Theoretical Final Exam SwissChO 2020

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.

- Finish your work immediately when the **STOP** signal is given.

- Only **answers written on the answer sheets** can be considered.

- This test has 19 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	$F = 96\,485 \text{ C mol}^{-1}$	$\Delta_r G^0 = -RT \cdot \ln(K) = -nFE^0_{\text{Zelle}}$	
Planck constant	$h = 6.626 \cdot 10^{-34} \text{ J s}$	Nernst equation	$E = E^0 + \dfrac{R \cdot T}{z \cdot F} \cdot \ln\left(\dfrac{c_{\text{ox}}}{c_{\text{red}}}\right)$
Speed of light	$c = 2.998 \cdot 10^8 \text{ m s}^{-1}$	Energy of a photon	$E = \dfrac{h \cdot c}{\lambda}$
Temperature	$0\,°\text{C} = 273.15 \text{ K}$	Lambert-Beer law	$A = \log\left(\dfrac{I_0}{I}\right) = \epsilon \cdot c \cdot L$

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											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
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 - ALUMINIUM COMPOUNDS   **15 POINTS**

The principal origin of aluminium is a mineral called bauxite, which is impure aluminum oxide.

  a) Give the formula of this oxide and its Lewis Structure

Aluminium chloride may be produced by two different methods:

  b) Through reaction of metallic aluminium and pure gaseous HCl. Give the equation of the reaction.

  c) Through reaction of gaseous Cl_2 passing over a solid mixture of charcoal and aluminium oxide. Give the equation of the reaction.

Aluminium chloride is a solid substance, but it is transformed into a gas by sublimation already at $177\,°C$.

  d) What is the volume in liters occupied by one mole of an ideal gas at $177\,°C$ and at $1\,bar$?

  e) $10.00\,g$ of aluminium chloride is heated to $177\,°C$ in a 2 liter container. The pressure of the resulting gas is $0.700\,bar$. What is the molar mass of the aluminium chloride in the gas phase?

  f) What is the formula of the gaseous substance?

  g) The structure of aluminium chloride may have the following geometry. Complete the drawing by adding electron pairs and charges so as to be in accordance with the octet rule.
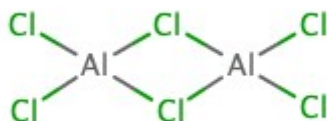

Figure 1: Potential structure of aluminium chloride.

If you take $1\,g$ of pure aluminium chloride $AlCl_3$ in a test tube, and you add a few drops of water, a violent hydrolysis reaction happens producing a white precipitate of aluminium hydroxide and a vapor composed of HCl.

  h) What is the equation of this hydrolysis ?

If you add more water, the previously produced HCl is dissolved and reacts with the precipitate, producing a hydrated ion, $[Al(H_2O)_6]^{3+}$

  i) What is the equation of this redissolution?

Aluminium chloride reacts with an equimolar mixture of benzene and chloromethane to produce a substituted benzene ring.

  j) Give the final organic molecule produced by this reaction

  k) If the reaction was carried out with twice as much of the chloromethane, what would be the final products?

Cryoscopy is a technique where the molar mass of any solute is determined by measuring the change in freezing point of a solvent in presence of the solute. If n moles of any solute are dissolved in $1.00\,\mathrm{kg}$ of benzene, the freezing point of benzene is $n \cdot 5.12\,^{\circ}\mathrm{C}$ lower than in the pure state. The compound $[\mathrm{Al(CH_3)_2F}]_x$ is a compound whose parameter x is an integer that is determined by cryoscopy. The experience shows that dissolving $1.00\,\mathrm{g}$ of the sample in $65.00\,\mathrm{g}$ of benzene leads to a lowering of the freezing point by $0.26\,^{\circ}\mathrm{C}$. Hint: Think about if the resulting change in freezing point after dissolving 1 mole in only $65\,\mathrm{g}$ benzene will be greater or smaller than for a full kg of benzene.

l) Calculate the value of parameter x.

PROBLEM 2 - SULFUR CHEMISTRY

15 POINTS

When burning in air, sulfur produces gaseous SO_2.

a) Draw the Lewis formula for SO_2.

