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**Theoretical Final Exam SwissChO 2019**

**INSTRUCTIONS**

- Write your name on each page and number these.
- You have three hours to solve the problems. Wait for the **START** signal before you begin.
- Use a new page for each problem.
- Write all necessary calculations legibly. Do not forget the units.
- Put your pages into the provided envelope at the end of the exam. Do not stick down the envelope.
- Finish your work immediately when the **STOP** signal is given.
- Leave your seat only when allowed to do so.
- Only **answers written on the answer sheets** can be considered.
- This test has 22 pages.

**Viel Erfolg!**

**Bonne chance!**

**Buona fortuna!**

**Good luck!**

## CONSTANTS AND FORMULAE

Avogadro constant	$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$	Ideal gas law	$pV = nRT$
Universal gas constant	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$	Gibbs energy	$G = H - TS$
Faraday constant	$F = 96\,485 \text{ C mol}^{-1}$	$\Delta_r G^0 = -RT \cdot \ln(K) = -nFE_{\text{Zelle}}^0$	
Planck constant	$h = 6.626 \cdot 10^{-34} \text{ J s}$	Nernst equation	$E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln \left( \frac{c_{\text{ox}}}{c_{\text{red}}} \right)$
Speed of light	$c = 2.998 \cdot 10^8 \text{ m s}^{-1}$	Energy of a photon	$E = \frac{h \cdot c}{\lambda}$
Temperature	$0^\circ\text{C} = 273.15 \text{ K}$	Lambert-Beer law	$A = \log \left( \frac{I_0}{I} \right) = \epsilon \cdot c \cdot L$

For the calculation of equilibrium constants all concentrations, refer to the standard concentration  $1 \text{ mol dm}^{-3} = 1 \text{ mol L}^{-1}$ . If not stated otherwise in a task, consider all gases ideal throughout this test.

Periodic Table of Elements

1 H 1.008																		2 He 4.003
3 Li 6.94	4 Be 9.01																	9 F 19.00
																		10 Ne 20.18
11 Na 22.99	12 Mg 24.31																	17 Cl 35.45
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80	
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29	
55 Cs 132.91	56 Ba 137.33	57–71		72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [212]
87 Fr [223]	88 Ra [226]	89–103		104 Rf [267]	105 Db [268]	106 Sg [269]	107 Bh [270]	108 Hs [270]	109 Mt [278]	110 Ds [281]	111 Rg [282]	112 Cn [285]	113 Nh [286]	114 Fl [289]	115 Mc [290]	116 Lv [293]	117 Ts [294]	118 Og [294]

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 140.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac [227]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [266]

## PROBLEM 1 - NICKEL

XX POINTS

**1.1** Nickel(II) phosphate is a light green solid that occurs naturally as the mixed mineral arupite where a fraction of cation sites is occupied by  $\text{Fe}^{2+}$ . The pure nickel salt has recently been found to be a viable material for constructing inorganic nanostructures such as nanorings and nanotubes. The unit cell of **pure** nickel(II) phosphate is orthorhombic with dimensions  $a = 5.824 \text{ \AA}$ ,  $b = 4.694 \text{ \AA}$  and  $c = 10.10 \text{ \AA}$ . It is depicted in Fig.1.

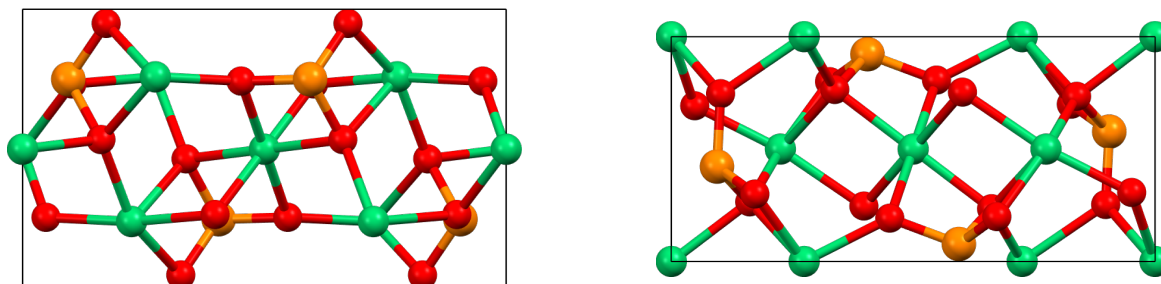


Figure 1: Front view (*left*) and top view (*right*) of the nickel(II) phosphate unit cell. Nickel is shown in green, phosphorus in orange, and oxygen in red.

- Calculate the metal content in pure nickel(II) phosphate in wt%.
- Calculate the density of pure nickel(II) phosphate in  $\text{g cm}^{-3}$ .

Industrially, nickel is obtained from naturally occurring nickel oxide  $\text{NiO}$  by the Mond process, invented by Ludwig Mond in 1890. The oxide is reduced by  $\text{H}_2$  at  $200^\circ\text{C}$  to its metallic form. Contained impurities such as iron oxide and cobalt oxide are reduced as well. To get rid of those impurities, the alloy is treated with gaseous carbon monoxide at  $60^\circ\text{C}$  to get exclusively nickel carbonyl, a complex of Ni and CO. This neutral complex, which has four carbon atoms for each nickel atom and a molecular mass of  $170 \text{ g/mol}$ , exists as a highly volatile liquid and can readily be decomposed at  $250^\circ\text{C}$  yielding pure metallic nickel.

- What is the chemical formula of the formed nickel complex? What is its structure based on VSEPR, considering that Ni formally carries no electron lone pairs?
- Provided all three reactions for nickel mentioned in the text above going from  $\text{NiO}$  to pure metallic nickel in as much details as possible.

Synthetically, nickel phosphate can be obtained by precipitation from solutions of  $\text{Ni}(\text{NO}_3)_2$  and phosphate salts at high pH. The  $pK_a$  values of phosphoric acid are  $pK_{a,1} = 2.14$ ,  $pK_{a,2} = 7.20$  and  $pK_{a,3} = 12.37$ . The solubility product of Ni(II) phosphate is  $K_L = 4.74 \times 10^{-32} \text{ M}^5$ . You prepare three solutions each having a total volume of  $250 \text{ mL}$ . Solution 1 is prepared from  $4.98 \text{ g Na}_2\text{HPO}_4$  and solution 2 from  $7.38 \text{ g Na}_3\text{PO}_4$ . Solution 3 is prepared by diluting a mixture of  $50 \text{ mL}$  of solution 1 and  $50 \text{ mL}$  of solution 2. The hydroxide concentration of a solution of a strong base, capable of accepting **two or more protons**, can be calculated using:

$$[\text{OH}^-] \simeq \sqrt{K_{b,1} \cdot c_0 + \left(\frac{K_{b,1}}{2}\right)^2} - \frac{K_{b,1}}{2}$$

where  $K_{b,1}$  is the first base dissociation constant and  $c_0$  is the total concentration of added base.

