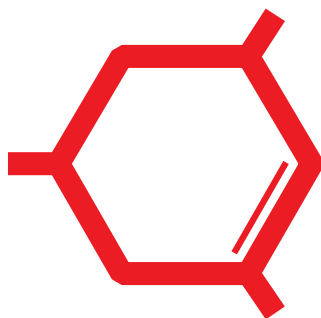




44th Austrian Chemistry Olympiad National Competition

Theoretical Part May 31st, 2018

.....
Name

		bp	/	rp	/	rp _{max}
1	Determining the Concentration of Lead(II) in 1950	/		/		8
2	Chromium and its Compounds: Electrochemistry & Kinetics	/		/		8
3	Organic Syntheses	/		/		17
4	Nitrogen and its Compounds	/		/		17
5	Chromium and its Compounds: Lattices, Nuclei and Complexes	/		/		10
Overall Score:				/		60

Please note:

- You have five hours to solve the problems and may use the following tools:
 - Non-programmable calculator
 - Collection of formulae and periodic table handed out to you
 - Concept paper
 - Writing utensil (pencil, blue- or black-coloured pen, ruler or set square, eraser)
- Wherever you ***need to calculate*** („Calculate...“), write the respective calculus into the corresponding boxes ***in a COMPREHENSIBLE way***, otherwise **you will lose scoring points**.

Please underline final results.

- Only **answers written into the boxes** will be used for scoring.
 - If you run out of space in an answer box, write the solution to the problem on concept paper. Write your ***name*** on top of that paper. *Clearly and unmistakably* mark the answer with the corresponding problem number x.xx

Problem 1

8 Points

Determining the Concentration of Lead(II) in 1950

An interesting method to determine lead(II) ions in aqueous solutions was developed in the 1950s. It will be described in the following paragraphs:

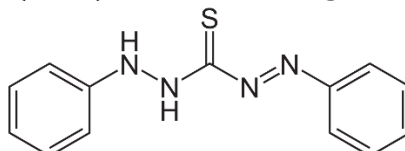
10.00 mL of the sample to be analyzed for its content of Pb^{2+} ions are transferred into a separatory funnel of a volume $V = 250\text{ mL}$. To this sample 75.00 mL of cyanide solution described below are added to mask interfering cations:

Preparing the cyanide solution:

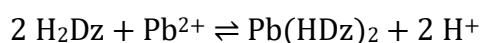
3.00 mL potassium cyanide solution (10.0%, density 1.07 g/cm^3) are added to 35.00 mL concentrated aqueous ammonia solution (35.0%, density 0.880 g/cm^3). Water is added to this mixture to reach a volume of 100 mL.

The pH of the mixture in the separatory funnel is lowered to $\text{pH} = 9.50$ by adding hydrochloric acid (6.00 M). This is followed by adding 7.50 mL of a solution containing the complexing agent Dithizone in tetrachloromethane (0.00500 % (w/V), density 1.594 g/cm^3) and 17.50 mL tetrachloromethane. During this step, Dithizone forms a coordination complex with the lead(II) ions that dissolves very well in tetrachloromethane. The mixture is agitated followed by waiting for phase separation. During this step the complex between lead and Dithizone transfers to the organic phase almost quantitatively. Finally, the absorbance of the organic phase is determined photometrically at a wavelength of $\lambda = 515\text{ nm}$. The molar extinction coefficient of the lead-Dithizone complex is $\epsilon = 66450\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

The complexing agent Dithizone (H_2Dz) is a bidentate ligand and has the following structure:



Equation for the coordination reaction:



The extraction follows:
$$K_{\text{Ex}} = \frac{[\text{Pb}(\text{HDz})_2]_{\text{org}} \cdot [\text{H}^+]^2}{[\text{H}_2\text{Dz}]_{\text{org}}^2 \cdot [\text{Pb}^{2+}]} = 5.60$$

	pK_a
Hydrochloric acid	-6.00
Ammonium ion	9.25
Hydrocyanic acid	9.40

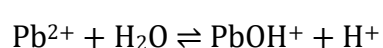
1.1 Calculate the volume of hydrochloric acid necessary to reach $pH=9.5$. Neglect any possible influence of potassium cyanide and lead(II) ions for your calculation.

1.2 Give the pH value for which you expect substantial formation of hydrocyanic acid (i.e. at which the concentration of hydrocyanic acid exceeds that of cyanide ions) and under which the solution should not fall below.

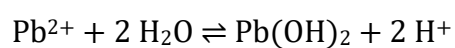
1.3 Calculate the maximum concentration of lead in a sample (in mol/L) that can be analyzed with this method.

1.4 Calculate the lead concentration of a sample for an absorbance of $A=0.328$ measured in a cuvette of 1cm path length. Assume complete complexation and extraction.

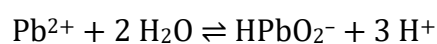
At pH = 9.50 lead ions are present in different compounds determined by the following equilibria:



$$K_1 = \frac{[\text{PbOH}^+][\text{H}^+]}{[\text{Pb}^{2+}]} = 3.00 \cdot 10^{-7}$$



$$K_2 = \frac{[\text{Pb}(\text{OH})_2][\text{H}^+]^2}{[\text{Pb}^{2+}]} = 3.00 \cdot 10^{-18}$$



$$K_3 = \frac{[\text{HPbO}_2^-][\text{H}^+]^3}{[\text{Pb}^{2+}]} = 7.00 \cdot 10^{-29}$$

1.5 Calculate the percentual amounts of the different lead-containing species at pH=9.5.

Base the next calculation on the following conditions: If you did not obtain a result in 1.1, assume that 25 mL of hydrochloric acid were added. Furthermore, assume that the extraction step does not change pH of the aqueous solution. Also, neglect the two lead-containing species $\text{Pb}(\text{OH})_2$ and HPbO_2^- . If you make further assumptions for your calculation, you need to show with your result that they were correct and valid (error < 1%).

1.6 Calculate the total concentration of all lead species in the aqueous phase after extracting with the abovementioned amount of dithizone in tetrachloromethane. Base your calculation on a sample that initially contained $c = 1.00 \cdot 10^{-6} \text{ mol/L Pb(II)}$.

Problem 2

8 Points

Chromium and its Compounds: Electrochemistry & Kinetics**A. Galvanic production of Chromium**

Chromium metal coatings can be produced by electrolysis in aqueous solutions of chromic acid (H_2CrO_4).

Electrolysis was carried out for 7.00 hours at a current of 1500 A. No changes occurred on the inert anode. At the cathode, hydrogen developed as a side product thus reducing the current yield for the deposition of chromium. At standard conditions (25°C, 1.00 bar) this resulted in the formation of 4.15 m³ hydrogen. Gas also developed on the anode.

2.1 Give balanced equations for all electrode processes.

Cathode:

Anode:

2.2 Calculate the current yield for the deposition of chromium on the cathode.

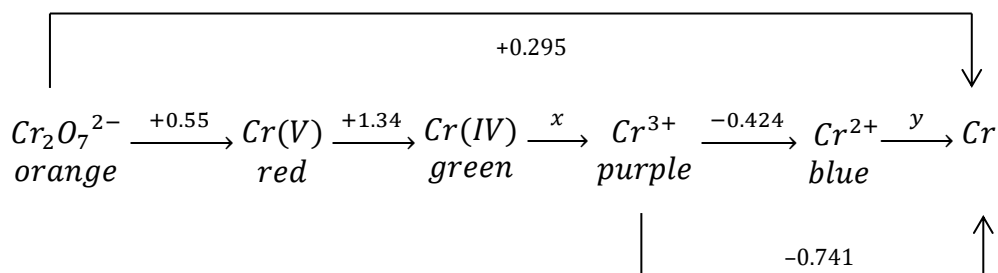
2.3 Calculate the mass of chromium deposited.