When treating an aqueous solution of SO_2 with zinc powder, or by electrolysis, SO_2 captures one electron per molecule and forms an unstable ion A, without undergoing any other change.

b) What is the Lewis structure of A?

c) What is the equation of the reaction of Zn with SO_2?

This ion A is not stable, as it has an uneven number of electrons. It slowly dimerizes producing an ion B (= 2 A), called dithionite, with a S-S bridge.

d) What is the Lewis structure of the ion B?

e) What is the equation of formation of ion B?

If the ion Na^+ is present in solution, the solution produces sodium dithionite by evaporation. Heated to $150\,°C$, the sodium dithionite decomposes into a mixture of salts containing the ions $SO_3{}^{2-}$, $S_2O_3{}^{2-}$ and some gaseous SO_2. The sodium ion Na^+ is not transformed in this reaction

f) Write down the equation of the spontaneous decomposition of sodium dithionite.

We will now discuss the properties of another oxide: SO_3. $1.000\,g$ of solid SO_3 is placed in a $1.000\,L$ container under vacuum. When heated to $630\,°C$, the substance is entirely vaporized.

g) What should be the theoretical pressure in the gas obtained this way?

The gas pressure is measured in the container with a manometer, and found to be higher than the theoretical value. It is exactly $1.000\,atm$ ($101\,325\,Pa$). This shows that SO_3 has partially decomposed into SO_2 and O_2.

h) Write down the equation of this reaction

i) Calculate the fraction x of the amount of SO_3 which is decomposed into SO_2 and O_2?

j) Calculate the equilibrium consant K_n in the unit mole.

PROBLEM 3 - CHEMISTRY OF SILICON   **15 POINTS**

This problem is divided into three independent parts. Each one can be answered independently from the others.

Part I
Silicon hydrides are called silanes. Most of them contain Si-Si bonds, but they become increasingly unstable as the number of silicon atoms increases. Here we would like to determine the strength of the Si-Si bond.

  a) Calculate the Si-Si bond dissociation energy D of Si_2H_6 from the following information:

   - Bond dissociation enthalpy of H-H: $436\,kJ/mol$

   - Bond dissociation enthalpy of Si-H: $304\,kJ/mol$

   - Heat of formation of Si_2H_6: $+\,80.3\,kJ/mol$

   - Heat of vaporization of elemental silicon: $450\,kJ/mol$

  b) Calculate the heat of formation of Si_3H_8. Is it more or less stable than Si_2H_6? If you were not able to solve a) use the value of 250 kJ/mol for the Si-SI bond dissociation energy.

Part II
The crystalline structure of silicon oxide (or silica) can be represented in the following way. Draw a grid with in total four identical squares (2x2 grid). On each intersection of lines and corners, add a silicon atom. In between two silicon atoms connected by a line, there is always one oxygen atom.

  c) Draw the 2x2 grid representing the structure of silicon oxide described in part II.

  d) What is the formula of this silicon oxide?

  e) If the bond energies of Si-O and O=O are respectively $368\,kJ/mol$ and $498\,kJ/mol$, what is the heat of formation of silica from solid silicon and gaseous O_2?

Part III
Cement chemistry. Ideally pure cement is a compound Ca_2SiO_4, which is made by heating a mixture of chalk $CaCO_3$ and sand SiO_2 at a temperature higher than $1000\,°C$. CO_2 is released in this process.

  f) What is the mass of $CaCO_3$ and SiO_2 in the initial mixture to be heated for producing $1000\,g$ of cement?

  g) Draw the Lewis structure of Ca_2SiO_4, where Si makes always single bonds with O. Also give the name of this compound.

When treated with water, the cement hardens and becomes "concrete". This transformation is a chemical reaction, where each atom Si loses one O atom. This atom combines with one Ca atom to produce CaO which then reacts with water to produce $Ca(OH)_2$. Thus, the cement molecule has lost one Ca and one O atom.

  h) Write down the equation of the reaction of water with the cement.

  i) The structure of the resulting concrete looks like a long chain of atoms. Draw its Lewis structure where all Si atoms are surrounded by single bonds formed with O atoms.

