the following mechanism for the formation of HO₃ has been proposed:



HO₃* represents an excited state of HO₃. For the following calculations, consider HO₃* and HO₃ as two different chemical compounds.

4.9 Give the rate law for each elementary reaction.

4.10 Derive an equation for the rate of formation of HO₃. Use the steady-state approximation for all intermediate products.

4.11 The expression obtained in 4.10 becomes more straightforward if we assume that k_2 is negligibly small. What is the simplified expression?

Problem 5 (M. Scherl)

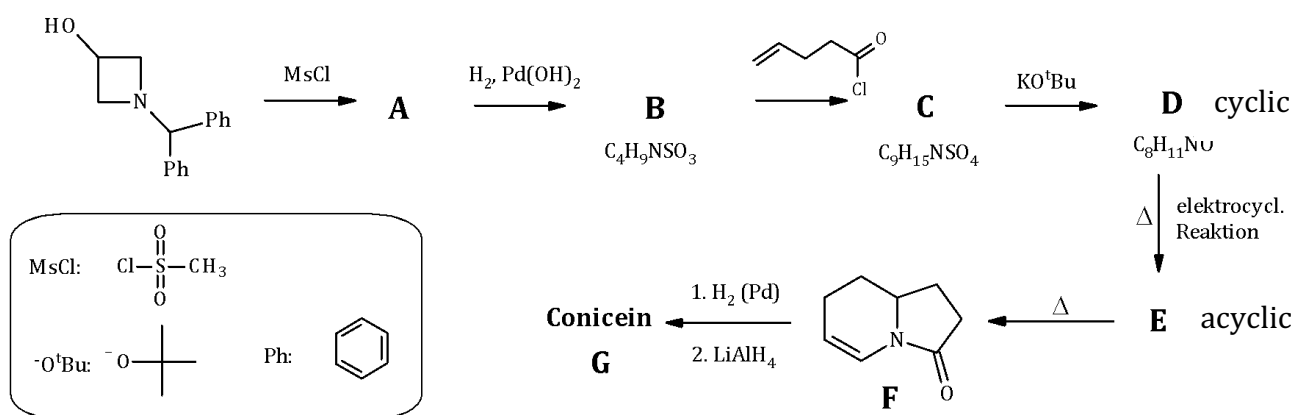
19 points

Organic synthesis

A. Synthesis of conicein (15 bp)

(Jung, M.E.; Choi, Y.M. J. Org. Chem. 1991, 56, 6729.)

This problem is about the synthesis of conicein, a heterocyclic alkaloid. In 1991 it was manufactured using elegant pericyclic reaction steps.



5.1 Draw the constitutional formulas of substances **A**, **B**, **C**, **D**, **E**, **F**, and **G**.

5.2 Draw "arrows" in the structural formula of **D**, which make the formation of **E** plausible.

5.3 Draw "arrows" in the structural formula of **E**, which make the formation of **F** (given) from reactant **E** plausible. Name the given reaction type in as much detail as possible. What is the name of this reaction?

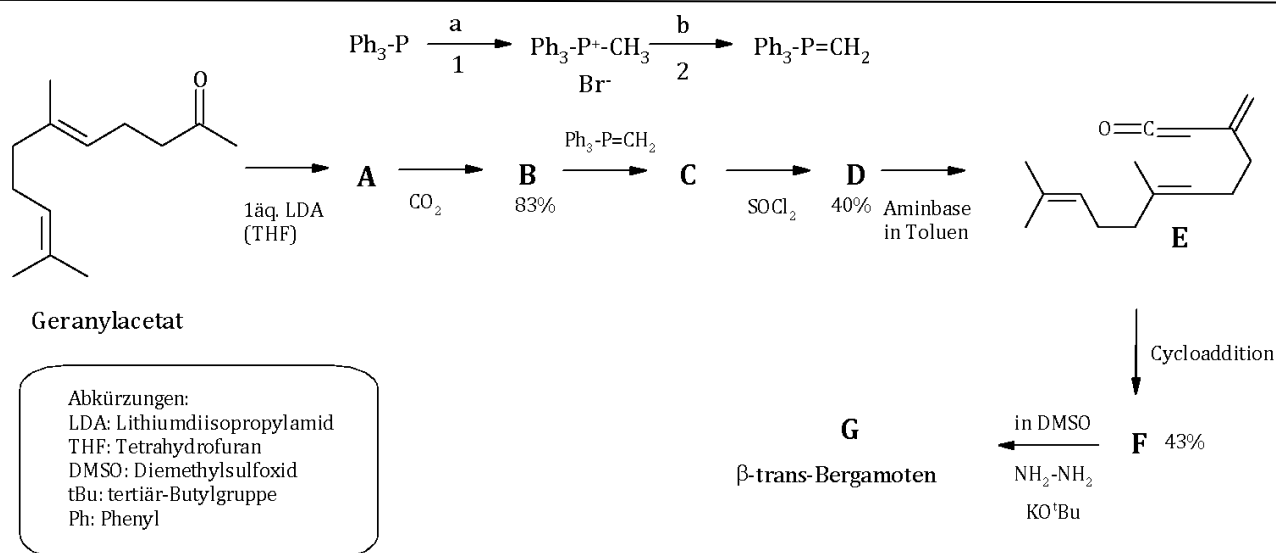
5.4 Write down the function of KO^tBu in the reaction $\text{C} \rightarrow \text{D}$. Name the mechanism according to which this reaction proceeds.

5.5 State the reason why the mesyl group was introduced into the structure of **A**. Write down a maximum of one sentence about it!

B. Synthesis of β -trans-Bergamotes (13,5 bp)

(Corey, E. J. Desai, M.C. Tet. Lett. 1985, 26, 3535.)

Bergamotes form a group of isomeric compounds that occur in various plants, especially in essential oils. This task deals with the synthesis of β -trans-Bergamotes. As a pheromone it acts defensively against the attack of herbivorous insects by attracting natural enemies of these insects.