- Calculate the pH value of all three solutions.
- You combine solution 3 with an equal volume of a  $2.57 \text{ mM Ni}(\text{NO}_3)_2$  solution. What is the final concentration of  $\text{Ni}^{2+}$  remaining in solution?

## PROBLEM 2 - FUEL CELL

XX POINTS

Classical fuel cells rely on hydrogen as a clean energy source. However,  $H_2$  is a non-trivial gas to be stored. Alternative systems using biomass and the vanadyl cation,  $VO^{2+}$ , have been developed. Here, we take a closer look at such a fuel cell using glucose as our model substrate. The design of the fuel cell has been depicted below in Fig.2.

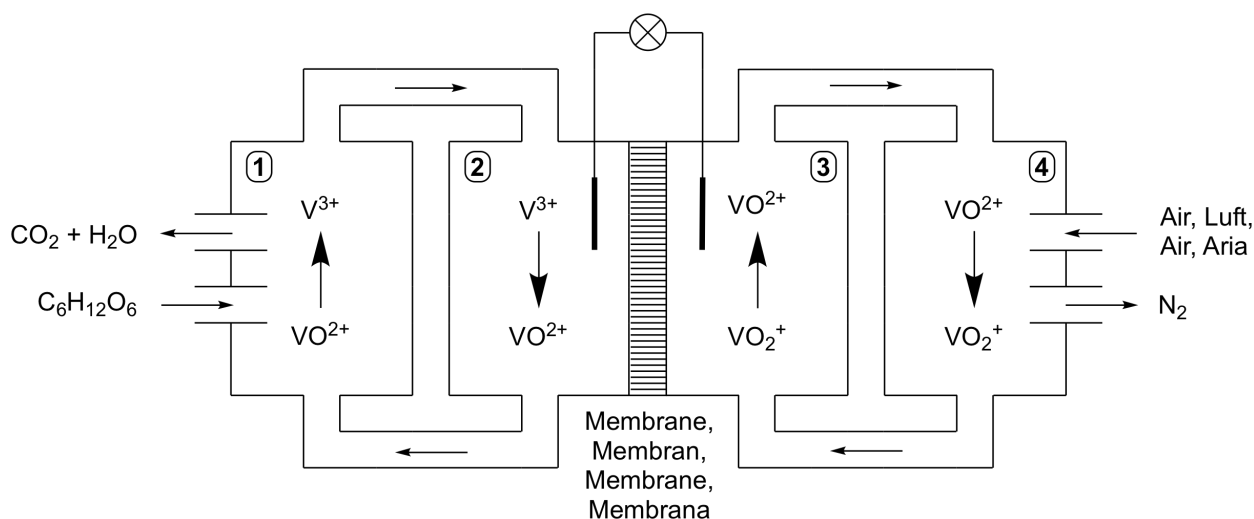


Figure 2: Schematic representation of a vanadyl mediated fuel cell consuming glucose.

At the beginning both cycles contain vanadyl in strongly acidic solution. In chamber 1,  $VO^{2+}$  get reduced to  $V^{3+}$  and glucose,  $C_6H_{12}O_6$ , gets oxidized to carbon dioxide and water. In chamber 4,  $VO^{2+}$  gets oxidized to  $VO_2^+$  by oxygen from the supplied air. In the central elements 2 and 3, constituting the galvanic cell, the produced  $V^{3+}$  and  $VO_2^+$  participated in the half cell reactions at the electrodes. The semi-permeable membrane is used to close the circuit. If the cell is operating,  $VO^{2+}$  is reformed and electricity flows through the circuit.

- Write the equations taking place in chambers 1 and 4.
- Write the half-cell equations for chambers 2 and 3. Assign anode and cathode to the chambers.
- Which ions cross the membrane in which direction when the cell is operating?

Running at full capacity, the chamber 1 consumes 5.00 g of glucose each minute and has a constant temperature of  $35^\circ C$ .

- How much air has to be pumped through chamber 4 during the time of this three hour exam? Assume that air contains 21 vol%  $O_2$  which is fully consumed. Assume that compressed air at 2 bar pressure is used.
- How many electrons pass from one chamber to the other each second?

We want to know whether such a cell can be used to illuminate this lecture hall fully during the exam. At full capacity, the left chambers contain  $[VO^{2+}] = 1.43 M$  and  $[V^{3+}] = 0.57 M$  while the right chambers contain  $[VO^{2+}] = 1.21 M$  and  $[VO_2^+] = 0.79 M$ . Both cycles have exactly the same geometry and contain a buffer keeping  $[H^+] = 1.00 M$ .

- Which voltage do you measure for the cell at full capacity?
- Write  $\Delta G$  as a function of  $\Delta G^\circ$  and of all concentrations. Is  $\Delta G$  pH dependent? What value for  $\Delta G$  do you get for an operating cell?

Table 2: Some standard reduction potential for vanadium.

Reaction	$E^0/V$
$V^{2+} + 2 e^- \rightarrow V$	-1.175
$V^{3+} + e^- \rightarrow V^{2+}$	-0.255
$VO^{2+} + 2 H^+ + e^- \rightarrow V^{3+} + H_2O$	-0.337
$VO_2^+ + 2 H^+ + e^- \rightarrow VO^{2+} + H_2O$	-0.991

- h) Assuming that the lamps in this lecture hall consume 1000 W worth of direct current. How many fuel cells are needed? The power output of a fuel cell is given by the product of voltage  $V$  and current  $I$ .

## PROBLEM 3 - MYSTERY BOTTLE

XX POINTS

During the annual check of the chemical inventory at your school, a bottle with an unreadable label is found. It contains one of the 4 compounds, shown in Fig.3, dissolved in methanol. Your task will be to properly label this solution. To not have to bother about the solvent, you take a small aliquot and remove MeOH under reduced pressure and at low temperature to obtain colorless needles.

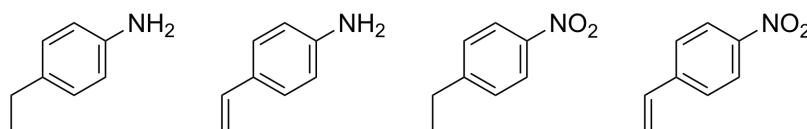


Figure 3: Possible chemical structure of the unknown organic compound.

- a) The unknown compound should have a chemical formula of  $C_aH_bN_cO_d$ . To identify the coefficients, you burn 0.053 g of the dried material at air and obtain 44 mL  $CO_2$  (g), 36  $\mu L$   $H_2O$  (l) and 5.5 mL  $N_2$  (g) when cooled to 25 °C. Calculate the ratio of a:b:c:d. Hint: It might be possible that you cannot make a prediction for all indices.

To preliminarily determine the compound, you record a mass spectrum of some of the dried material, depicted in Fig.4.