PROBLEM 4 - COORDINATION CHEMISTRY   **13 POINTS**

The tetrachloroplatinate ion $(PtCl_4^{2-})$ is a common precursor for the synthesis of platinum complexes. $PtCl_4^{2-}$ adopts square-planar coordination geometry.

a) Give the oxidation state of the metal and the total valence electron count of $PtCl_4^{2-}$.

In square-planar complexes, ligand exchange kinetics are often governed by the identity of the ligand trans to one being exchanged. This "trans-effect" can be of high importance for the synthesis of more complicated compounds, as the trans effect can be used to predict which ligand in a given complex will be replaced the fastest. The following example shows the trans effect in a reaction:
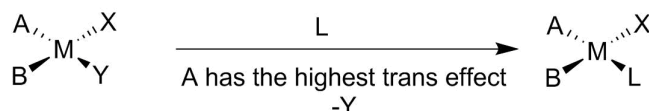
Since Ligand A has the highest trans-effect, the ligand trans to it, Y, will be replaced the fastest in a ligand-exchange reaction.

The strengths of the trans-effect of four ligands are ordered below:

$$NO_2^- > Cl^- > NH_3 \geq Py \tag{1}$$

b) Predict the expected products **A**, **B** and **C**, assuming that in each step only one ligand is exchanged. Make sure to consider the overall charge of the complex.
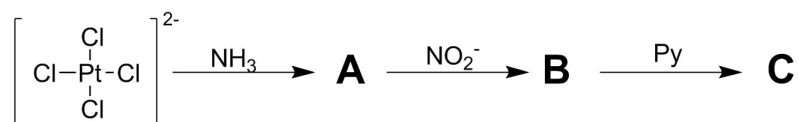
The spectrochemical series can be used to predict the differences in color of similar complexes, below a set of different ligands, ordered according to ascending ligand field splitting:

$$SCN^- < Cl^- < N_3^- < NCO^- < H_2O < NC^- < Py < NH_3 < en < NO_2^- < CO \tag{2}$$
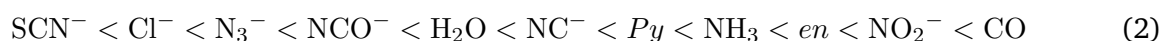
c) How do you expect the color of the complexes to develop during the first reaction step? Elaborate how the crystal field splitting changes during the substitution and how this influences the wavelength of the absorbed light and observed color.

d) Phosphine ligands have an even stronger trans-effect than NO_2^-. Predict the product of the reaction between $PtCl_4^{2-}$ and 2 equivalents of triphenylphosphine, PPh_3.

e) When 1 equivalent dppe is used, a different product is obtained. Draw the product and explain why it is different than the product obtained in d.)

Dppe:
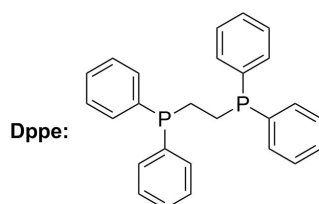
PROBLEM 5 - BASIC QUANTUM CHEMISTRY   **13 POINTS**

In this task we will have a look at the different isotopologues of chlorine gas Cl_2. Chlorine in nature occurs as two major isotopes ^{35}Cl and ^{37}Cl with a natural abundance of 75% and 25% respectively. In this task the diatomic molecule Cl_2 will be treated by the harmonic oscillator and rigid rotor approximations. The formulas below will prove useful in this regard:

Reduced mass μ of a diatomic molecule:

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \tag{3}$$

Harmonic vibrational wave number $\tilde{\nu}$, where k is the force constant of the bond:

$$\tilde{\nu} = \frac{1}{2\pi c} \cdot \sqrt{\frac{k}{\mu}} \tag{4}$$

Energy of a harmonic Oscillator, with n = 0,1,2, ... :

$$E_n = h \cdot \tilde{\nu} \cdot c \cdot (n + \frac{1}{2}) \tag{5}$$

Rotational constant of a diatomic molecule:

$$B = \frac{h}{8 \cdot \pi^2 \cdot c \cdot I} \tag{6}$$

where I is the momentum of Inertia given by $I = \mu \cdot R^2$, with the bond length R of the diatomic molecule.