**Hints:**

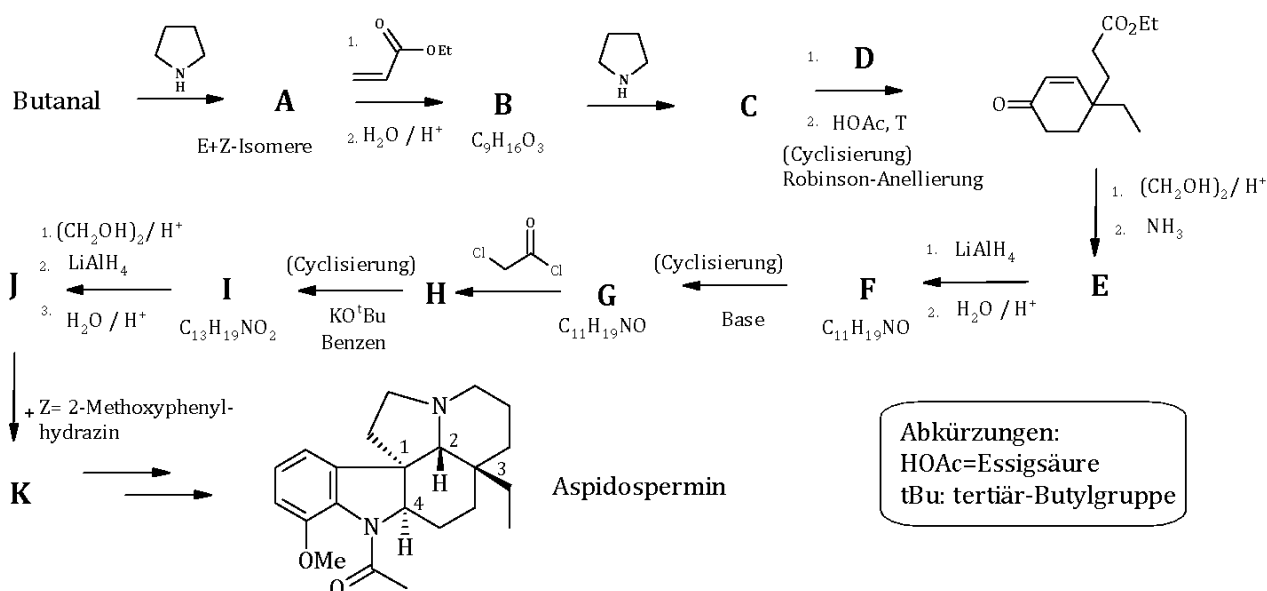
In step **E** to **F** a [2+2]-Cycloaddition with the π electrons of the ketene and a C=C double bond takes place. That results in a derivative of the bicycle „Bicyclo[3.1.1]heptane“. Substance **F** shows an intense IR absorption at 1710 cm^{-1} , substance **G** does not.

5.6 Suggest one reagent a and one reagent b for reaction 1 or 2 in the upper reaction scheme.
5.7 Specify the reaction mechanism according to which reaction 1 in the upper reaction scheme proceeds.
5.8 Draw the resonance structure of the product of reaction 2 in the upper reaction scheme, representing the Ylide.
5.9 Suggest one suitable and one unsuitable solvent for reaction 2 in the above reaction scheme.
5.10 Draw the constitutional formulae of substances A , B , C , D , and the structural formulae of F and G in the correct conformation (no planar rings!)

C. Synthesis of Aspidospermin (25 bp)

(Stork, G.; Dolfini, J.E. J. Am. Chem. Soc. 1963, 85, 2872-2873.)

This task involves the synthesis of aspidospermine, a monoterpenoid indole alkaloid. Aspidospermine is one of over 100 known aspidosperm alkaloids and was first isolated from the quebracho tree, which is native to Chile.



5.11 Draw the structural formulae of **butanal**, **A-K**, and **Z** (11 pieces), taking into account the correct stereochemistry.

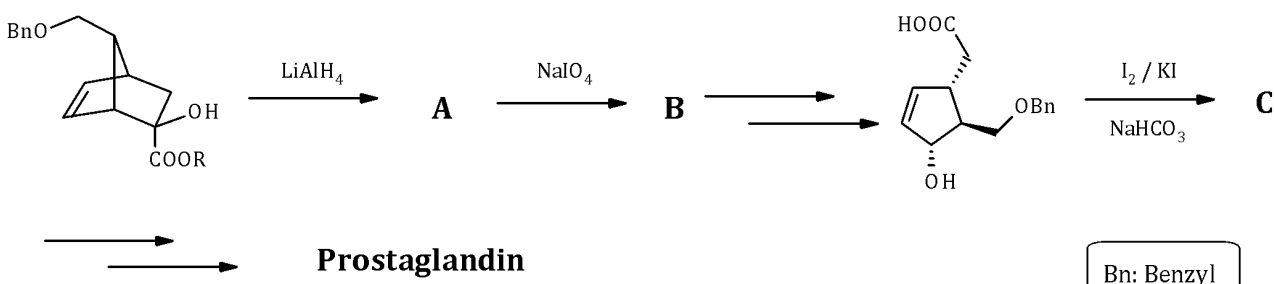
5.12 Name the mechanism by which **K** is formed from **J**.

5.13 Determine the absolute configurations of the stereogenic centers 2-4 in the product **Aspidospermine**. Write only 2 = ...; 3 = ...; etc., do not draw the structure of **aspidospermine**!

D. Synthesis of Prostaglandin-Fragments (10 bp)

(Corey, E. J.; Ensley, H.E. J. Am. Chem. Soc. 1975, 97, 6908.)

Prostaglandins are derivatives of eicosan and act as tissue hormones in the animal and human organism. They play an essential role in an inflammatory reaction, a form of nonspecific immune defense. This problem involves the synthesis of a special prostaglandin fragment.



5.14 Draw the structural formulae of **A**, **B**, and **C**, taking into account the correct stereochemistry.

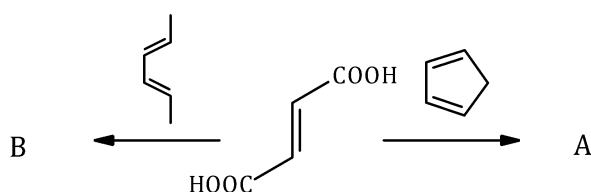
5.15 Name the function of NaHCO_3 in the reaction that leads to the formation of **C**.

5.16 Write down the cyclic intermediate that leads to the formation of **C** and draw "arrows" that make the opening of the cycle with the formation of **C** plausible.