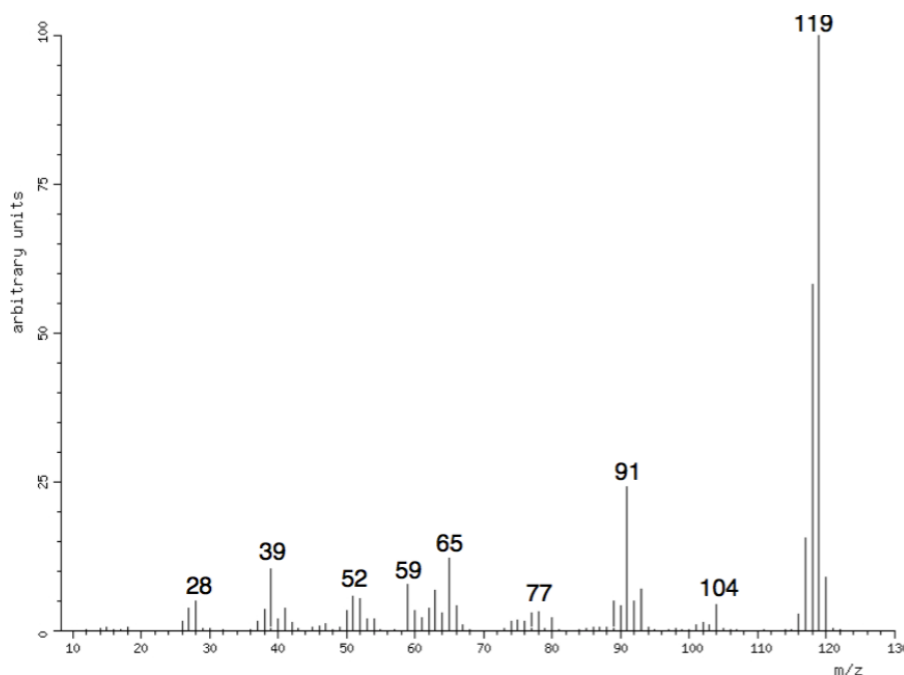


Figure 4: Mass spectrum of the unknown substance, recorded by EI at 75 eV.

- b) Identify and label the molecule peak as  $[M^{\bullet+}]$ .
- c) What is the chemical formula of the unknown substance?
- d) Ethyl and vinyl benzene derivatives show a characteristic fragmentation product in their mass spectrum. The corresponding cation, tropylium, contains only carbon and hydrogen and is aromatic. Draw the structure of tropylium and label the corresponding peak.



To get further confidence in the identified label you record an infrared spectrum of the dried material, shown in Fig.5.

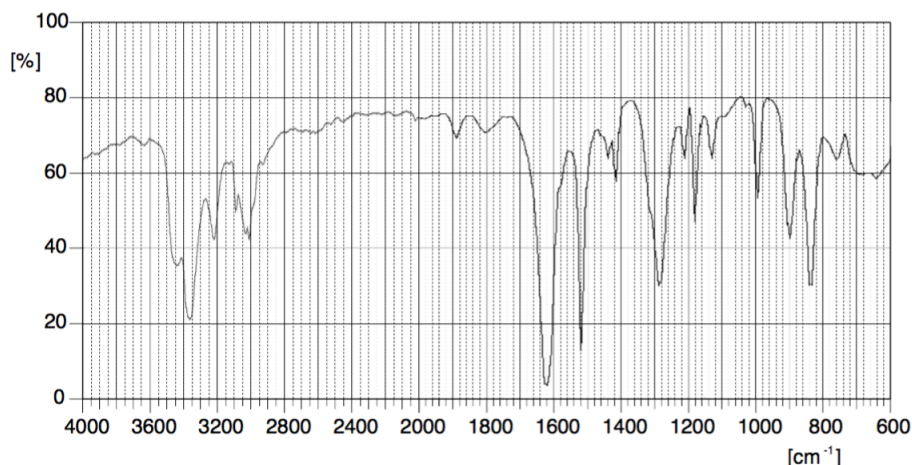


Figure 5: IR spectrum of the unknown substance, recorded as KBr disc.

- e) Use the table provided (cf. IChO) to assign all visible vibrations above  $1250\text{ cm}^{-1}$ .

Still lacking confidence in the identification of the dried material, you record its  $^1\text{H}$  NMR spectrum in  $d_6$ -acetone. The substance's peaks are shown in Fig.6.

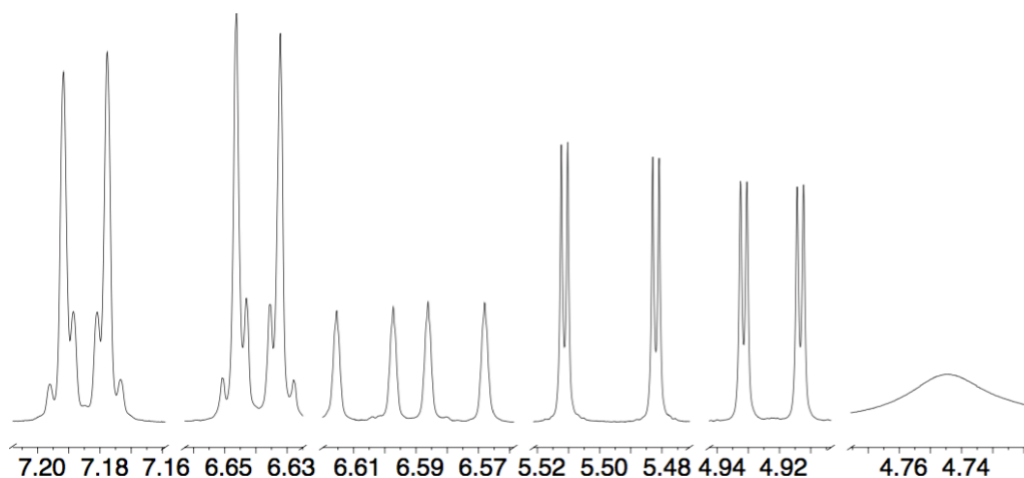


Figure 6:  $^1\text{H}$  NMR spectrum of the unknown substance recorded at 600 MHz in  $d_6$ -acetone. **INTEGRAL MISSING!**

- f) Using the  $^1\text{H}$  NMR spectrum, state how many hydrogen atoms correspond to each peak. Also state the peak's multiplicity.
- g) The peaks around 6.59, 5.50 and 4.93 ppm can be described as (*dd*), corresponding to a characteristic fragment in the identified substance. Calculate the coupling constants for all three *dd* peaks.
- h) Assign all peaks to protons in the identified structure.

Table 3: Hint: Chemical shift of aromatic protons can be calculated using the formula  $\delta = 7.26 + \Sigma I$ .

Substituent	$I_{ortho}$	$I_{meta}$	$I_{para}$
Ethyl	-0.15	-0.06	-0.18
Vinyl	+0.06	-0.03	-0.10
Amino	-0.75	-0.25	-0.65
Nitro	+0.95	+0.26	+0.38

Having identified the compound, you want to determine the concentration of the unknown sample. You record a UV/VIS spectrum of a standard of known concentration prepared from the dried needles and manage to identify  $\lambda_{max} = 274 \text{ nm}$  with  $\epsilon_{max} = 16\,490 \text{ cm}^{-1} \text{ M}^{-1}$ .