a) Calculate the statistical distribution of the 3 possible Cl_2 isotopologues based on the natural abundance of the respective isotopes.

b) Below you can see a comparison of a harmonic potential (black) and an anharmonic potential (red) used to model the vibrations of a diatomic molecule. What process cannot be explained based on the harmonic model, but is considered in the anharmonic one?
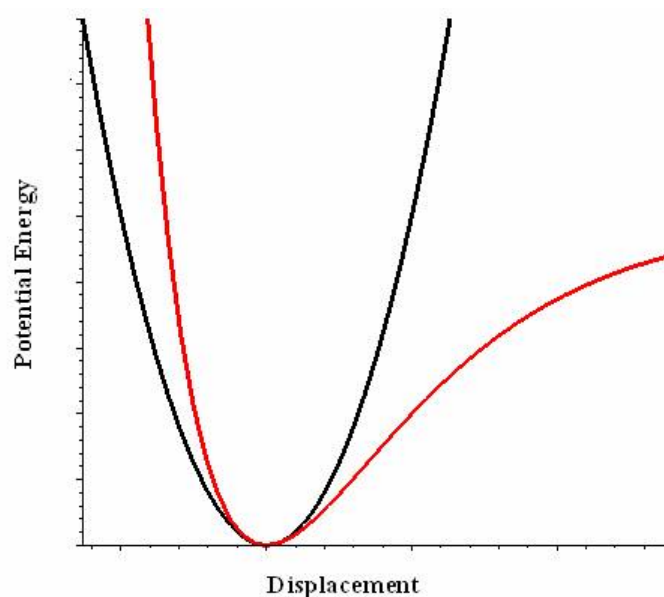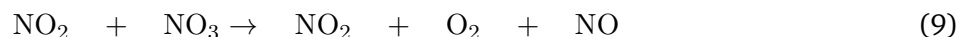
c) In the following we will have a look at the chlorine isotopologues based on the harmonic approximation. Calculate the reduced mass in the unit u (atomic mass unit) for the three different species.

d) $^{35}Cl_2$ has got a harmonic wave number of $559.72\,\mathrm{cm}^{-1}$. Calculate the wavenumber for the vibration of the other two isotopologues by assuming that the force constant k is equal for all species. Hint: you do not need to calculate k explicitly to solve this task.

e) Considering the statistical distribution you determined in a) calculate the weighted average for the stretching wave number in a Cl_2 molecule.

f) By looking at the formula for the energy in a harmonic oscillator which of the 3 isotopologues will have the lowest zero-point energy (i.e. n = 0) and will thus be the hardest to dissociate?

g) $^{35}Cl_2$ has got a rotational constant $B = 0.243\,\mathrm{cm}^{-1}$. Use this information and the formulae above to determine the equilibrium bond distance of a $^{35}Cl_2$ molecule. Hint: make sure to convert the reduced mass calculated in c) and the given rotational constant into SI units first.

PROBLEM 6 - KINETICS OF NITROGEN PENTOXIDE   **12 POINTS**

Consider the following reaction (1):

$$2N_2O_5(g) \quad \rightleftharpoons \quad 4NO_2(g) \quad + \quad O_2(g) \tag{7}$$
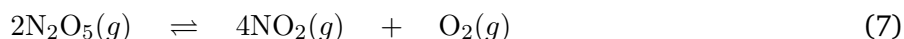
The proposed reaction mechanism of (1) consists of 3 different elementary reaction steps, equations (2) – (4):

$$N_2O_5 \quad \rightleftharpoons \quad NO_2 \quad + \quad NO_3 \tag{8}$$

$$NO_2 \quad + \quad NO_3 \rightarrow \quad NO_2 \quad + \quad O_2 \quad + \quad NO \tag{9}$$

$$NO \quad + \quad NO_3 \quad \rightarrow \quad 2NO_2 \tag{10}$$

Note that NO_2 serves as necessary collision partner in (3) and therefore cannot simply be canceled out of the equation.

a) Write down the rate law for $[N_2O_5]$

b) Write down the rate law for $[NO]$ and apply the steady state approximation to find a simplified expression for $[NO]$.

c) Write down the rate law for $[NO_3]$ and apply the steady state approximation to find a simplified expression for $[NO_3]$

d) Use your result from b.) to simplfy the equation derived in c.)

e) Finally, use your result in d.) to simplfy the rate law for $[N_2O_5]$ derived in a.) also, give the expected reaction orders in $[NO]$, $[NO_2]$, $[NO_3]$ and $[N_2O_5]$.