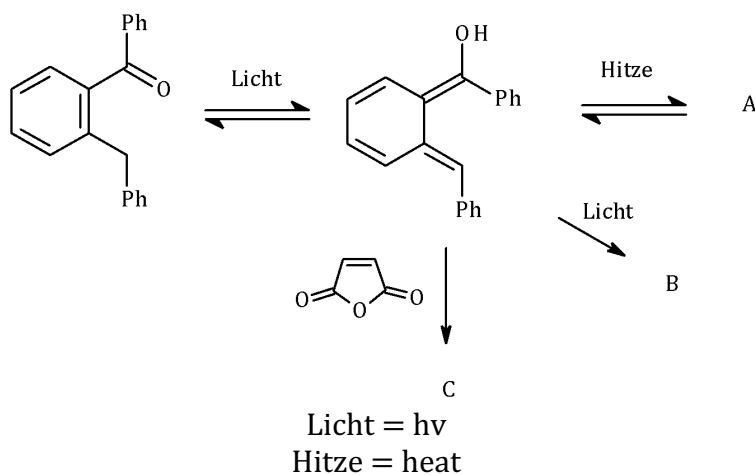
5.17 Name the mechanism by which the reaction to substance **A** proceeds and name the function of LiAlH_4 .

E. At the organic end it becomes purely pericyclic (9 bp)

In the following problems, remember the Woodward Hoffmann rules and the terms con- and disrotatory.



5.18 Draw the structural formulas of **A** and **B**, taking into account the correct stereochemistry.



5.19 Draw the structural formulae of **A**, **B**, and **C**, taking into account the correct stereochemistry.

Problem 6 (St. Seywald)

6 points

Structural elucidation of oriental spices

The history of herbs and spices goes back almost to the beginning of humankind. Among other things, caraway seeds have been found in the remains of the Neolithic (3,000 BC) lakeside settlements in Switzerland. In 2300 BC, an Egyptian tablet shows the use of cassia and thyme in beer production. Around 700 BC, a cuneiform script library of the Assyrian ruler Assurbanipal describes dill, fennel, cardamom, saffron, sesame, and thyme. Thus the following pages of the competition take their place in the ancient cultural history of the description of spices. Of course, we will not use hieroglyphics or cuneiform script to decipher the information.

A. Caraway

The main components of caraway seeds are *D*-(+)-Carvone (over 50%), *D*-(+)-Limonene (over 30%), myrcene und α -phellandrene. *D*-(+)-Carvone is (*S*)-2-Methyl-5-(prop-1-en-2-yl)-cyclohex-2-enone.

6.1 Draw the structural formula of *D*-(+)-Carvone and mark the stereogenic center with an *.

The table indicates some properties that can be measured on substances

	Property
<i>A</i>	Boiling point
<i>B</i>	UV spectrum
<i>C</i>	Refractive Index
<i>D</i>	Melting point
<i>E</i>	Optical rotation
<i>F</i>	Dipole moment
<i>G</i>	NMR spectrum in an achiral environment
<i>H</i>	IR spectrum

6.2 Specify the letters of all properties that can be used to distinguish between *D*-(+)-Carvone and *L*-(-)-Carvone.

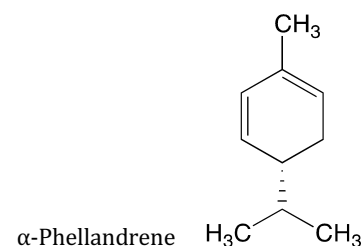
 α -Phellandrene

¹H-NMR Spektrum (500 MHz, CDCl₃):

δ (in ppm) = 6.14 (d, *J* = 10.4, 1.0 Hz, 1H), 5.78 – 5.91 (m, 2H),

1.95 – 2.10 (m, 2H), 1.80 – 1.91 (m, 1H), 1.63 – 1.76 (m, 4H),

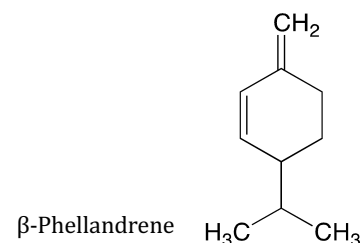
0.84 (dd, *J* = 6.2, 1.5 Hz, 6H).



6.3 Name the shown α phellandrene according to IUPAC (do not forget the stereo descriptor!)

6.4 Draw the structure of α phellandrene in your answer sheet and assign the above-mentioned shifts from the $^1\text{H-NMR}$ to the respective protons by adding the δ values.

Besides the α phellandrene, there exists the isomer β phellandrene.



6.5 Specify the **total number** of stereoisomers of both phellandrene molecules mentioned.

B. Thyme

The main components of the essential oil of thyme are thymol (25-50%), carvacrol (a constitutional isomer of thymol, 3-10%), and p-cymene. Here we will take a closer look at two other constituents of thyme oil, let us call them **A** and **B**. The isomers **A** and **B** have the molecular formula $\text{C}_{10}\text{H}_{18}\text{O}$.

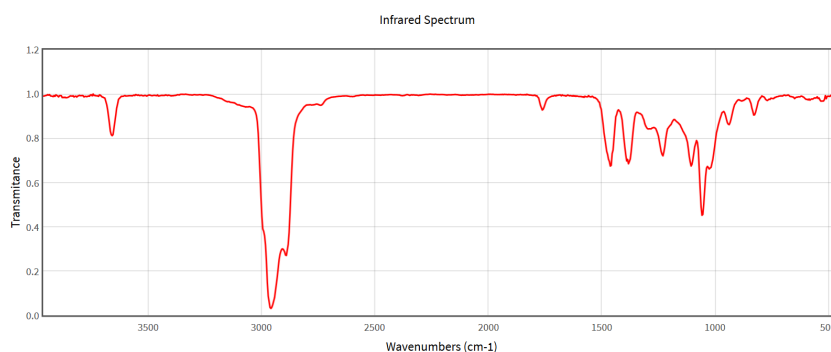
Substance A is bicyclic; it is 1,7,7-Trimethyl-bicyclo[2.2.1]heptan-2-ol. In the bicyclic nomenclature, bridgehead C is given number 1, followed by bridges starting with the longest and ending with the shortest.

6.6 Draw the **four** configuration-isomeric structures of **A**, indicating the absolute configuration of each structure for all stereogenic centers (e.g., 12*R*, 14*S*).

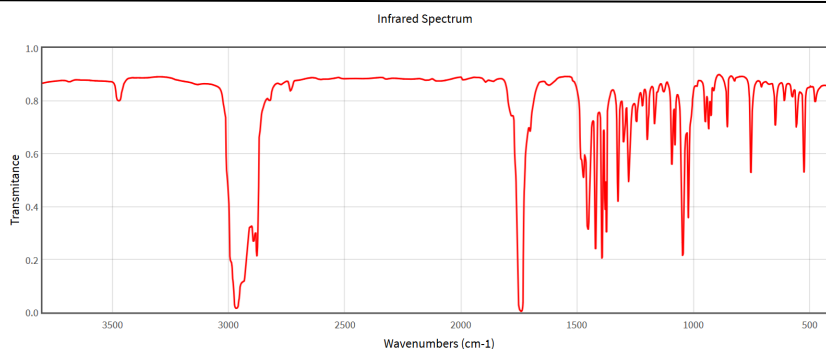
Three IR spectra of bicyclic compounds are given below.