- i) Observing a transmission of 27 % over a distance of 1 cm from a 1000 x dilution of the unknown solution, what concentration has the unknown solution?

## PROBLEM 4 - CHIRALITY TO THE BUILDING BLOCKS OF LIFE

XX POINTS

Amino acids are the essential ingredients for the chemistry of life itself as we know it. Fig.7 shows the structures of tyrosine (Tyr), cysteine (Cys) and threonine (Thr). These amino acids are highly interesting because of their variety of nucleophilic reactivity and subsequent frequent involvement in post-translational modification.

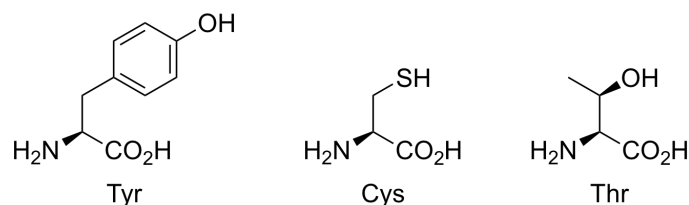


Figure 7: Chemical structures of some amino acids.

- Assign the absolute configuration for each stereogenic center in Tyr, Cys and Thr.
- How many diastereomers of threonine exists? Draw all of them. How do these structures relate pairwise to one another?

Benzyl bromide, PhCH<sub>2</sub>Br, is a common electrophile to protect strong nucleophiles such as hydroxyl, sulfhydryl and amino groups. To selectively protect the hydroxyl group of Tyr, PhCH<sub>2</sub>Br is added to a mixture of tyrosine, NaOH and CuBr<sub>2</sub>. The amino acid thereby forms a chelating complex with Cu<sup>2+</sup> having a copper to amino acid ratio of 1:2. The complex has a square planar coordination and carries a net charge of -2 at pH > 10.

- Order amino, carboxyl, hydroxyl, sulfhydryl groups according to their nucleophilicity given their dominant protonation state in strongly basic aqueous solution.
- Draw the two diastereomers of the tyrosine copper complex. Are the complexes optically active?

If you try to use the same protocol to protect the hydroxyl of threonine, incomplete conversion is observed. For the sulfhydryl group of cysteine, you find that no benzylated product is formed. Instead you recover the unprotected amino acid and unreacted benzyl bromide.

- Explain the lack of reactivity of cysteine towards benzyl bromide using a chemical structure.

Using NiCl<sub>2</sub> instead of CuBr<sub>2</sub> leads to the same result for the protection of cysteine. However, another complex is formed in solution with a Ni<sup>2+</sup> to amino acid ratio of 1:3. The complex has an octahedral coordination geometry at nickel and cysteine shows the same binding mode for Ni<sup>2+</sup> as for Cu<sup>2+</sup>.

- How many diastereomers of this complex could theoretically exist? You do not need to draw them.

## PROBLEM 5 - DISTORTING MANGANESE

XX POINTS

In this question, we take a closer look at the ligand field splitting of  $\text{Mn}^{2+}$  complexes. According to crystal field theory, the destabilization of metal  $d$ -orbital by the introduction of ligands can be thought of as a stepwise process. Introducing 6 ligands as a cloud of homogeneously distributed negative charge, all  $d$ -orbitals experience the same destabilization. The localization to 6 evenly spaced point charges then leads to the splitting of different  $d$ -orbital, as depicted in Fig.8. The common graphical representation of  $d$ -orbitals is given in Fig.9.

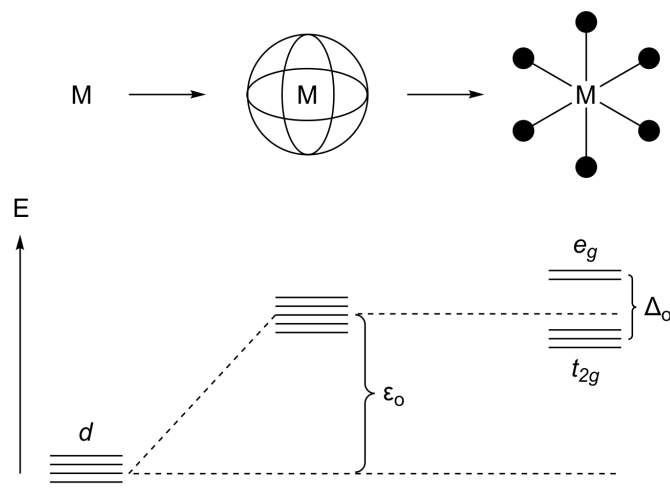


Figure 8: Ligand field splitting by the introduction of a homogeneous cloud corresponding to 6 ligands and subsequent localization to point charges along the axes of the coordinate system.

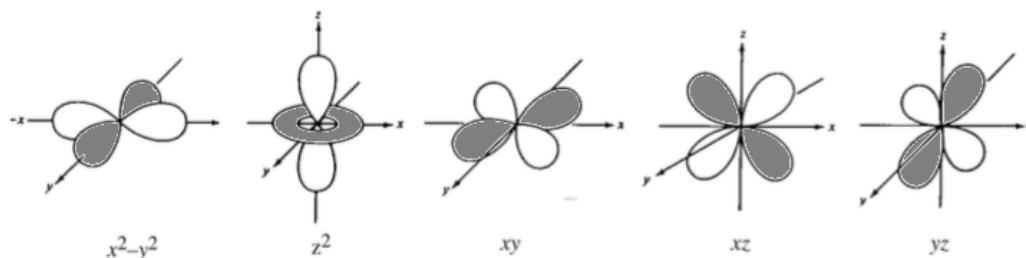


Figure 9: Graphical representation of the set of  $d$ -orbitals. The labels denote the plane in which these orbitals mostly lay, as span by the two unit vectors.

- a) Denote which orbitals correspond to  $t_{2g}$  and which to  $e_g$  assuming that the ligands come to reside on the axes of the coordinate system.

The ligand field splitting energy  $\Delta_o$  depends on the  $\sigma$ -donation properties of the ligands. Stronger donors lead to a larger splitting. We will compare  $[\text{Mn}(\text{OH}_2)_6]^{2+}$  and  $[\text{Mn}(\text{CN})_6]^{4-}$ . The first complex has a  $\Delta_o = 8500 \text{ cm}^{-1}$  while the second absorbs at  $\lambda_{\text{max}} = 330 \text{ nm}$ . They do not have the same number of unpaired electrons.

- b) Determine the oxidation number of the complexes. How many  $d$ -electrons do the complexes have?
- c) Draw the proper energy schemes for both complexes (on a common energy scale) and fill in their  $d$ -electrons.
- d) What color are the complexes? Assume the  $t_{2g} \rightarrow e_g$  transition to be color determining.