2.4 Calculate the volume of the gas having developed on the anode at standard conditions (25°C, 1.00 bar).

B. Electrochemistry of Chromium and its Compounds

Chromium (from Greek χρωμα = color) received its name from that fact that its compounds and ions show many different colors.

Below, you find an incomplete Latimer diagram for some of these coloured ions at pH = 0. All potentials are given in Volt.



2.5 Calculate the missing potentials x and y .

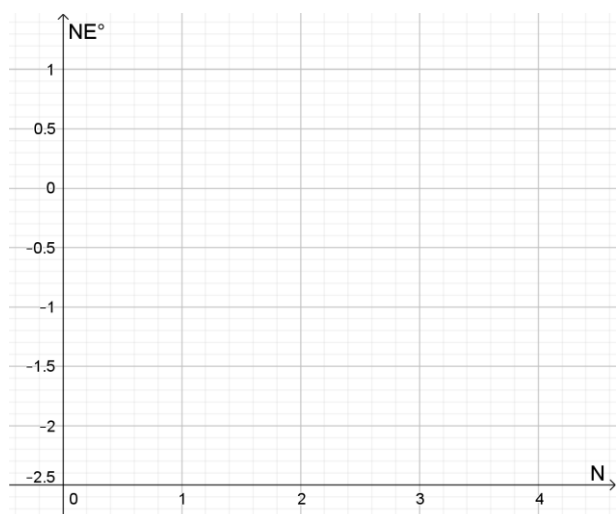
2.6 Demonstrate that Cr(IV) can disproportionate to Cr(III) and Cr(VI) via suitable calculation.

2.7 Calculate the equilibrium constant for this disproportioning reaction at 25°C.

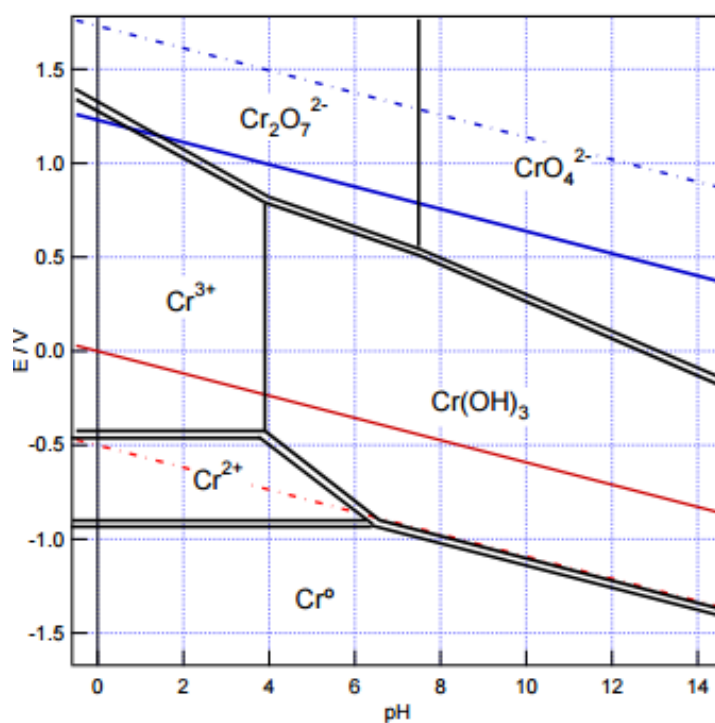
2.8 Does Cr(II) tend to disproportionate to Cr(III) and Cr(0)? Tick the correct box and give a reason for your choice based on the Frost diagram of the relevant species.

☐ yes, tends to disproportionate

☐ no, does not tend to disproportionate



The so-called Pourbaix diagram (see right) results from plotting the redox potentials of all chromium species against pH. It is based on the condition that the activities of all species participating in any equilibrium are $a=1$, except for H^+ (H_3O^+).



2.9 Name two species showing pH-independent redox reaction in the diagram, at least within a certain pH-range.

2.10 Name two species showing protolysis that does not depend on potential.

Analytical Chemistry often uses the redox system dichromate/chromium(III). Its standard potential is $E^\circ(\text{Cr}_2\text{O}_7^{2-}|\text{Cr}^{3+}) = +1.33 \text{ V}$.

2.11 In which pH range does $\text{Cr}_2\text{O}_7^{2-}$ react to Cr^{3+} ?

2.12 Formulate the half equation for the redox pair $\text{Cr}_2\text{O}_7^{2-}|\text{Cr}^{3+}$.

2.13 Derive an equation $E = f(\text{pH})$ for the line between the two species $\text{Cr}_2\text{O}_7^{2-}$ and Cr^{3+} at 298 K. (Assumption: the activities of the chromium species do not change).

2.14 Use this derived linear function to calculate E at $\text{pH}=2$.

C. Kinetics – Chromium and Ethanol

Oxidizing $\text{CH}_3\text{CH}_2\text{OH}$ with Chromium(VI) formerly was the basis to determine the ethanol content in breath ("chemical alco test"). The reaction can also be used in analysis. Diluted $\text{K}_2\text{Cr}_2\text{O}_7$ solutions in strongly acidic solution (in this case 3.6 M HCl) yield HCrO_4^- ions, the oxidizing compound during the reaction.

2.15 Formulate a balanced equation for the reaction of HCrO_4^- with ethanol to Cr^{3+} und ethanoic acid.

At the given conditions the rate law for the overall reaction is:

$$v = - \frac{d[\text{HCrO}_4^-]}{dt} = k \cdot [\text{HCrO}_4^-]^x$$

with reaction order x being an integer. After waiting for different reaction times t , $[\text{HCrO}_4^-]_t$ was determined by iodometric titration. Iodine reacted with thiosulfate ($c = 0.020 \text{ mol/L}$) following $2 \text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightleftharpoons 2 \text{I}^- + \text{S}_4\text{O}_6^{2-}$. As usual, the end point was marked by adding starch. Iodine previously had been formed by reaction of remaining HCrO_4^- with iodide. Hence it was possible to calculate $[\text{HCrO}_4^-]_t$ from the amount of thiosulfate solution used during titration.

For each analysis a sample volume of 10.0 mL was used. This led to the following values:

Reaction time t / min	0	10	20	30	40
Titration volume $V(\text{S}_2\text{O}_3^{2-})$ / mL	---	11.7	9.10	7.15	5.60
$[\text{HCrO}_4^-]_t$ / mol/L	0.0100	0.0078	0.0061	0.0048	0.0037
$\ln[\text{HCrO}_4^-]_t$	- 4.61	-4.85	-5.10	-5.35	-5.59
$\frac{1}{[\text{HCrO}_4^-]_t}$	100	128	165	210	268

2.16 As an example, calculate the concentration $[\text{HCrO}_4^-]_t$ for a titration volume $V(\text{S}_2\text{O}_3^{2-}) = 10.3 \text{ mL}$.