6.7 Which of the three IR spectra listed belongs to substance **A**? Enter the name given (IR-1, IR-2, or IR-3).

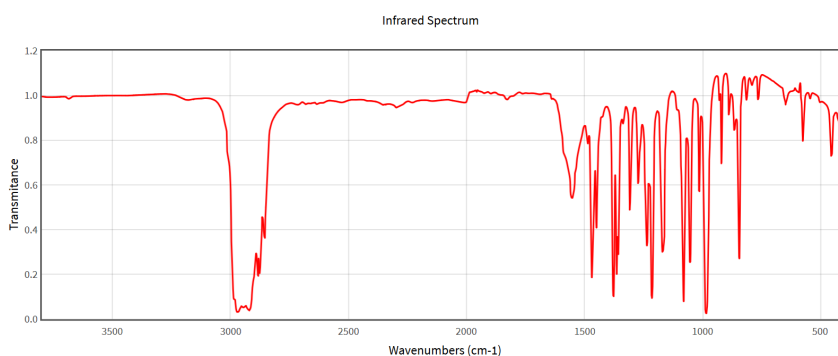
IR-1



IR-2

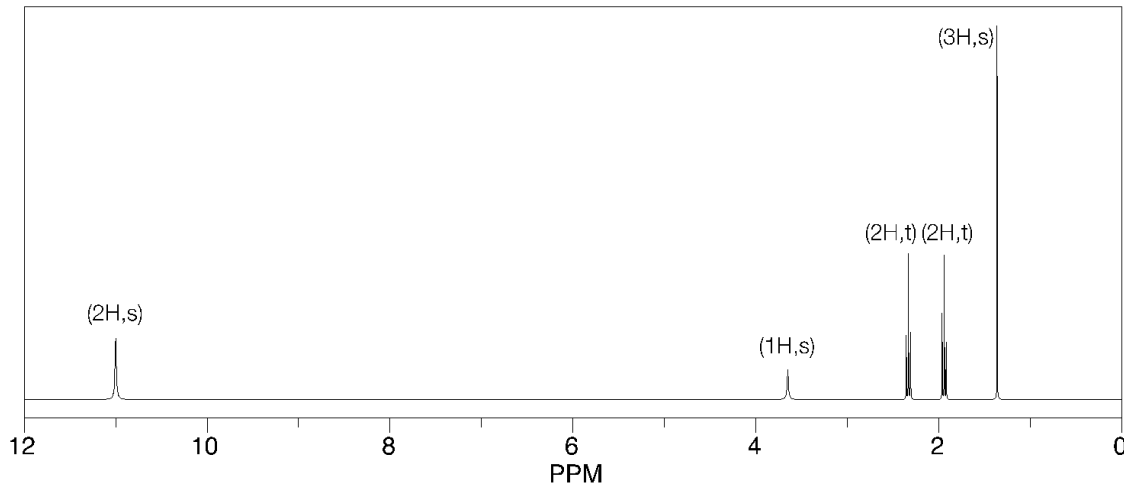


IR-3



¹H- and ¹³C-NMR and IR spectra of **substance B** are given (see next page). If the ozonolysis of **B** is carried out with oxidative processing, three products are obtained: Acetone (propanone), **X**, and **Y**. p

The elemental analysis of **Y** yields 44.44% C, 6.23% H, and 49.33% O (*m/m*). The following ¹H-NMR spectrum (in DMSO-d₆ as solvent) was also recorded from **Y**:



6.8 Specify the formulas of **X** and **Y**.

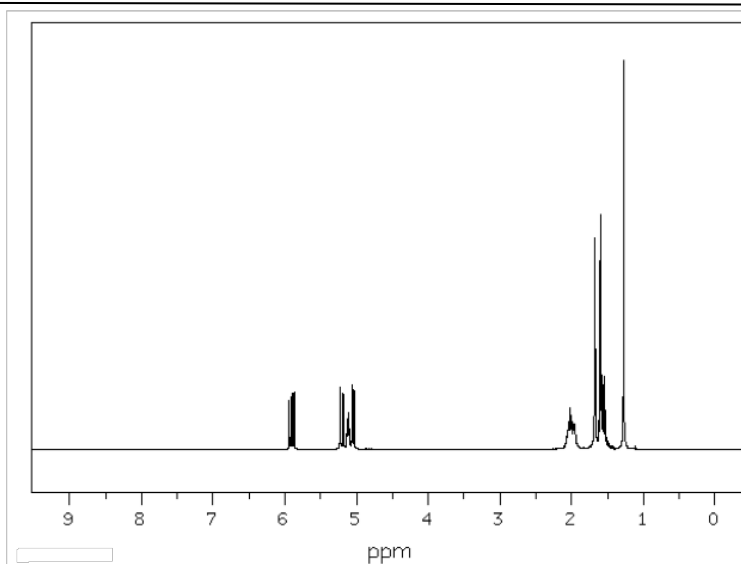
6.9 Draw a constitutional formula of **Y**.

6.10 Draw a constitutional formula of substance **B**.

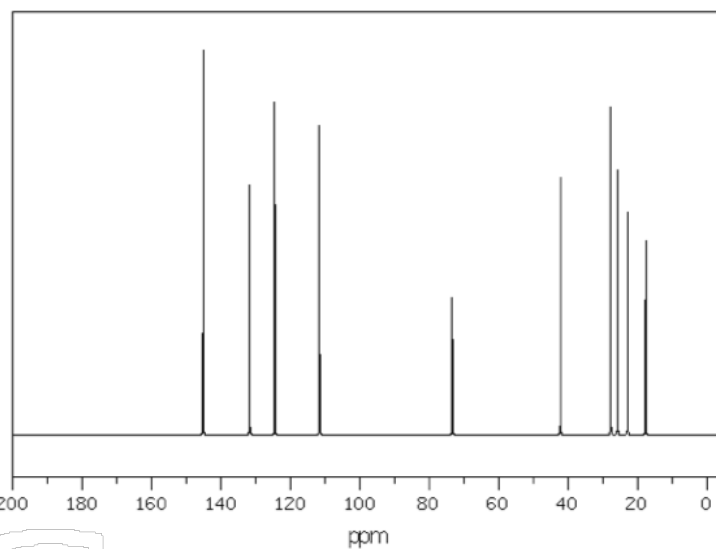
Spectra of substance B:

¹H-NMR-Spektrum(400 MHz, CDCl₃):

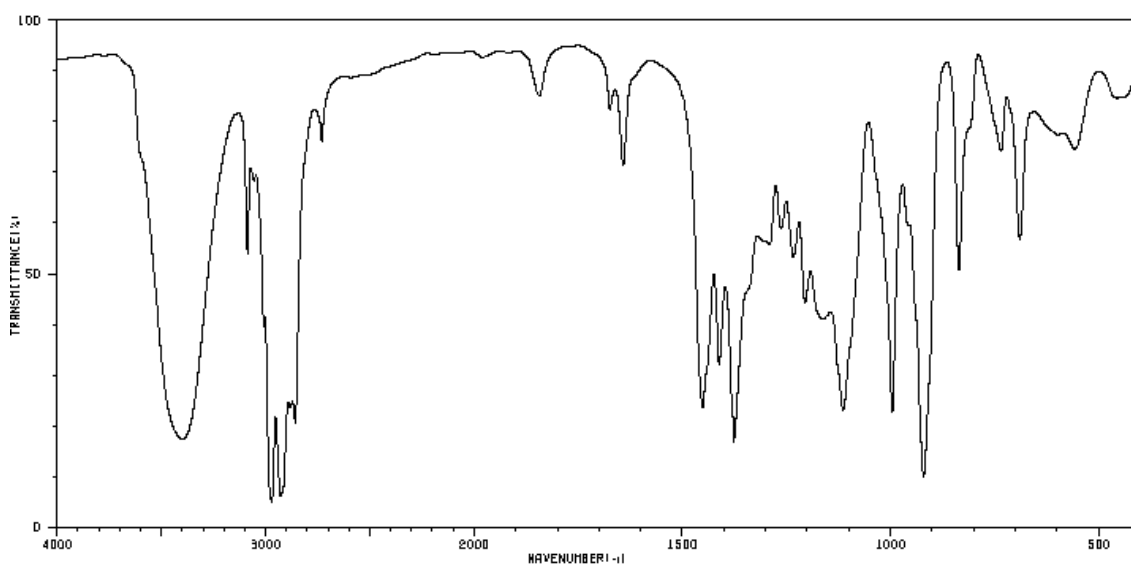
$\delta = 1.27$ (3H), 1.54 (1H), 1.58 (1H), 1.60 (3H), 1.68 (3H, $J = 0.9$ Hz), 1.96 (2H, $J = 0.9$ Hz), 2.02 (1H), 5.05 (1H, $J = 10.7$ Hz, -1.3 Hz), 5.12 (1H), 5.21 (1H, $J = 17.3$ Hz, -1.3 Hz), 5.90 (1H, $J = 17.3$ Hz, 10.7 Hz)

**¹³C-NMR-Spektrum**(25.16 MHz, CDCl₃):

$\delta = 17.66, 22.85, 25.71, 27.80, 42.19, 73.40, 111.66, 124.48, 131.73, 145.15$

**Selected ¹H-¹³C couplings:**

H	C (H-C bound)
5.90	145.15
5.12	124.48

IR-Spektrum:

Problem 7 (G. Schellander)

9 points

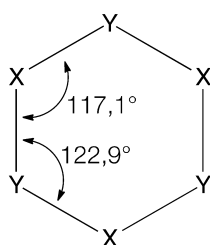
Thermo- and quantum-chemical consideration of some B, P, and N compounds

Borazine

The Lewis acid BH_3 reacts with the Lewis base NH_3 to form the aminoborane $\text{H}_3\text{B}-\text{NH}_3$. Organic-oriented people immediately think of the isoelectronic ethane $\text{H}_3\text{C}-\text{CH}_3$. Hoping for further parallels to carbon chemistry, they are not disappointed. Borazine $\text{B}_3\text{N}_3\text{H}_6$ with its hexagonal backbone is also called inorganic benzene.

7.1 For borazine, draw three resonance structures with all electron pairs and any formal charges. Also use mesomeric limiting formulas that suggest the aromaticity of the structure.

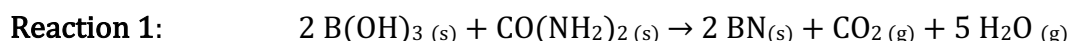
The internal angles in Borazine are not quite the same, as the following sketch shows and as the correct Lewis formula suggests:



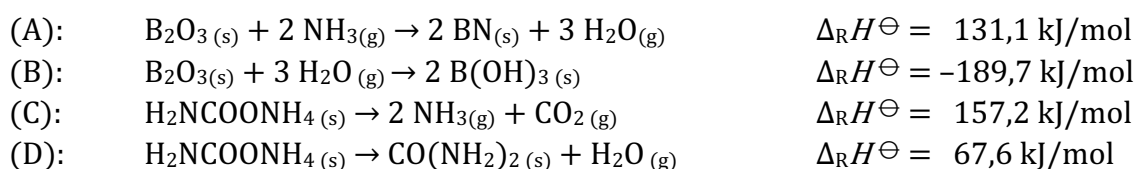
7.2 Write the correct element symbols (N or B) for X and Y.

Boron Nitride

A further interesting compound is the boron nitride BN. It exists - like carbon itself - in several modifications. The graphite-analogous hexagonal BN (h-BN) is formed in a reaction of boric acid H_3BO_3 (or $\text{B}(\text{OH})_3$) and urea $\text{CO}(\text{NH}_2)_2$, among others:



Four reactions (based on boron trioxide or ammonium carbamate) and their reaction enthalpies are given at 298 K:



7.3 Calculate the value $\Delta_{\text{R}}H_{298}^\ominus$ for reaction 1 using the given data. Show how you include reactions (A) to (D) in the calculations.