In 1937, Hermann Arthur Jahn and Edward Teller reported first studies about the spontaneous symmetry distortion (breaking in non-linear) in molecules with degenerate electronic ground states. For octahedral complexes, this distortion occurs when a contraction or elongation along the z axis lowers the total energy by tweaking the orbital energies, see Fig.12. For small distortions, the  $e_g$  orbitals thereby split symmetrically around their initial energy level by  $\delta_1$  while the  $t_{2g}$  orbitals do so asymmetrically by  $\delta_2$ , where  $\Delta_o > \delta_1 > \delta_2$ . It is known that one of our complexes spontaneously contracts.

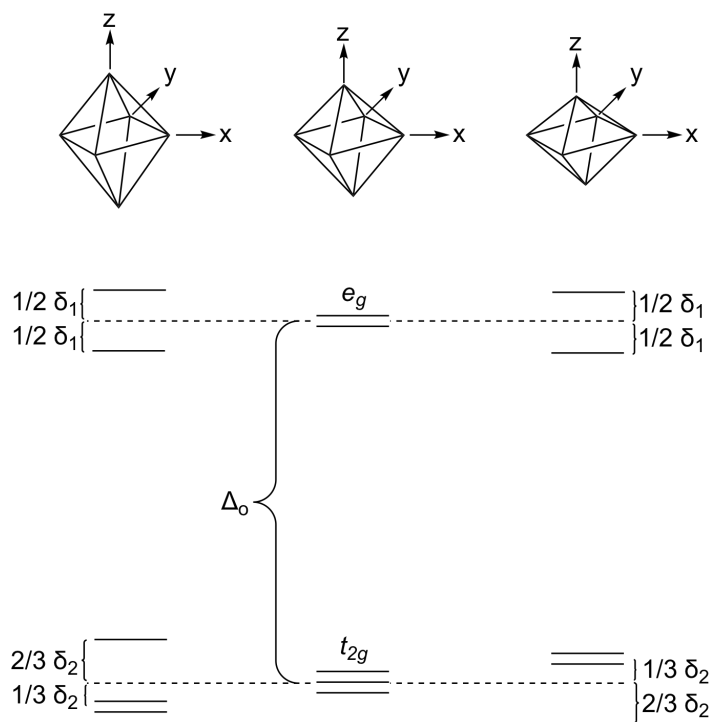


Figure 10: Schematic splitting known as Jahn-Teller effect.

- Which d-orbital get stabilized by compressing an octahedral complex along the z axis?
- Use your orbital diagrams from d) to argue whether complexes  $[\text{Mn}(\text{OH}_2)_6]^{3+}$  and  $[\text{Mn}(\text{CN})_6]^{3-}$  are distorted or not.
- How much stabilization energy does the distortion contribute in terms of  $\delta_1$  and  $\delta_2$  if a distortion is occurring?

## PROBLEM 6 - THE IODINE-HYDROGEN REACTION

XX POINTS

The formation of hydrogen iodide (HI) from hydrogen ( $\text{H}_2$ ) and iodine ( $\text{I}_2$ ) is one of the best investigated reactions in the gas phase. In the year 1894, Bodenstein performed kinetic experiments and found the effective rate law for the formation of HI:

$$r_{eff} = -\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = k_{eff}[\text{H}_2][\text{I}_2]$$

where  $k_{eff}$  is an effective rate which is readily measurable in an experiment. For the exact mechanism, several alternatives have been proposed and investigated. In the following we will have a look at two of them.

In mechanism A iodine is first cleaved reversibly to elementary iodine atoms, reaction (1). In a second step (2), these react with hydrogen to form hydrogen iodide. Both reactions are considered to be elementary reactions:



The dissociation and reformation of iodine in the first reaction step is much faster than the second step. Therefore, you can assume the first reaction to be in a rapid pre-equilibrium.

- Write down the rate law for the second reaction i.e. the formation of hydrogen iodide.
- Write down the equilibrium constant of the rapid pre-equilibrium.
- Substitute your expression for the equilibrium constant in the rate law and show that mechanism A is in accord with the experimental rate law by finding an expression for  $k_{eff}$ , which does only depend on the three given rate constants  $k_1$ ,  $k_{-1}$  and  $k_2$ .

In an alternative mechanism B reaction (1) is followed by two subsequent elementary reactions (3) and (4). In this mechanism  $\text{H}_2\text{I}$  is a very reactive intermediate which we will treat using the steady-state approximation.



- Write down the rate law for the formation of hydrogen iodide according to elementary reaction (4).
- Apply the steady-state approximation on  $\text{H}_2\text{I}$  by determining the derivative of its concentration with respect to time and setting it equal to 0.
- Rearrange the obtained equation to obtain an expression for the concentration of  $\text{H}_2\text{I}$ .
- Substitute this in the rate law for reaction (4) and show that also this mechanism is in accord with the experimental rate law by using the equilibrium constant from b) and additionally making the approximation that  $k_4$  is very small.
- In analogy to c) determine an expression for  $k_{eff}$  which only depends on the rate constant of the given elementary reactions.
- Propose another mechanism for the hydrogen-iodine reaction, which also fulfills the experimental rate law and give the corresponding elementary reaction(s).

## PROBLEM 7 - OXYGEN IN SPACE

XX POINTS

Oxygen is the third most abundant chemical element in the universe, after hydrogen and helium. The naturally most abundant isotope  $^{16}\text{O}$  is synthesized at the end of the helium process in massive stars. The nuclear reaction involves the fusion of a  $^{12}\text{C}$  nucleus and a  $^4_2\text{He}$  nucleus and releases a gamma photon of energy  $1 \times 10^{-14} \text{ J}$  as byproduct.

- Write the chemical equation for generation of  $^{16}\text{O}$ .
- Using the simplified energy-momentum relation  $E = mc^2$ , how much energy is released during the fusion of  $12.0 \text{ g } ^{12}\text{C}$  with a stoichiometric amount of  $^4_2\text{He}$ ? How many TNT equivalent does this correspond to?

Hints: Use isotope masses of  $4.002602 \text{ u}$  for  $^4_2\text{He}$ ,  $12.000000 \text{ u}$  for  $^{12}\text{C}$  and  $15.994917 \text{ u}$  for  $^{16}\text{O}$ . A ton of TNT releases  $4.184 \times 10^9 \text{ J}$  upon detonation.

Europa is the smallest of the four Galilean moons orbiting Jupiter. It is special since it contains a thin atmosphere, containing mostly  $\text{O}_2$ . The surface pressure on Europa is  $0.1 \mu\text{Pa}$  and the temperature fluctuates between  $40 \text{ K}$  and  $100 \text{ K}$ . From here, we want to calculate the triple point of oxygen ( $p_t, T_t$ ) depicted in the phase diagram in Fig. 11. A landed space probe collects a sample of solid oxygen at  $40 \text{ K}$  and stores it in an empty container of  $2.00 \text{ L}$  volume. The sample sublimates until an equilibrium is reached when the pressure has increased to  $93.5 \text{ mPa}$ .