2.17 Determine the reaction order x , by plotting concentration vs time in a suitable graph. Choose reasonable dimensions on each axis.



2.18 Calculate the rate constant k and give the result with correct units.

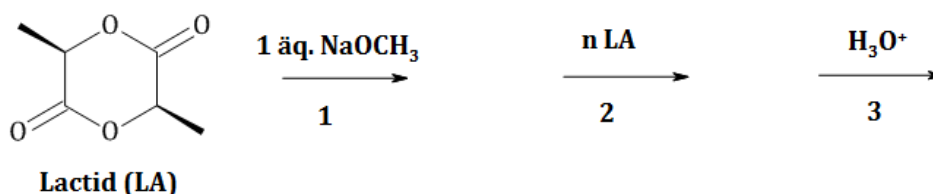
Problem 3

17 Points

Organic Syntheses

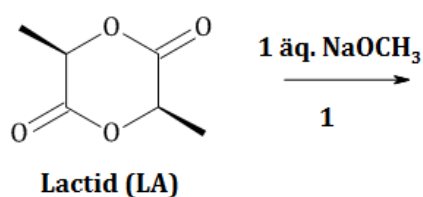
A. Polymerization

Poly lactides, short PLA, are polymerized through so-called *ring opening polymerization* (ROP). They were first described in 1845 by Théophile-Jules Pelouze, who observed that oligomers and polymers form during the isolation of lactic acid. PLA-based thermoplasts gain increasing popularity because they are biodegradable. For instance, they compete with standard PE foils as mulch films in agriculture and gardening. A process leading to PLA from lactides was developed in 1932 and patented in 1954 by DuPont, a large chemical company.



3.1 Draw the configuration formulae of all possible stereo-isomers of lactide and determine the absolute configuration of each stereogenic center.

3.2 Formulate mechanisms (including arrows for attacking species) for initiation (1), propagation (2, with $n(\text{LA}) = 1$) and termination (3) of the ring-opening polymerization of lactide (LA). Keep **stereochemistry** in mind! Mark the repetitive unit in the product (after step 3) in the usual way.



3.3 Tick the correct answer

Polymerization leads to

- | |
|--------------------------|
| ☐ |
| ☐ |
| ☐ |
| ☐ |
- a polyamide.
 a polyester.
 a polyanhydride.
 a polycarbonic acid.

3.4 Give the IUPAC-name/s of the product/s of acidic hydrolysis of lactide. Include stereodescriptors, if necessary.**B. Synthesis of a caffeic acid derivative**

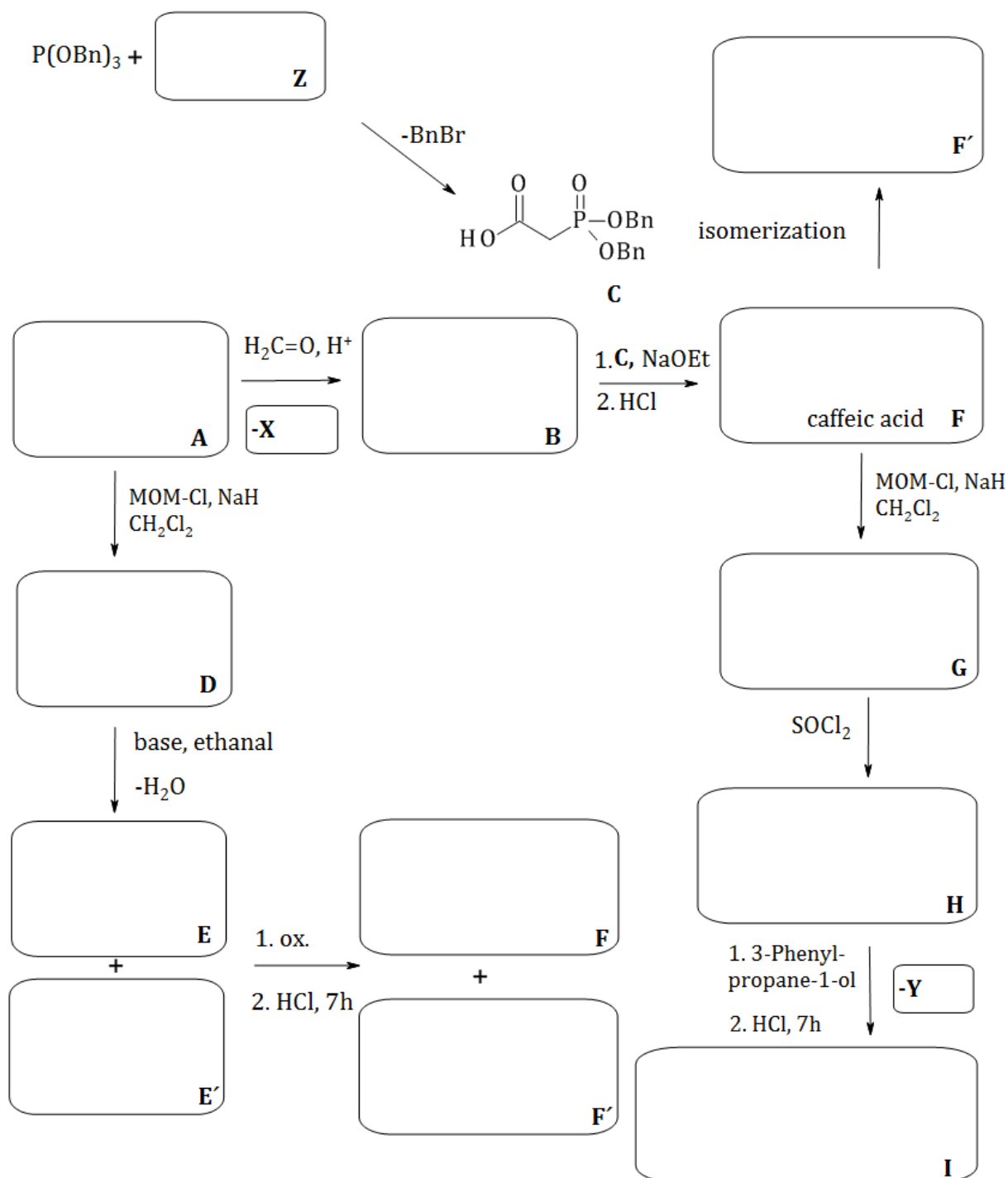
This problem focuses on the synthesis of the caffeic acid derivative **I**, whose cytoprotective properties against cytotoxicity induced by H₂O₂ was tested together with 20 other esters of caffeic acid.

You have the following hints for solving the problem:

- Compound **A** is called 3,4-dihydroxybenzene carbaldehyde.
- **E** and **E'** are stereoisomers.
- **F** and **F'** are stereoisomers.
- Compound **F** can be transformed to **F'** via isomerization reaction.
- **F** and **F'** have the following elemental composition (w/w):
60.00% C, 4.48% H, 35.52% O.
- The following well-known abbreviations are used:
Ph = Phenyl,
Bn = Benzyl (Phenylmethyl),
MOMCl = CH₃OCH₂Cl,
PDC = Pyridinium dichromate.