PROBLEM 7 - STRUCTURE ANALYSIS VIA NMR   17 POINTS

In this problem we will discuss two compounds, **X** and **Y**. Both compounds have the sum formula $C_5H_{10}O_2$, and contain a strong peak in the IR spectrum in the region of $1750\,\text{cm}^{-1}$.

   a) Using the given information from the IR-spectrum, which structural unit or functional group is present in both molecules?

   b) How many double bonds or rings will a molecule with the sum formula $C_5H_{10}O_2$ contain?

The 1H-NMR spectra of compounds X and Y are given on the next page, using them answer the following questions:

   a) By analyzing the peak integrals and their fine structure (multiplicity) note down all fragments you can clearly identify for both substances.

   b) By making use of the peak position (i.e. the chemical shift) assemble the fragments in the correct manner to give the structure of both **X** and **Y**.
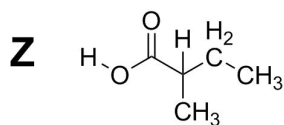
Compound X
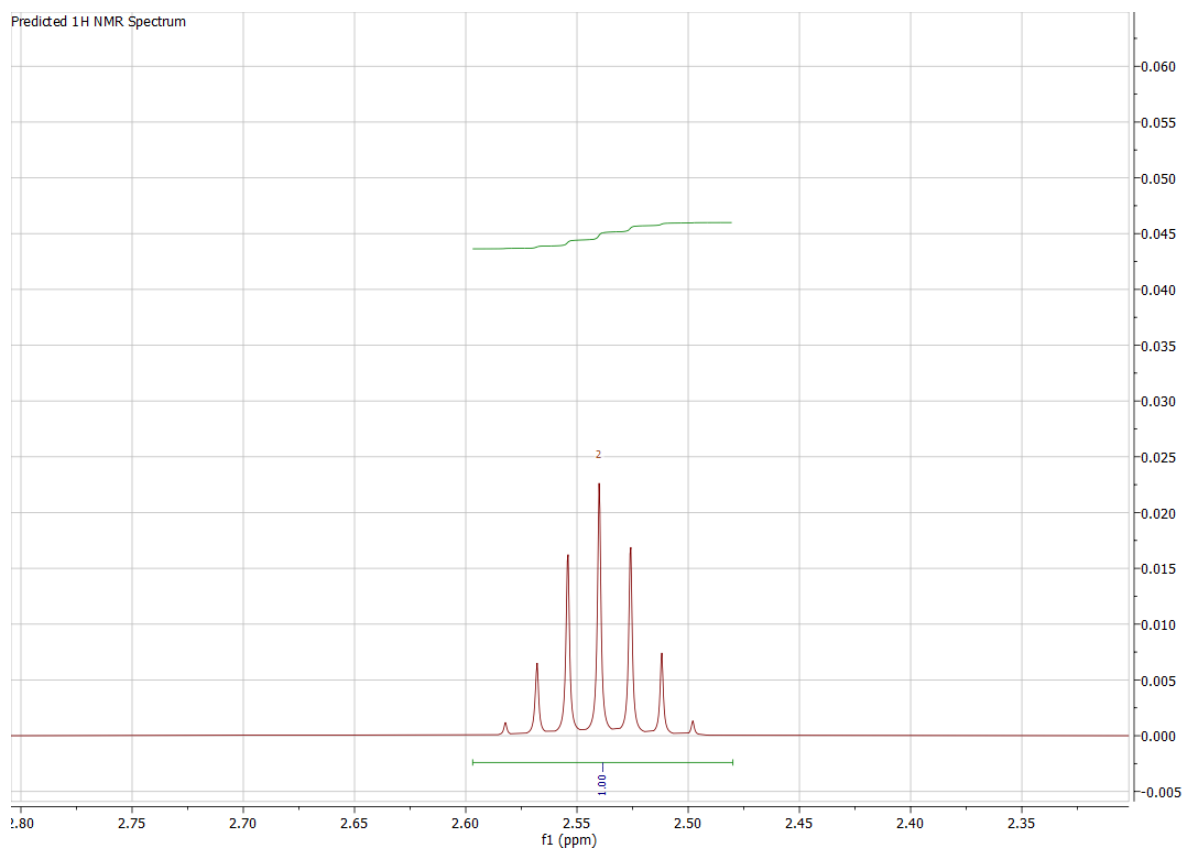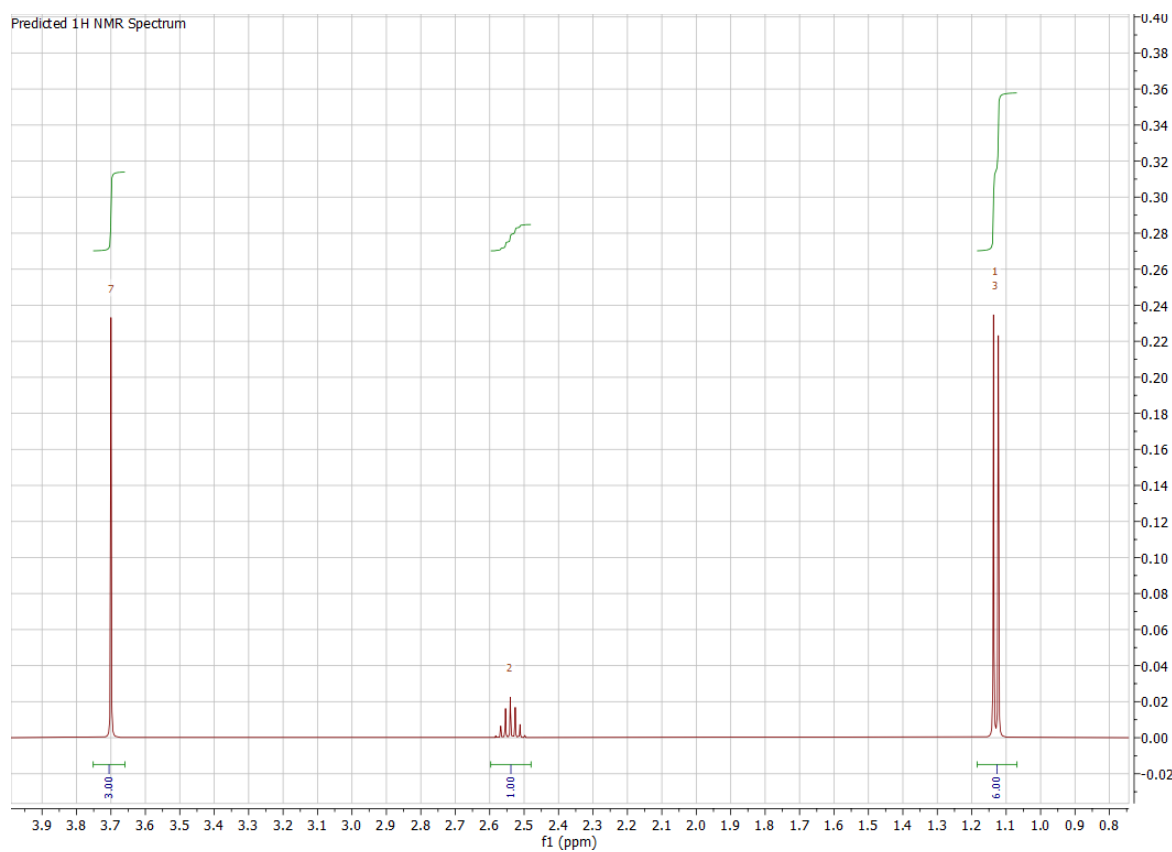
Compound Y
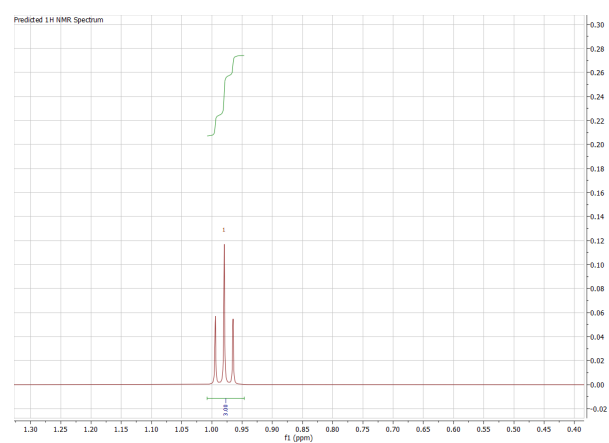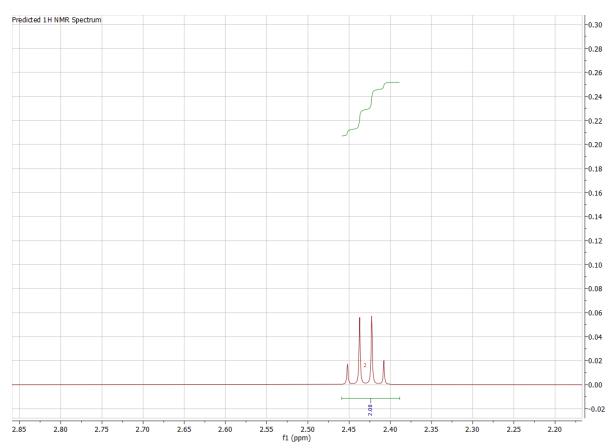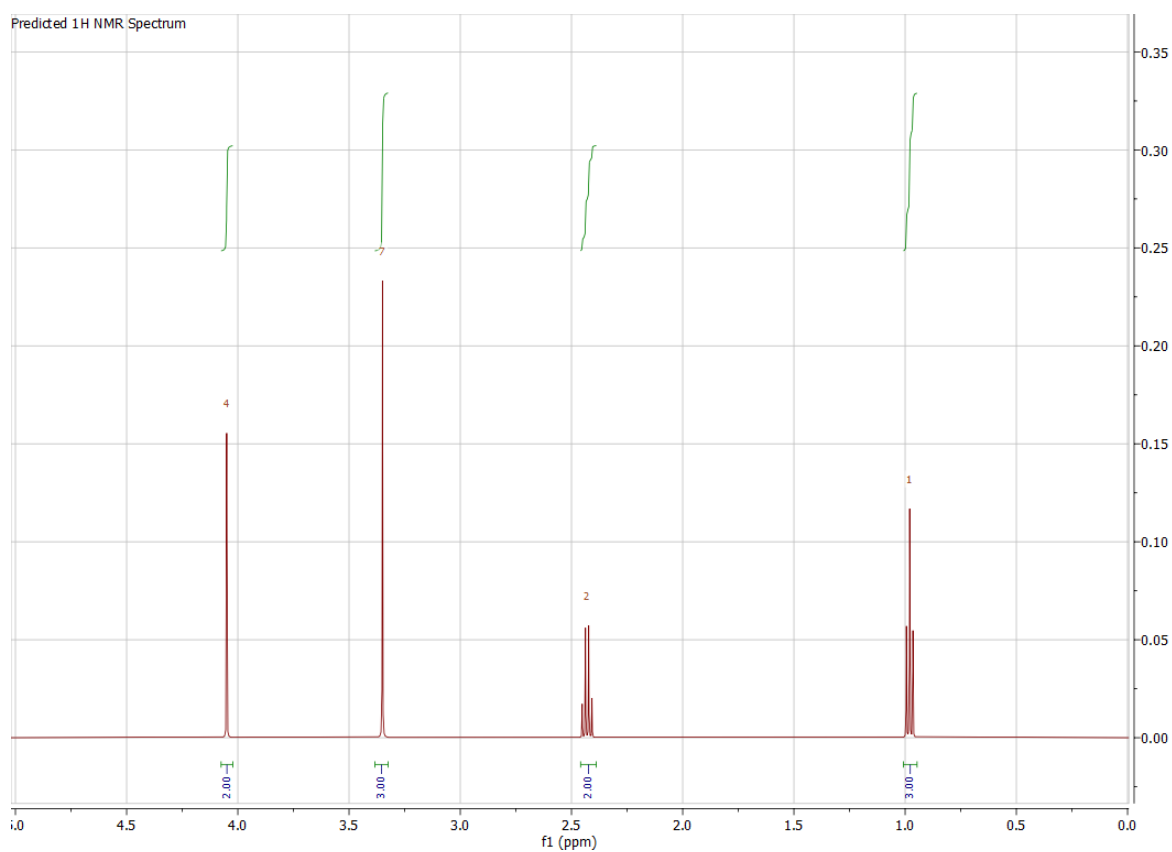
Shown below is yet another molecule of the same sum formula, compound **Z**.