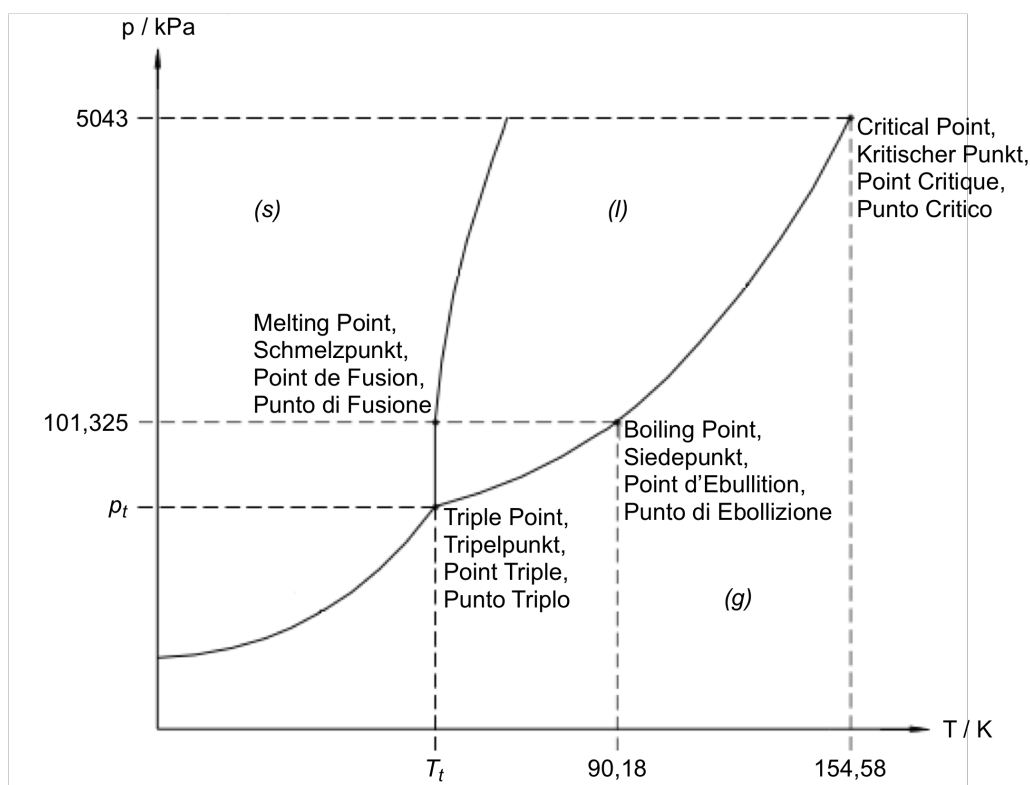


Figure 11: Phase diagram of diatomic oxygen,  $\text{O}_2$ .

The Clausius-Clapeyron equation relates pressure and temperature changes for phase transitions:

$$\ln \left( \frac{p_2}{p_1} \right) = -\frac{L}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

where  $p_i$  is the pressure at temperature  $T_i$ ,  $L$  is the specific enthalpy of vaporization or specific heat of sublimation and  $R$  is the universal gas constant. For oxygen, the heat of vaporization is 7.44 kJ/mol and the heat of sublimation is 9.26 kJ/mol.

- c) The temperature of the container is increased by 10 K. The container would burst at internal pressures about 100 Pa. Does it hold?

The triple point is a special combination of pressure and temperature at which a compound can exist in an equilibrium of its solid, liquid and gaseous phase at once. The boiling point of  $O_2$  at 1 atm is 90.18 K.

- d) Calculate the pressure and temperature of oxygen's triple point.

At high altitudes in Earth's atmosphere, oxygen is converted to ozone, which protects us from ultraviolet light emitted by the sun. Some properties of the involved allotropes of oxygen are listed below.

- e) Write the chemical equation for the interconversion of  $O_2$  and  $O_3$ .
- f) Calculate the enthalpy of formation of  $O_3$  based on bond dissociation enthalpies  $E_b$ . Why does the value of  $O_3$  do not correspond to what is experimentally measured?

You simulate the Earth's upper atmosphere in a container in your laboratory. You fill an empty container of volume 10.0 L with 12.38 mg of pure  $O_2$  and cool it to 220 K.

- g) What is the equilibrium constant of the reaction from  $O_2$  to  $O_3$ ?
- h) What is the partial pressure of  $O_3$  in the system once the equilibrium has reached? Hint: Expand the equation and neglect the term of the unknown of order 3.

Table 4: Thermodynamic properties of allotropes of oxygen.

Bond order	$E_b$ /kJ/mol	
O–O	213	
O=O	498	
Substance	$\Delta H_f$ /kJ/mol	$\Delta S_f$ /J/(molK)
$O_2$	0	205
$O_3$	143	239



## PROBLEM 8 - INTO THE ELECTRON CLOUD

XX POINTS

Benzene is a highly symmetrical molecule having the chemical formula  $C_6H_6$ . Its  $\pi$  system can be represented in two different ways of alternating single and double bonds, called resonance structures.

- Draw the two resonance structures of benzene.
- Benzene shows reflection symmetry, rotational symmetry as well as inversion symmetry. Indicate on plane, axis or point for each type of symmetry.

The resonance structures are used to account for the shortcoming of the Lewis model in describing the physical properties of benzene. For example, it can be measured that all bond length in benzene are the same having a value of 139 pm, being somewhere in between single and double bonds. Quantum chemical models have no problem in describing this observation. In this question, we will focus on two equivalent approaches to describing the pi system of benzene. Paying tribute to the cyclic nature of benzene, we can formulate the following differential equation:

$$-\frac{\hbar^2}{2m_e} \frac{d^2 \Psi_n(\phi)}{d\phi^2} = E_n \Psi_n(\phi)$$

A possible solution for the orbital energies thereof has the form:

$$E_n = \frac{\hbar^2 n^2}{2m_e R^2}$$

where  $n = 0, \pm 1, \pm 2, \dots$  represents the different energy levels,  $m_e = 9.109 \times 10^{-31}$  kg is the electron mass and  $R$  denotes the radius of the modeled circle.

- Calculate the expected radius of benzene in pm **based on the average bond length**.
- Calculate the energy levels for  $|n| \leq 4$  and draw a schematic energy diagram and fill in the  $\pi$  electrons of benzene according to Hund's rule.
- Benzene adsorbs light most efficiently at 255 nm. In the schematic diagram, this corresponds the difference between the lowest unoccupied energy level and the highest occupied level. Use this difference to calculate the radius  $R$  of the model. Is it smaller or bigger than the experimentally observed radius of benzene?

The treatment of electrons in benzene as particles on a ring only works for low  $n$  since the number of constituting carbon  $2p$  orbitals is finite. Their linear combination results 6 delocalized orbitals for the  $\pi$  system, depicted below.