3.5 Write down the formulae of **F and **F'**.**

3.6 Insert the structural formulae of **A**, **B**, **D**, **E**, **E'**, **F**, **F'**, **G**, **H**, **I**, and **Z** including correct stereochemistry into the boxes shown in the reaction scheme. In the same way add the empirical formulae of **X** and **Y**. Abbreviate possible benzyl-, phenyl- or MOM-residues as *Bn*, *Ph* or *MOM*.



3.8 Write down the stereochemical relation of **E** and **E'** as well as **F** and **F'**.

3.9 Formulate the reaction mechanism of the isomerization from **F** to **F'** and suggest appropriate reaction conditions.

3.10 What is the role of NaOEt in the first step when producing **F** from **B** and **C**? Draw the constitution formula of the reactive intermediate formed during this reaction. Name the reaction mechanism between this intermediate and the other reactand. How is this name reaction called?

3.11 Formulate a detailed reaction mechanism (use "R" for residues) for the formation of **E** and **E'** from **D** and ethanal. Use arrows for attacking species. Name the reaction mechanism.

3.12 Which is the underlying name reaction for the formation of **D** from **A**? Name the corresponding reaction mechanism. Explain why this step is necessary within the reaction scheme.

C. Woodward synthesis of Colchicine

Colchicine is the main alkaloid of the autumn crocus (*Colchicum autumnale*). It is one of the most prominent natural products. On the one hand being a potent phytotoxin, it shows substantial potential as a pharmaceutical drug on the other hand: It is a mitose inhibitor that prevents formation of the spindle apparatus during cell division.

First attempts of total synthesis in the 1950s set milestones for the synthesis of natural products. Only very few target compounds have been synthesized in such multifaceted ways as colchicine. The reaction sequence shown in this problem was developed by Woodward, a renowned organic chemist (1963). The special feature of this synthesis was that it strategically introduces the nitrogen functionality at C-7 at a very early stage of the protocol. [1] Woodward was awarded the Nobel Prize in Chemistry 1965 for his achievements.

[1] Graening, T. and Schmalz, H. (2004), Colchicin-Totalsynthesen im Vergleich: Eine Reise durch 50 Jahre Organische Synthesechemie. Angewandte Chemie, 116: 3292-3318. doi:[10.1002/ange.200300615](https://doi.org/10.1002/ange.200300615)

Hints:

- Compound **A**: Methyl-(*E*)-3-aminobut-2-enoate
- N_2H_4 / H_2O_2 / Cu^{2+} : specific reducing agent for non-aromatic double bonds
- PDC: Pyridinium dichromate

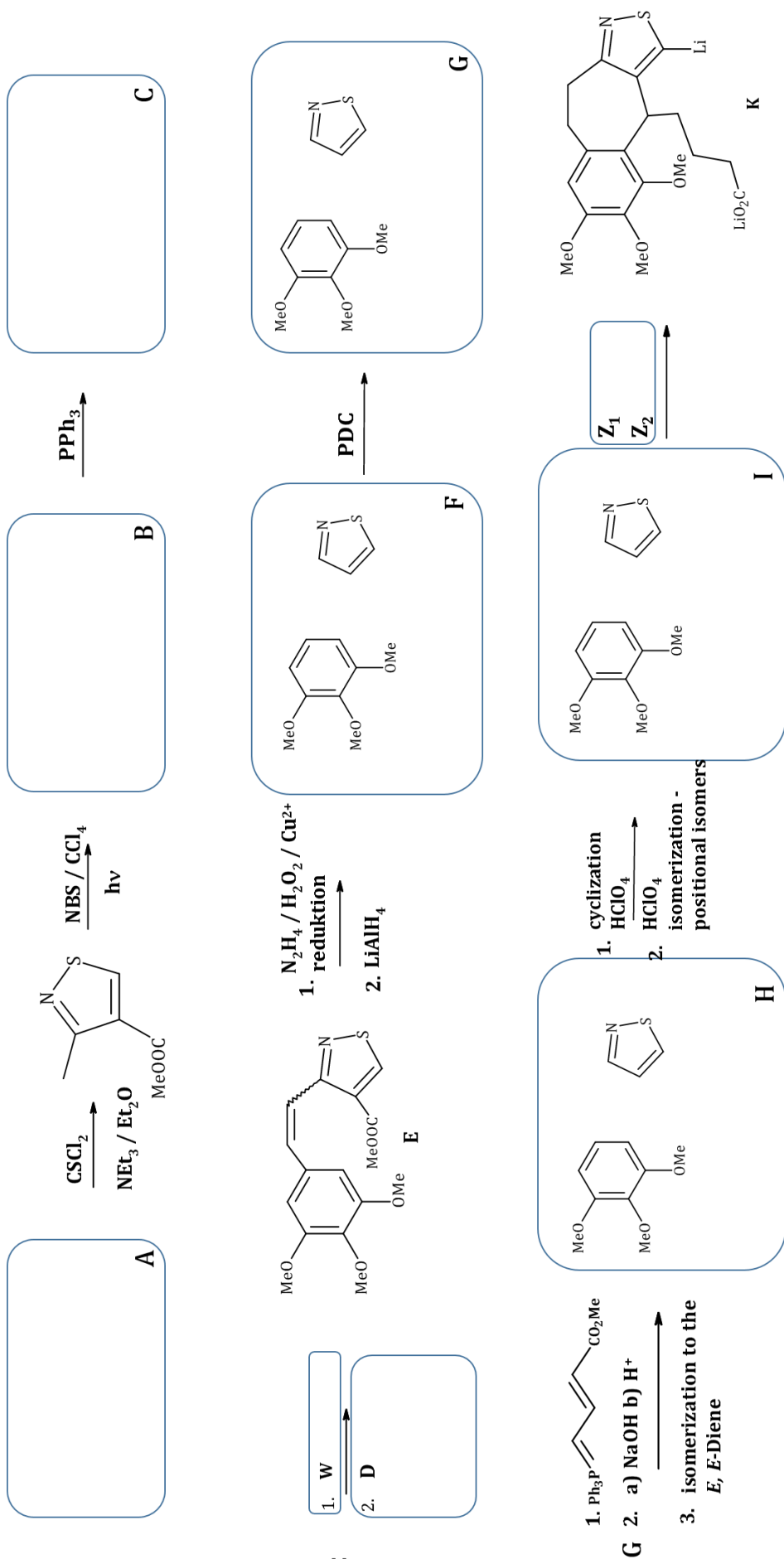
3.13 Insert the structural formulae of A, B, C, D, F, G, H, I, L, M, N, O, P, and R into the boxes shown in the reaction scheme. In the same way add the empirical formulae of W, X, and Y. Several boxes already contain substructures of the respective compound, which you only need to complete.