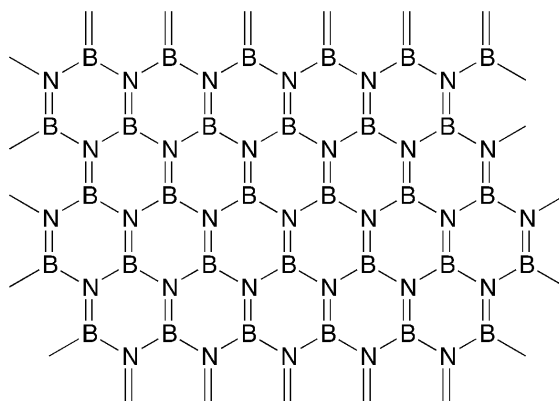
In reality, reaction 1 takes place at temperatures significantly higher than 25°C . Here are the isobaric heat capacities:

Compound	$C_p / \text{Jmol}^{-1}\text{K}^{-1}$
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$\text{BH}_3\text{O}_3(\text{s})$	86,1
$\text{BN}(\text{s})$	19,7
$\text{CH}_4\text{N}_2\text{O}(\text{s})$	94,0
$\text{CO}_2(\text{g})$	37,1
$\text{H}_2\text{O}(\text{g})$	33,6

7.4 Calculate $\Delta_R H^\ominus$ for reaction 1 at 900°C .

Graphene as a “single graphite layer” is well known. Single BN layers are also being investigated. There are similarities, but also differences. The figure below shows the structure of such a layer. The B-N bond distance is $1,45\text{\AA}$.



Let us take a look on the π electrons in a square section of an infinitely large imaginary layer. That means that we do not have to take phenomena at the edges into account.

7.5 Calculate the number of π electrons in a square section with side length $L = 300\text{\AA}$ and the number N of electronic states. Round N to a whole number.
If you get no result here, calculate with $N = 2500$ states.

Let us approach the description of these π electrons in the model of free electron gas (where the mutual repulsion is neglected), describing them as independent particles in a square two-dimensional box potential.

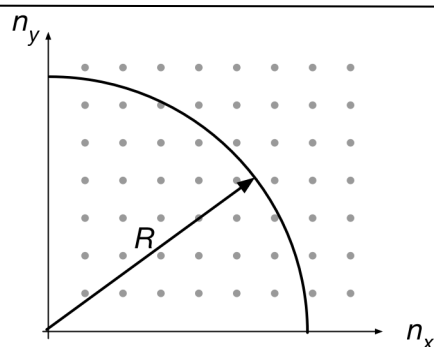
For these electrons, the Schrödinger equation provides the following energy levels:

$$E_{n_x, n_y} = \frac{h^2}{8m_e L^2} (n_x^2 + n_y^2) \quad (1)$$

7.6 Arrange the first 11 energy levels of a square box potential E_{n_x, n_y} in order of increasing energy. Start at E_{11} , end at E_{33} . If two energy levels are degenerate, insert = in between (e.g. $E_{51} = E_{78}$)

Now we are dealing with a very, very large number of states that are close together. The states are occupied up to the so-called Fermi energy E_F , states above this are empty. We want to neglect the zero-point energy here, so we set $E_{11} \approx 0$.

For the states we use a graphical representation in an abstract state plane. Its points provide all combinations of quantum numbers and thus represent all possible states:

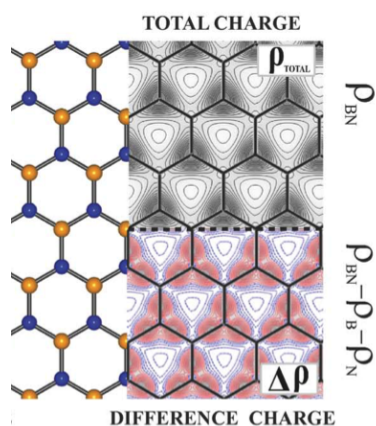


All states within the radius R are occupied. The number of occupied states thus corresponds to the area of the quarter circle shown. Besides the circle equation: $R^2 = n_x^2 + n_y^2$

7.7 Using equation (1) express R^2 as a function of Fermi energy.

7.8 Calculate the Fermi energy.

While in graphene the electrons are distributed quite evenly, they are not so in BN, as a look at the density distribution of the negative charge shows.



aus:
M. Topsakal, E. Aktürk, and S. Ciraci,
First-principles study of two- and one-dimensional
honeycomb structures of boron nitride
Phys. Rev. B 79 (2009) 115442

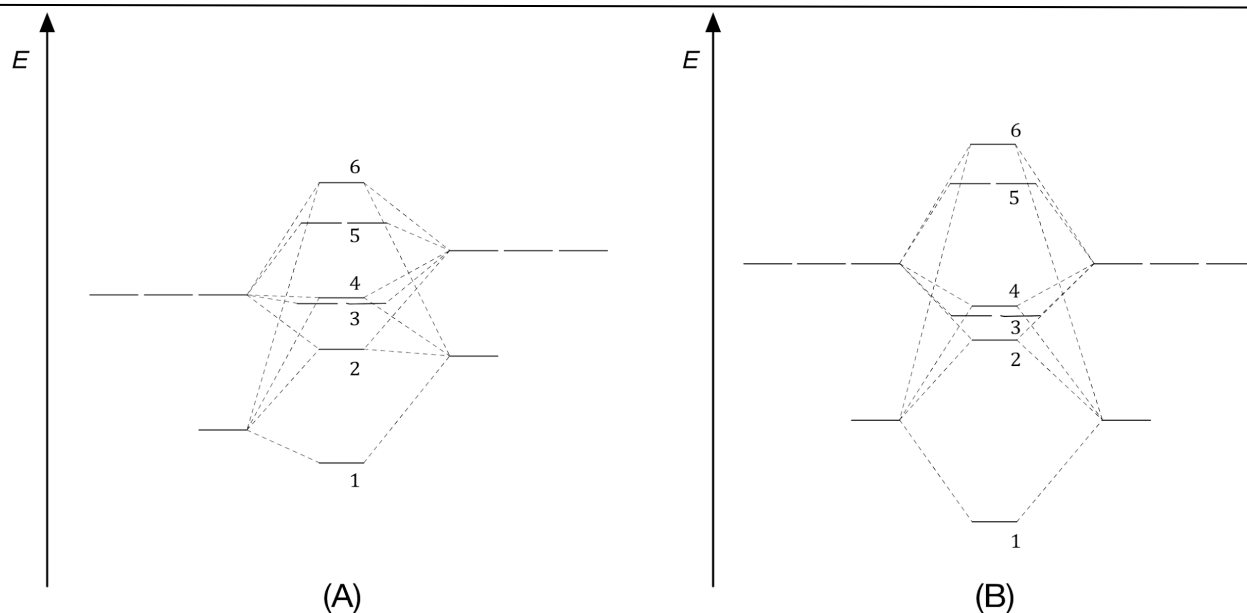
7.9 Which balls (yellow, blue) stand for which element (B or N)?