The following formula describe the linear combinations mathematically:

$$\begin{aligned}\pi_1 &= 0.408\chi_1 + c_{1,2}\chi_2 + c_{1,3}\chi_3 + c_{1,4}\chi_4 + c_{1,5}\chi_5 + c_{1,6}\chi_6 \\ \pi_2 &= 0.577\chi_1 + 0.289\chi_2 + c_{2,3}\chi_3 + c_{2,4}\chi_4 + c_{2,5}\chi_5 + c_{2,6}\chi_6 \\ \pi_3 &= 0.577\chi_1 - 0.289\chi_2 + c_{3,3}\chi_3 + c_{3,4}\chi_4 + c_{3,5}\chi_5 + c_{3,6}\chi_6 \\ \pi_4 &= 0.408\chi_1 + c_{1,2}\chi_2 + c_{4,3}\chi_3 + c_{4,4}\chi_4 + c_{4,5}\chi_5 + c_{4,6}\chi_6 \\ \pi_5 &= c_{5,1}\chi_1 + 0.500\chi_2 + c_{5,3}\chi_3 + c_{5,4}\chi_4 + c_{5,5}\chi_5 + c_{5,6}\chi_6 \\ \pi_6 &= c_{6,1}\chi_1 + 0.500\chi_2 + c_{6,3}\chi_3 + c_{6,4}\chi_4 + c_{6,5}\chi_5 + c_{6,6}\chi_6\end{aligned}$$

where  $\pi_i$  denotes the linear combination and  $c_{i,j}$  is the coefficient of atom orbital  $j$  to  $\pi_i$ .

- Using the provided diagram and considering the symmetry of the molecule, determine all missing coefficients  $c_{i,j}$ .

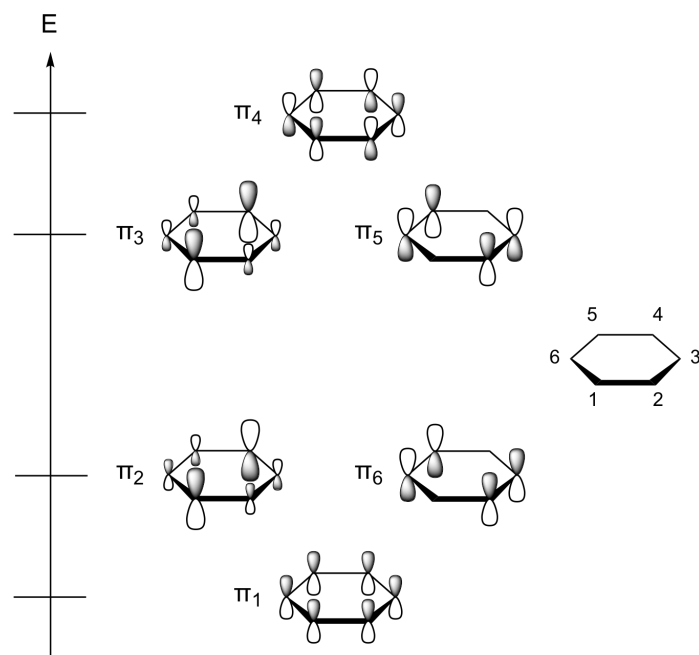


Figure 12: Schematic representation of the  $\pi$  orbitals in benzene.

The corresponding energies can be calculated by using the formula:

$$E_i = \alpha + 2\beta \cos\left(\frac{2\pi(i-1)}{N}\right)$$

where  $N$  is the number of  $\pi$  centres and  $i$  is the energy level. The parameters  $\alpha$  and  $\beta$  denote the self-interaction and interaction between neighbouring  $2p$  orbitals. Their values are  $\alpha = -11.4 \text{ eV}$  and  $\beta = -18 \text{ eV}$ .

g) Calculate the energy for all  $\pi_i$ .

h) Qualitatively correlate  $E_k$  with the energies  $E_n$ . For which values of  $n$  does the infinite model break down?

Hint:  $E_k$  needs a cosine argument in radians. To convert from radians to degrees, use:  $2\pi = 180^\circ$ .

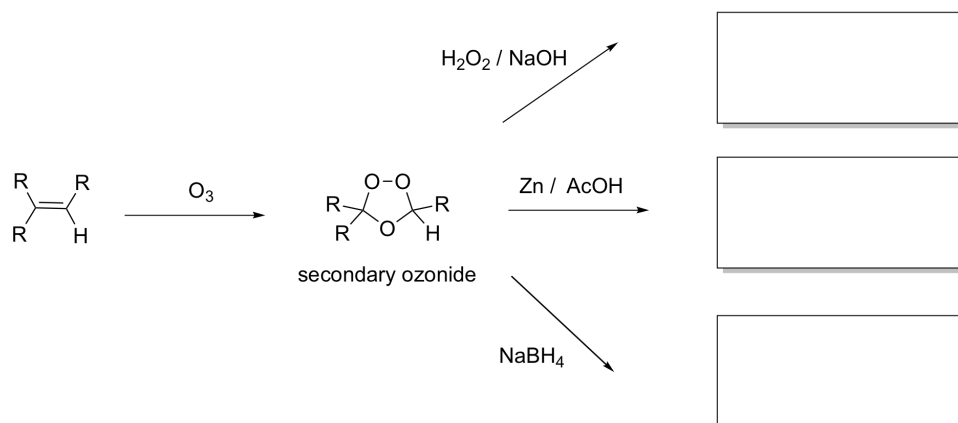
## PROBLEM 9 - ORGANIC REACTIONS WITH C=C DOUBLE BONDS

XX POINTS

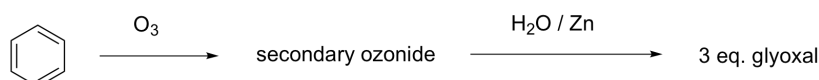
## OZONOLYSIS OF C=C DOUBLE BONDS

Ozone ( $O_3$ ) is a very strong oxidizing agent which can cleave C=C double bonds. During the reaction, a so called secondary ozonide is formed (see general scheme below). Depending on the following work up conditions different products can be obtained.

- a) Draw out the different products of the ozonolysis obtained under the given workup conditions.



Benzene can be treated with ozone as well. By this one can gain three equivalents of glyoxal (ethanedial).



- b) Draw out the Lewis structure of glyoxal.
- c) Draw the secondary ozonide produced from treating benzene with three equivalents of ozone.

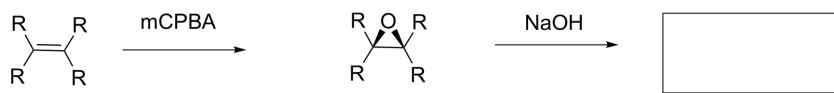
Now consider the benzene derivative 1,2-xylene (1,2-dimethylbenzene). When 1,2-xylene is treated with ozone one obtains three different products.

- d) Draw the structure of 1,2-xylene.
- e) Write down the structural formula and the systematic names of all three compounds which you can obtain from the ozonolysis of 1,2-xylene **after reductive workup using Zn / AcOH**.
- f) In which ratio are these three products obtained when you assume that all C=C double bonds are cleaved with an equivalent probability?