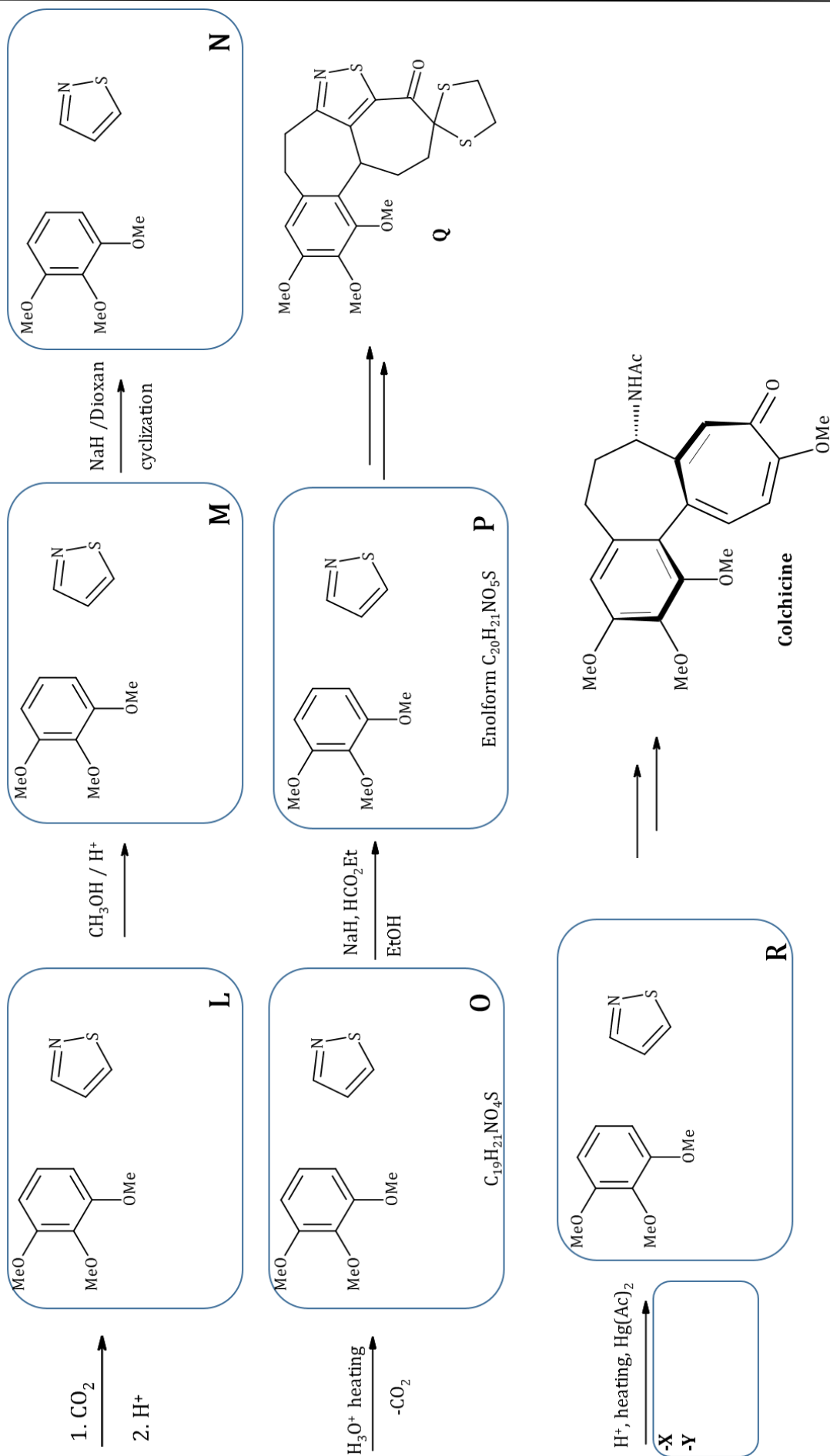
3.14 Suggest reagents Z_1 and Z_2 for transforming I to K.

3.15 Which name reaction is the basis of the step from H to I (cyclization)? Name the corresponding reaction mechanism.

3.16 Which type(s) of chirality are present in colchicine? Also state their number.

3.17 Give the stereodescriptor(s) of colchicine.





Problem 4

17 Points

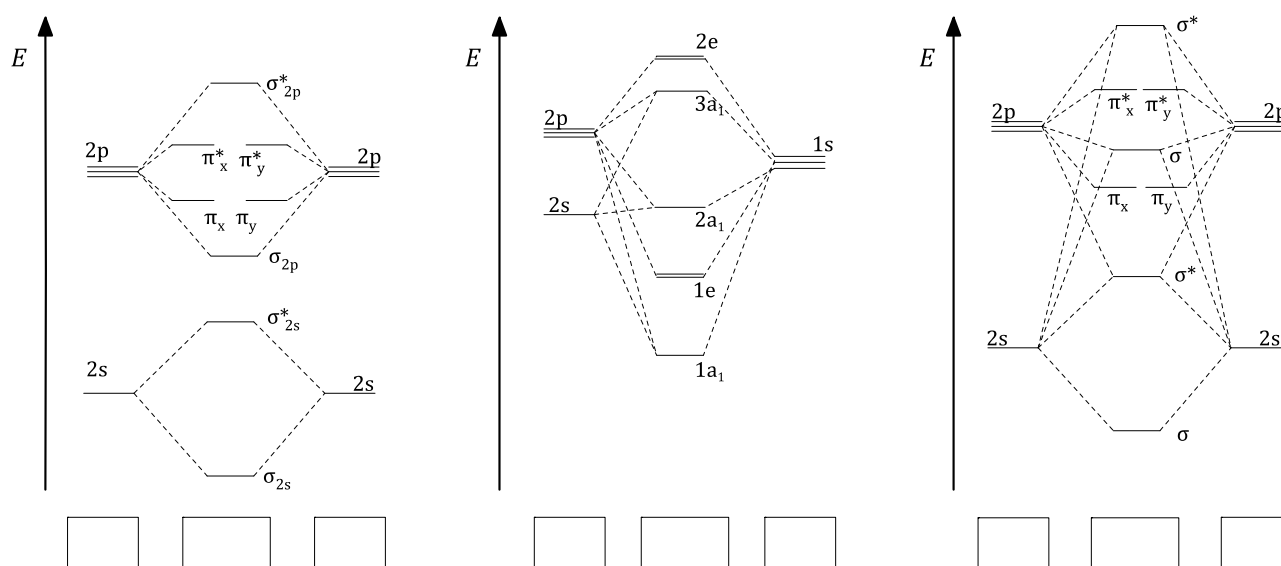
Nitrogen and its Compounds

This problem deals with Nitrogen and some of its compounds. It elucidates aspects of chemical properties and molecular structure as well as thermodynamic and kinetic aspects.

A. The Nitrogen Molecule – a Comparison

In contrast to molecular oxygen molecular nitrogen is rather inert. Comparing the corresponding MO schemes can explain this inertness. The following figure shows MO schemes of N_2 , O_2 , and NH_3 , one of the most important nitrogen compounds, respectively.

4.1 Label the schemes by writing the correct element symbols and molecular formulae into the respective boxes. Populate the schemes with electrons (arrows).



4.2 State magnetic behavior and bond order:

Nitrogen N_2

Bond order: _____

☐ diamagnetic

☐ paramagnetic

Oxygen O_2

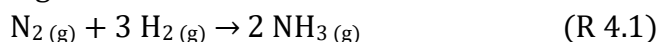
Bond order: _____

☐ diamagnetic

☐ paramagnetic

B. Ammonia

Every year some 180 million metric tons of ammonia are produced, which makes it one of the most important commodity chemicals. Almost all ammonia is synthesized through the Haber-Bosch process based on the following reaction:



Find some thermodynamic data at 298 K you will need during the following calculations:

	$\Delta_f H^\circ / \text{kJ/mol}$	$S^\circ / \text{J/molK}$	$C_p^\circ / \text{J/molK}$
$\text{N}_2(\text{g})$	0	191.6	29.1
$\text{H}_2(\text{g})$	0	130.7	28.8
$\text{NH}_3(\text{g})$	-45.9	192.8	

4.3 Calculate the overall quantity of heat Q_1 released during worldwide production of ammonia at isobaric conditions at 298 K in Joule.