Phosphornitrid

Phosphorus and nitrogen form various compounds. The simplest binary compound is the phosphorus mononitride PN, sometimes also called nitridophosphane - in a way an analog to N_2 .

7.10 Draw the Lewis formula of PN. Is it isoelectronic with N_2 ? (yes/no)

Two MO diagrams are shown. One of them belongs to the PN. For the questions below, the MOs are simply numbered from the lowest drawn one - which does not have to be the lowest one of the molecule.



7.11 Indicate which MO diagram belongs to the PN by writing the correct letter.

Tip: Draw the correct MO diagram for the following questions and fill it with the correct number of valence electrons.

7.12 Indicate the number(s) of degenerate MO-s in diagram (B).

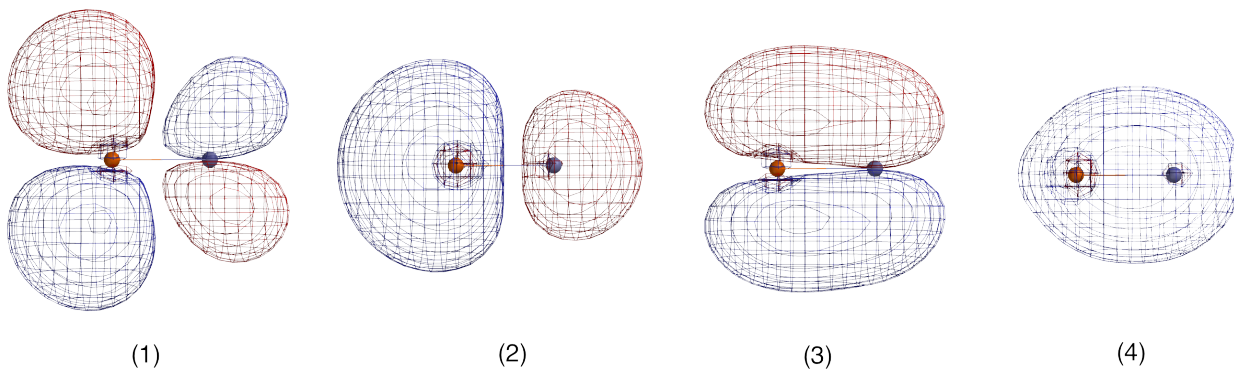
7.13 Which MO of PN represents an antibonding π MO?

7.14 Specify the magnetic behaviour of PN (diamagnetic/paramagnetic)

7.15 Enter the number of the HOMO of PN.

7.16 Specify the bond order of PN.

The following orbital images show calculated MO-s of PN.



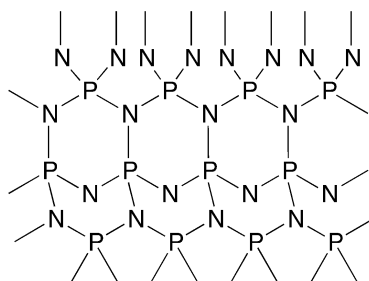
7.17 For each MO depicted, indicate whether it is a σ or π -MO and whether it is bonding or antibonding. For example, write "(5) σ , antibonding".

7.18 Arrange the orbitals in order of increasing energy by writing the numbers (1), (2), etc.

A wavenumber of $\tilde{\nu} = 1390 \text{ cm}^{-1}$ was calculated for the stretching vibration in PN.

7.19 Calculate the force constant k for the PN bond. Use the relative atomic masses of P and N from the PSE.

A further PN connection also occurs in several modifications. A section of its grid can be displayed in this way:



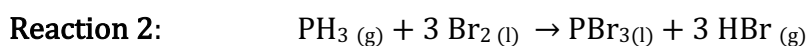
7.20 Specify the empirical formula of this compound (with the smallest integer coefficients)

The Van't Hoff equation makes it possible to determine from equilibrium constants at different temperatures $\Delta_R H^\ominus$ and $\Delta_R S^\ominus$ by plotting $-\ln K$ against $1/T$.

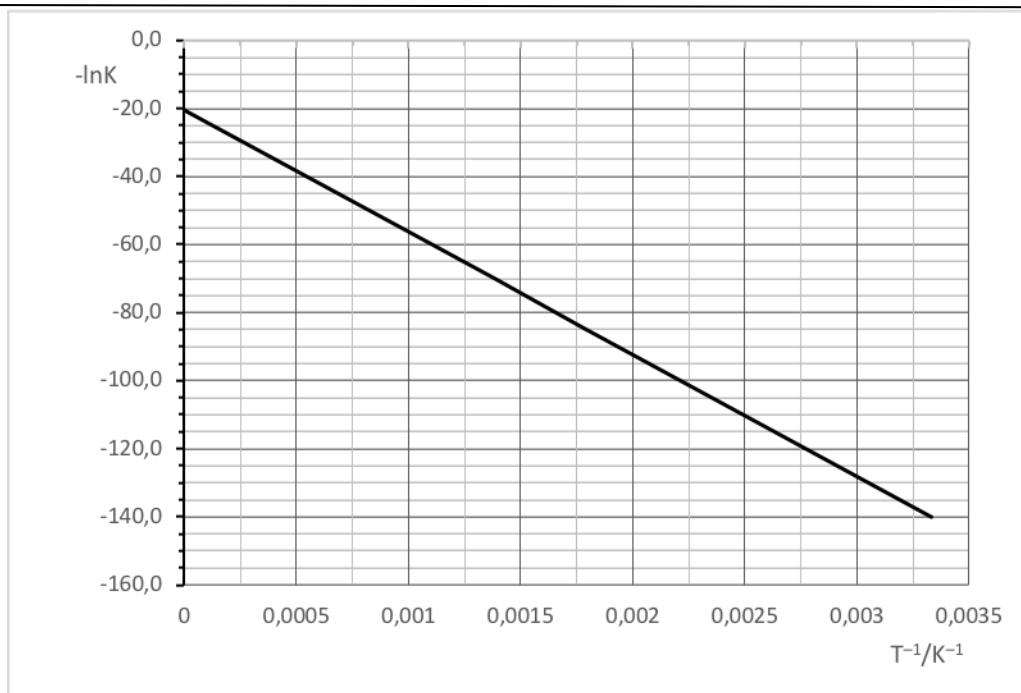
7.21 From the Van't Hoff equation, give the expression for the slope of this plot and its SI unit.