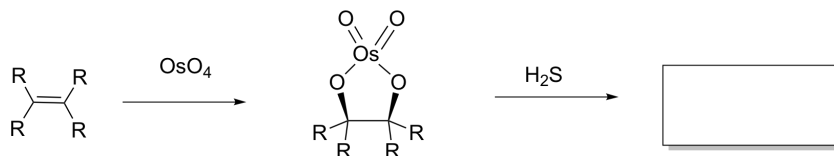
## EPOXIDE RING OPENING VS DIHYDROXYLATION

C=C double bonds can also react with mCPBA (meta-chloroperoxybenzoic acid) to yield epoxides. Upon treatment with sodium hydroxide this epoxide ring can be opened by the nucleophilic attack of a hydroxide ion.

- g) Draw out the structure of mCPBA.
- h) Draw the product of the epoxide ring opening reaction. Pay attention to the correct stereochemistry.



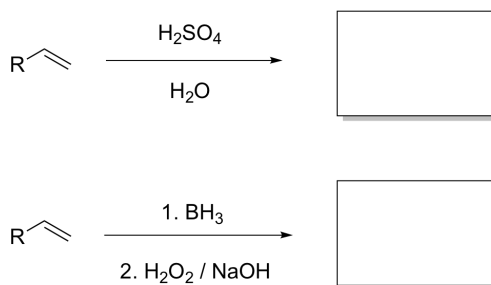
Alternatively, a C=C double bond can also be treated with osmium tetroxide ( $\text{OsO}_4$ ) to yield an intermediary syn-osmate-ester, which can then further be reduced to yield a 1,2-diol. Therefore, this reaction is also referred to as a so-called dihydroxylation reaction.



- i) Draw out the product of the dihydroxylation reaction with osmium tetroxide.
- j) Compare this product to the one obtained in h). How do they compare in terms of stereochemistry?

#### ADDITION OF $\text{H}_2\text{O}$ TO A C=C DOUBLE BOND

In both the following reactions you get a formal addition of  $\text{H}_2\text{O}$  to the C=C double bond.

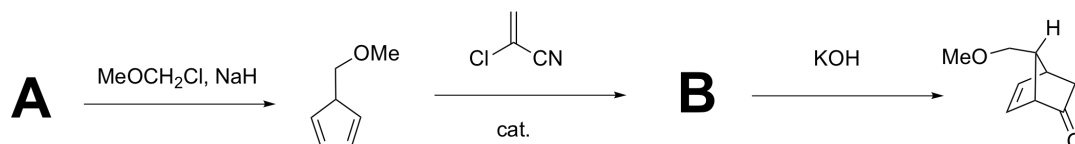


- k) Draw out the two different products formed.
- l) What is the name of the rule which predicts the selectivity in the first example? Explain the obtained selectivity e.g. by drawing a mechanism for the first reaction.

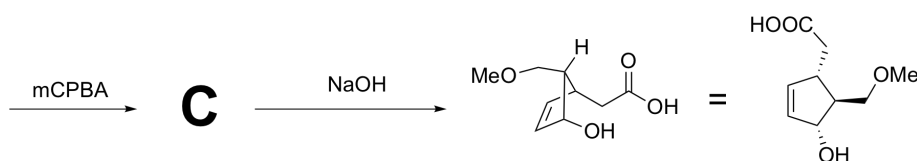
PROBLEM 10 - THE TOTAL SYNTHESIS OF PROSTAGLANDIN F2 $\alpha$ 

XX POINTS

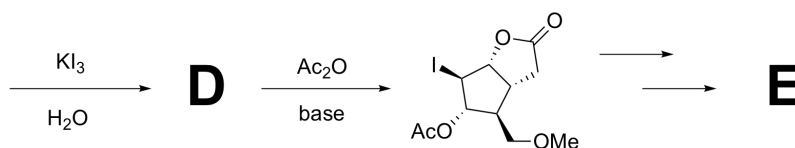
In 1969 E. J. Corey and his co-workers published the first total synthesis of a prostaglandin. Prostaglandins are a group of physiologically active lipid compounds having diverse hormone-like effects and are found overall in humans and other animals.



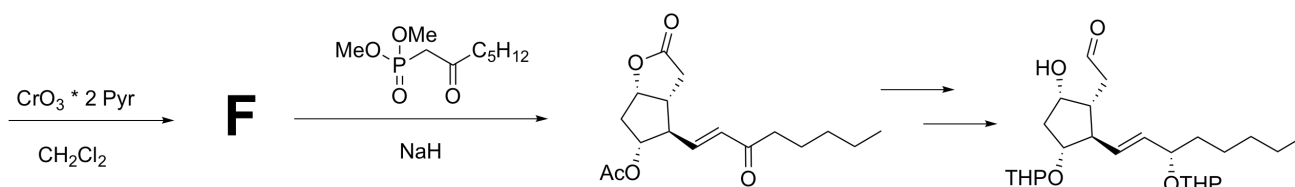
Starting from **A**, a nucleophilic substitution reaction leads to the shown diene, which can further undergo a Diels-Alder reaction with 2-chloroacrylonitrile to yield compound **B**. **B** is then further hydrolyzed to yield a bicyclic ketone as product.



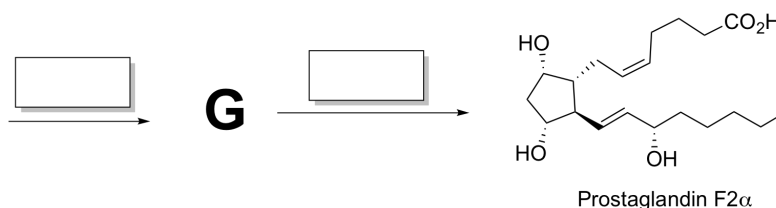
This ketone was then treated with mCPBA in a Baeyer-Villiger Oxidation to yield the lactone **C**. The lactone ring was further opened in the next step using sodium hydroxide.



In a next step treatment with KI<sub>3</sub> led to a iodolactonization product **D** which was further acylated in the follow up reaction step. After removal of the iodine and the methyl group a primary alcohol **E** was obtained.



Collins Oxidation with the pyridine-chromium (VI) complex led to the selective formation of the corresponding aldehyde **F**. This compound then was further used in a Horner-Wadsworth-Emmons reaction with a phosphonate and sodium hydride as shown above. The substrate was further converted and the acid-labile THP protecting group was introduced. This finally yielded the aldehyde shown.



A subsequent Wittig-Reaction yielded **G**, which could further be transformed in one step to the final Prostaglandin F2 $\alpha$ .

- a) Draw out the chemical structure for the compounds **A-G**.
- b) Give all necessary reagents for the last two conversions finally yielding Prostaglandin F2 $\alpha$ .
- c) Draw the positively charged intermediate which is formed during the iodolactonization yielding compound **D**. Why is it necessary to use KI<sub>3</sub> instead of just elementary iodine (I<sub>2</sub>)?
- d) Make a comparison between the Horner-Wadsworth-Emmons reaction and the Wittig reaction, which are both encountered in this total synthesis. Name one similarity and one essential difference in terms of educts and formed products.