Rumors say that a new death star will feature in the movie „Star Wars: Episode XIX – the Force of Chemistry“, due to be released in 2076. This gigantic weapon will produce the abovementioned 180 million metric tons of ammonia in a gigantic bomb calorimeter to be used later for destroying the assigned planetary target.

4.4 Calculate the overall quantity of heat Q_2 released for one batch of ammonia in the bomb calorimeter at 298 K.

4.5 Calculate the sum mass of educts the death star needs to hold for one load of ammonia.

Let us now return to science without fiction. The Haber Bosch process is often discussed when introducing chemical equilibrium.

4.6 Calculate K_p for the formation of ammonia following equation R 4.1 at 298 K.

Ammonia synthesis often takes place at 400°C to achieve higher reaction rate.

4.7 Calculate K_p for ammonia formation at 400°C assuming that $\Delta_R H$ and $\Delta_R S$ have the same values as at 298 K.

In reality reaction enthalpy of course depends on temperature. The following values for the equilibrium constant for the reaction in (R 4.1) can be found:

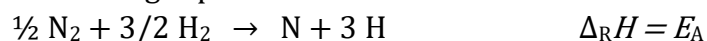
T	K_p
500 K	1.14×10^{-1}
600 K	2.11×10^{-3}
700 K	1.12×10^{-4}

4.8 Based on these values calculate $\Delta_R H_{650}$ as accurately as possible.

4.9 Calculate C_p of NH_3 . Assume that the C_p values of H_2 , N_2 , and NH_3 are independent of temperature.

C. Bond breaking in Nitrogen and Kinetic Isotope Effect

One limitation of ammonia synthesis lies in the fact that the activation energy of the uncatalyzed reaction is extraordinarily high. One can estimate its value from the reaction enthalpy of the dissociation of N_2 and H_2 in the gas phase:



The following enthalpies are given:



4.10 Calculate E_{A} based on a suitable thermodynamic cycle.

Let us briefly assess if the kinetic isotope effect (KIE) plays a role during bond breaking in nitrogen. Regard the N_2 molecule a harmonic oscillator for that purpose. Nitrogen comprises two stable isotopes, whose masses are given below for your calculations:

	Mass in amu	Frequency of occurrence
^{14}N	14.0031	99.634 %
^{15}N	15.0001	0.366 %

4.11 Give the frequency of occurrence for the following molecules in %.

$^{14}N-^{14}N$: _____ $^{14}N-^{15}N$: _____ $^{15}N-^{15}N$: _____

Let us compare $^{14}N-^{14}N$ and $^{14}N-^{15}N$ regarding the KIE.

4.12 Calculate the reduced masses μ for each molecule below in amu and kg using five significant figures. Demonstrate the calculation in detail for one of them.

$\mu(^{14}N-^{14}N) =$ _____ amu = _____ kg
 $\mu(^{14}N-^{15}N) =$ _____ amu = _____ kg

The stretching vibration of the $^{14}N-^{14}N$ molecule occurs at a wavenumber of 2456 cm^{-1} .

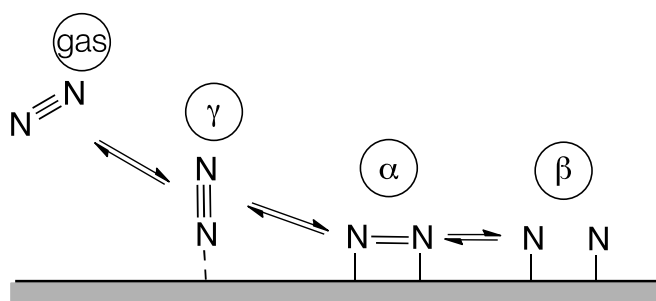
4.13 Calculate the force constant k of the N-N bond in gaseous nitrogen.

4.14 Calculate the zero point energies E_0 of $^{14}\text{N}-^{14}\text{N}$ and $^{14}\text{N}-^{15}\text{N}$ in J.

4.15 Calculate the ratio of rate constants k_{1414}/k_{1415} for bond breaking in $^{14}\text{N}-^{14}\text{N}$ and $^{14}\text{N}-^{15}\text{N}$, respectively.

D. Catalysis

Since its earliest days, ammonia synthesis is based on an iron-based catalyst found by Alwin Mittasch as the result of tedious chemical legwork. It took until the 1980s that Gerhard Ertl (Nobel Prize for Chemistry 2007) elucidated in detail how this catalyst works. The individual steps during heterogeneous catalysis are complex. During the initial steps, adsorption of nitrogen to the iron surface plays a key role.

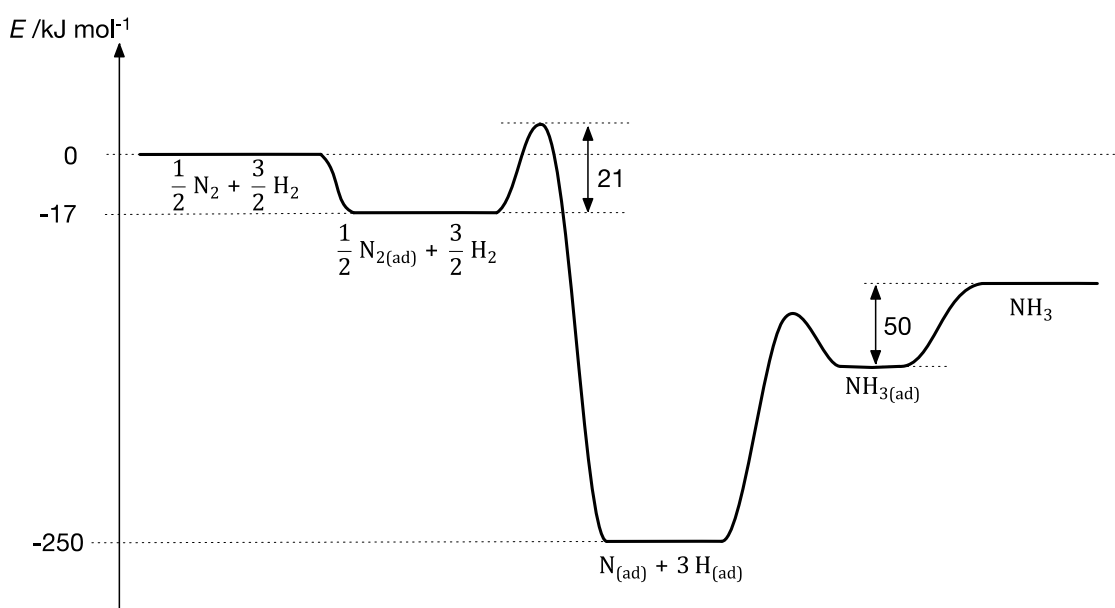


The scheme above (modified from Ertl, Angew. Chem. 102 (1990) 1258-1266) demonstrates how nitrogen adsorbs to the catalyst surface in several steps followed by dissociation ($\alpha \rightarrow \beta$). For this process the following relation is valid: The stronger the bond between nitrogen and catalyst surface, the weaker is the N-N bond.