7.22 From the Van't Hoff equation, give the expression for the y-intercept of this plot and its SI unit.

For the reaction



there's one of those Van't Hoff plots:



7.23 Enter the values of the slope and y-intercept from the plot.

7.24 Specify $\Delta_R H^\ominus$ and $\Delta_R S^\ominus$ for reaction 2.

Also known are bond dissociation enthalpies D^\ominus_{298} in kJ/mol:

Br-Br: 193

Br-H: 366

H - P: 297

and Evaporation enthalpies $\Delta_{\text{vap}} H^\ominus_{298}$ in kJ/mol:

Br₂: 30,9

PH₃: 14,6

PBr₃: 12,9

7.25 Calculate the bond dissociation enthalpy $D^\ominus_{298}(\text{P-Br})$

Problem 8 (G. Schellander)

6 points

Hydrogen – atomic, exotic and molecular

Atomic hydrogen

In 1888 the Swedish physicist Johannes Rydberg presented the formula for the wavenumbers of the spectral lines in the hydrogen spectrum, which is named after him today:

$$\tilde{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1)$$

For hydrogen, the value of the Rydberg constant $R_H = 109678 \text{ cm}^{-1}$. The formula gives the ionization energy of the H atom in the ground state correctly (13,6 eV), as well as the wavenumbers or wavelengths of the spectral lines for various series.

A spectral series of the H atom starts at 7459,9 nm and has its shortest wavelength line at 2279,4 nm.

<i>8.1 Find the quantum number n_1 of this series. Provide your calculations.</i>
<i>8.2 Specify the wavelengths of the first three lines of this series, i.e., for (1) $n_2 = n_1 + 1$, (2) $n_2 = n_1 + 2$ and (3) $n_2 = n_1 + 3$</i>
<i>8.3 Indicate in which range of the electromagnetic spectrum these lines are located (γ, X-ray, UV, VIS, IR)</i>

The Rydberg constant can be divided into two parts and thus can be generalized. It is

$$R_H = \frac{\mu_H}{m_e} R_\infty, \quad \text{where } R_\infty = \frac{m_e e^4}{8 \epsilon_0^2 h^3 c} = 10973732 \text{ m}^{-1} \quad (2)$$

where μ_H is the reduced mass of the hydrogen atom (one proton and one electron), m_e is the electron mass, and all other natural constants have their usual meaning.

The Schrödinger equation also provides expressions for energy levels of electrons in the hydrogen atom as well as in hydrogen-like ions with the nuclear charge number Z and the reduced mass μ .

$$E_n = - \frac{Z^2 \mu e^4}{32 \pi^2 \epsilon_0^2 \hbar^2 n^2} \quad (3)$$

<i>8.4 Show that the Rydberg formula (1) can be obtained from the relation (3) by deriving from (3) the wave number for a transition between the levels n_1 and n_2 in hydrogen ($Z = 1$).</i>

8.5 Calculate the Rydberg constant R_{Li} for the Li^{2+} -Ion in cm^{-1} .
For the mass of the Li atomic nucleus use 6,941 u.

Exotic hydrogen

In so-called "exotic atoms", individual elementary particles are replaced by others. For example, in muonic hydrogen the muon μ ($m_\mu = 206,8m_e$) replaces the electron. Both particles are leptons with the same charge, and for this example, we want to disregard the short life of the muon particle (approx. 2,2 μs).

8.6 Calculate the ionization energy of the muonic H atom in kJ/mol

The wave function $\Psi_{(1,0,0)}$, i.e., the 1s orbital, shows a maximum of the radial residence probability at the radius of the first Bohr orbit a_0 . This Bohr radius is usually given as

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \quad (4)$$

Here the atomic nucleus is neglected, otherwise the reduced mass of the system nucleus-electron would have to stand instead of the electron mass.

8.7 Which of the following expressions correctly represents the value corresponding to Bohr's radius for the muonic hydrogen? Write down the letter.

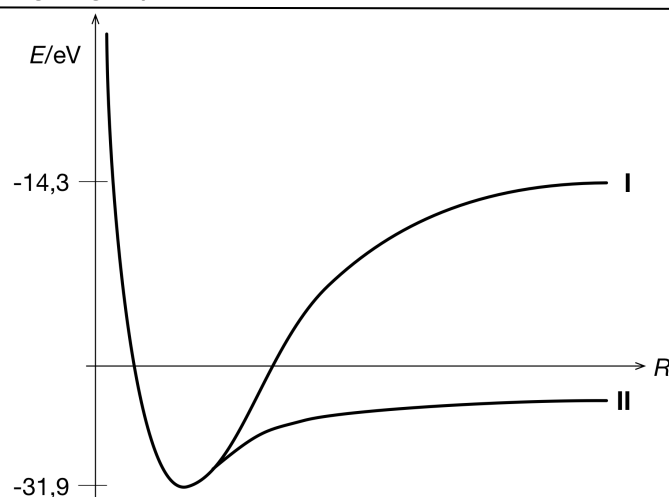
(A) $\frac{4\pi\epsilon_0\hbar^2}{m_\mu e^2}$ (B) $\frac{4\pi\epsilon_0 m_p \hbar^2}{m_\mu m_p e^2} + \frac{4\pi\epsilon_0 m_\mu \hbar^2}{m_p m_\mu e^2}$ (C) $\frac{4\pi\epsilon_0\hbar^2}{\mu_e e^2} + \frac{4\pi\epsilon_0\hbar^2}{\mu_p e^2}$

Molecular hydrogen

The hydrogen molecule H_2 is known to be stable against dissociation which can take place in two ways:



The diagram schematically shows the total energy of the system of two H atoms against the nuclear distance R . The zero-point of the energy scale corresponds to unbound protons and electrons, so atoms and molecules have the same energy scale. The two curve branches I and II represent the courses for the above-mentioned dissociations.



8.8 Which curve branch stands for which bond splitting? Assign (a) and (b) to the curve branches (I) and (II) correctly.

8.9 Specify the energies required for fissions (a) and (b) in eV. Neglect the zero-point energy of the H_2 molecule.

The homolytic cleavage (a) could also take place photolytically, in which case the photon would have to bring along the dissociation energy as minimum energy.

8.10 Does this minimum energy correspond to a minimum wavelength λ_{min} or a maximum wavelength λ_{max} ?

8.11 Calculate this λ for the photolysis of H_2 in nm.

8.12 Calculate the electron affinity of the H-atom in kJ/mol from the available data. Write a positive number if the process $H + e^- \rightarrow H^-$ is exothermic.