Hence during adsorption stretching vibrations of the N-N molecules occurred at two further wave numbers. Assign them to the correct situation (see figure).

4.16 The oscillation at ... cm^{-1} corresponds to situation (tick the correct one):				
1500 cm^{-1}	☐ gas	☐ α	☐ β	☐ γ
2100 cm^{-1}	☐ gas	☐ α	☐ β	☐ γ

The figure below sketches a strongly simplified version of the energy diagram for synthesizing ammonia:

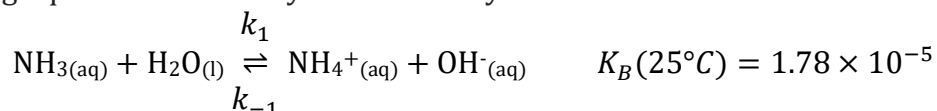


4.17 What is the activation energy of the catalyzed reaction?

4.18 What is the enthalpy of formation of $\text{NH}_{3(ad)}$?

E. Ultrafast Reaction of Ammonia in Aqueous Solution

The following equilibrium is always reached very fast:



Let us assume the equilibrium concentration of $\text{NH}_{3(aq)}$ being $0,15 \text{ mol dm}^{-3}$ for an experiment.

A sudden temperature change increases the amounts of $\text{NH}_4^+_{(aq)}$ and $\text{OH}^-_{(aq)}$ by a small amount. After $\tau = 7,61 \text{ ns}$ relaxation time the deviations from equilibrium x have reached $\frac{1}{e}$ of their initial values x_0 : $x_\tau = \frac{x_0}{e}$.

Water concentration $[\text{H}_2\text{O}]$ remains constant and hence does not occur in any equation.

4.19 State the rate law for the change in concentration of NH_3 .

$$-\frac{d[\text{NH}_3]}{dt} =$$

4.20 State a term for $\frac{dx}{dt}$, assuming that x denotes the momentary deviation from equilibrium concentration.

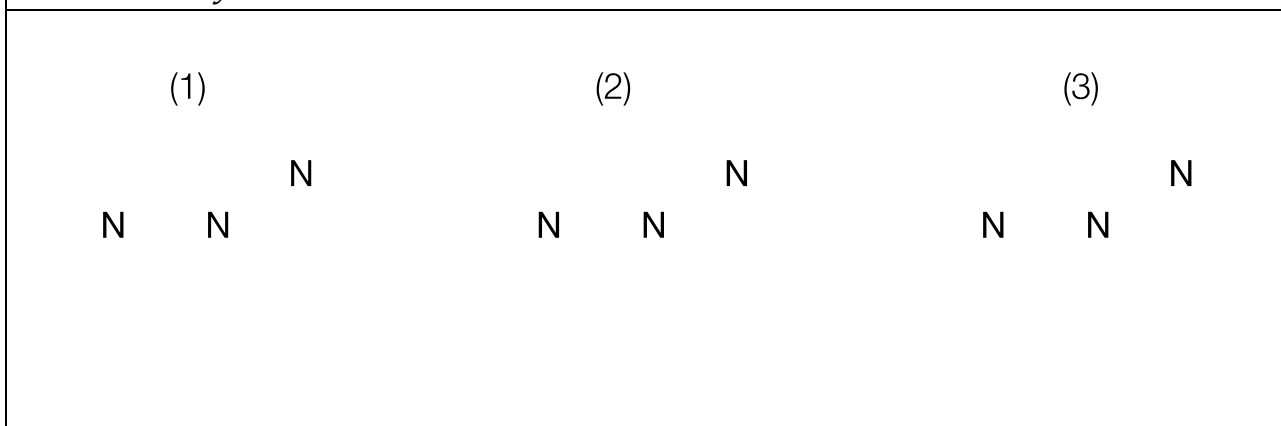
4.21 Calculate the rate constants k_1 and k_{-1} .

F. Further Compounds containing N and H

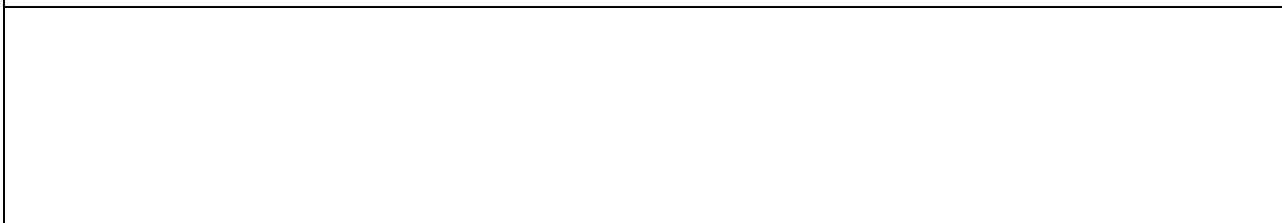
In addition to ammonia, other compounds containing N and H exist. For instance, you may already have heard of hydrazine, which is used as rocket fuel. If a molecule contains only σ -bonds, it is called an azane. There are also unsaturated N-H compounds containing one or more N=N-double bonds called azenes. The number of N atoms is denoted with the usual prefixes for numerals (di, tri...).

For the triazene N_3H_3 one can draw three isomers: (1) and (2) are different configurational isomers and (3) constitutional isomers.

4.22 Add the missing H-atoms and complete the Lewis formulae. Assign formal charges, if necessary.



4.23 There is also a triazane with the empirical formula N_3H_3 . Draw its constitutional formula.



Problem 5

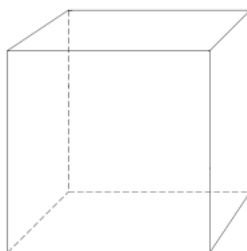
10 Points

Chromium and its Compounds: Lattices, Nuclei and Complexes

A. Chromium as a Metal

Chromium crystallizes in a body-centered cubic lattice. It has a density of $\rho = 7.14 \text{ g cm}^{-3}$.

5.1 Draw the chromium atoms as spheres into the unit cell of the body-centered cubic unit cell. Also state the number of atoms per unit cell.



Number of atoms per unit cell:

5.2 Calculate the lattice parameter a in pm.

The chemical element chromium comprises different nuclides ranging from mass number 41 to 68. ^{50}Cr , ^{52}Cr , ^{53}Cr , and ^{54}Cr are stable isotopes. The unstable isotope ^{51}Cr is applied intravenously, for instance to determine the volumes and masses of red blood cells. ^{51}Cr disintegrates through electron capture. It has a molar mass of $M = 50.945 \text{ g mol}^{-1}$. A sample of mass $m = 2.00000 \text{ g}$ shows an activity of $A = 6.84701 \cdot 10^{15} \text{ Bq}$.

5.3 Give a balanced, complete disintegration equation for electron capture. Note both mass number and atomic number for every nuclide.

5.4 Calculate the half-life of ^{51}Cr in hours from the data given.

1500 mg of an alloy containing silver, copper, and chromium were dissolved. The resulting solution containing Ag^+ , Cu^{2+} , and Cr^{3+} ions was diluted to a volume of 500 cm^3 . One tenth of that solution was used for the following experiments:

After removing silver and copper from the solution, chromium was oxidized with hydrogen peroxide to chromate in alkaline solution (OH^-). The sample was then acidified followed by adding $25,00 \text{ cm}^3$ of 0.100 molar iron(II) salt solution. Thereby, iron(II) quantitatively reduced chromate to chromium(III) leading to iron(III). Remaining iron(II) was quantitatively titrated by 17.20 cm^3 of 0.0200 molar KMnO_4 -solution.

5.5 Formulate balanced ion equations for:
 a) Oxidation of chromium(III) by hydrogen peroxide,
 b) Reduction of chromate by iron(II), and
 c) Oxidation of Iron(II) by permanganate.
 Explicitly state every stoichiometric coefficient, including "1".

a)

b)

c)

5.6 Calculate the fraction of chromium in the alloy in $\%(w/w)$.

B. Chromium in Complexes and Ionic Lattices

Chromium can exist in several oxidation states. Chromium(III)-ions form the tris-glycinato-chromium(III) complex with glycinate ($\text{NH}_2\text{-CH}_2\text{-COO}^-$), a bidentate chelating ligand.

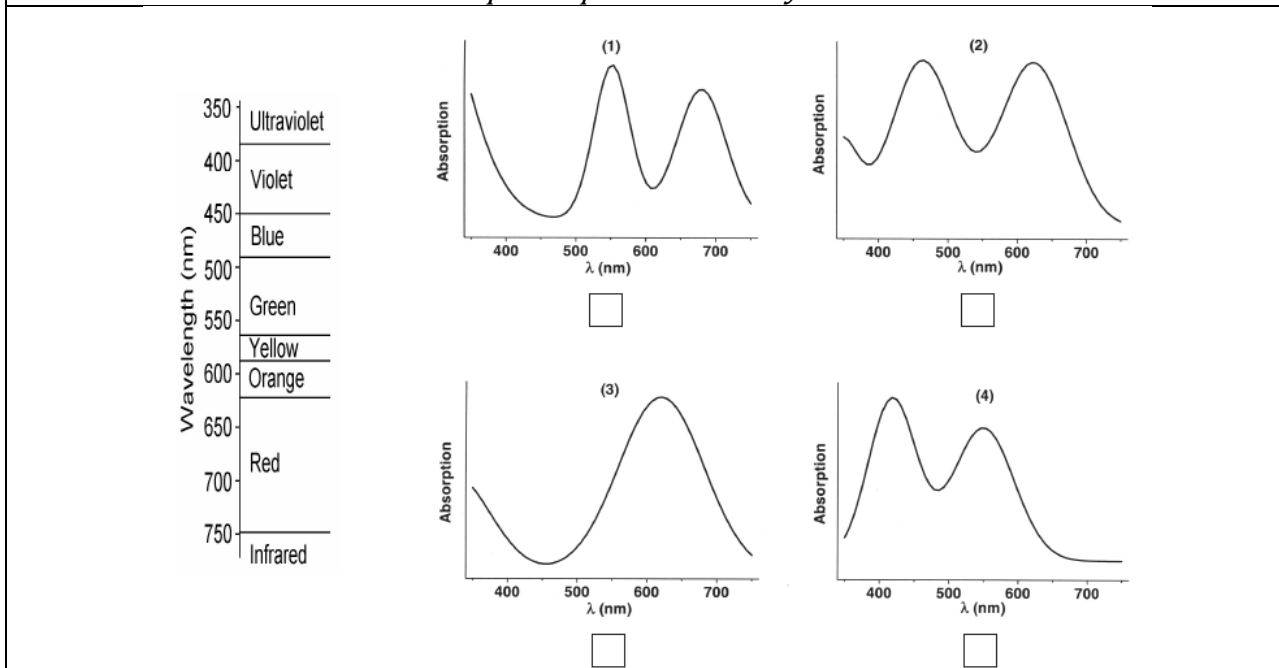
5.7 State the name of the coordination polyhedron formed by the complex. State the donor atoms explicitly and use only the skeletal structure of the ligands otherwise.

Coordination polyhedron:

5.8 State the number of possible geometrical isomers (=diastereomers!) for the tris-glycinato-chromium(III) complex and all corresponding stereo descriptors. Consider that each ligand molecule contains two different donor atoms.

Chromium(III) ions cause the red color of ruby, a gemstone.

5.9 Tick the box below the absorption spectrum of ruby.



The empirical formula of another chromium complex is $\text{CrCl}_3\text{H}_{12}\text{O}_6$. 0.533 g of this compound were dissolved in 100 cm³ water followed by adding 10 cm³ nitric acid ($c = 2 \text{ mol dm}^{-3}$). Then an excess of silver nitrate solution was added. The resulting precipitate was filtered, washed, dried, and weighed: $m_{\text{precipitate}} = 0.287 \text{ g}$.

1.06 g of the sample lost 0.144 g mass when gently heating to 100°C in dry air.

5.10 Write down the correct and complete formula of the complex. The structural drawing should make clear which ligands are located in which coordination sphere of chromium.

Many compounds of type AB_2O_4 crystallize in the so-called spinel-type crystal structure.

In normal spinels, O^{2-} -ions form a cubic face-centered structure. One eighth of the tetrahedral voids is occupied by – mostly bivalent – A-ions. Half the octahedral voids are occupied by – mostly trivalent – B-ions.

Inverse spinels also consist of compounds AB_2O_4 and the same crystal lattice. However, the A-ions in this case occupy one quarter of the octahedral voids, the B-ions one quarter of the octahedral and one eighth of the tetrahedral voids. Hence again one half of the octahedral voids and one eighth of the tetrahedral voids are occupied..

One can predict if a spinel is normal or inverse by comparing the ligand field stabilization energies LSFE of the two species. For FeCr_2O_4 , a spinel, there are two possibilities: Normal spinel $\text{Fe}^{\text{T}}\text{Cr}^{\text{O}}\text{Cr}^{\text{O}}\text{O}_4$, and inverse spinel $\text{Fe}^{\text{O}}\text{Cr}^{\text{T}}\text{Cr}^{\text{O}}\text{O}_4$; here, ⁰ and ^T denote octahedral and tetrahedral voids, respectively. Fe^{2+} comprises 6 d electrons, Cr^{3+} 3 d electrons. In all cases high spin complexes are preferred over low-spin complexes.

5.11 Occupy the d-orbital schemes of tetrahedral and octahedral voids of Cr^{3+} and Fe^{2+} , respectively. Do this by inserting arrows in the usual way.

Cr^{3+} Tetraederlücke	Cr^{3+} Oktaederlücke	Fe^{2+} Tetraederlücke	Fe^{2+} Oktaederlücke
_____ _____ _____ t_2 _____ _____ e_g			
_____ _____ e _____ _____ _____ t_{2g}		_____ _____ e_g _____ _____ _____ t_{2g}	_____ _____ _____ t_2 _____ _____ e

5.12 Determine whether FeCr_2O_4 is a normal or an inverse spinel. For that purpose, calculate the LSFE for both Fe^{2+} and Cr^{3+} in both types of voids in units of Δ_0 . Then, calculate the LFSE for normal and inverted spinel and state your decision.