c) Label the different hydrogen atoms clearly with **1-5** and then fill in the following table:

Number	Integral	Multiplicity
1		
2		
3		
4		
5		

d) **Z** contains a chiral center. Is it possible to find out, if a sample of **Z** is enantiopure only with a simple ^{1}H-NMR measurement?

PROBLEM 8 - ORGANIC RIDDLE   **16 POINTS**

Coniferol, a component in lignin, has the molecular formula $C_{10}H_{12}O_3$. It is not soluble in water or aqueous $NaHCO_3$.

Bromine dissolved in $CHCl_3$ will discolor forming compound **A**, $C_{10}H_{12}O_3Br_2$, when being added to Coniferol.

Reductive ozonolysis of Coniferol produces vanillin (4-hydroxy-3-methoxybenzaldehyde) and compound **B** ($C_2H_4O_2$).

Coniferol and excess benzoyl chloride (C_6H_5COCl) react under basic conditions to form compound **C**. This compound quickly discolors $KMnO_4$ (aq) and is insoluble in dilute sodium hydroxide solution.

Hot HI converts ArOR into ArOH and RI, furthermore hot HI can result in the substitution of activated alcohols. Addition of hot HI to coniferol results in the formation of **D** ($C_8H_9O_2I$) and MeI.

In aqueous basic solutions of CH_3I, coniferol will form compound **E** ($C_{11}H_{14}O_3$) that is insoluble in strong bases but will discolor a $Br_2/CHCl_3$ solution.

The following signals can be observed in the ^{1}H-NMR spectrum of Coniferol: 7.20 (1H, d), 6.94, (1H, d), 6.86 (1H, S), 6.37 (1H, d), 6.14 (1H, m), 5.71 (1H, s) 4.36 (2H, m) 3.80 (3H, s), 2.58 (1H, t). The signals at 2.58 and 5.71 disappear upon addition of D_2O.

   a) Draw the structures of Coniferol and compounds **A, B, C, D** and **E**.

   b) There are multiple stereoisomers of compound **A**. Draw the Fischer projection of every possible isomer and denote all of the stereocenters with R or S. Hint: if you were not able to find the full structure of **A**, you can work with partial structures and use abbreviations for missing residues.
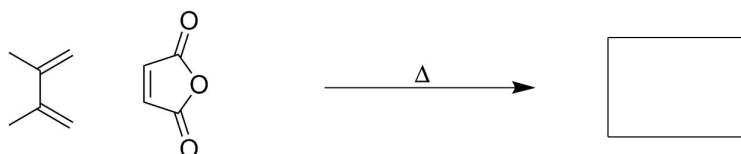
PROBLEM 9 - PERICYCLIC REACTIONS   **12 POINTS**
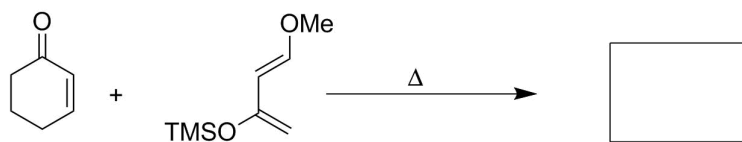
Part I - The Diels Alder reaction
Disregard the stereochemistry in the products in this part.
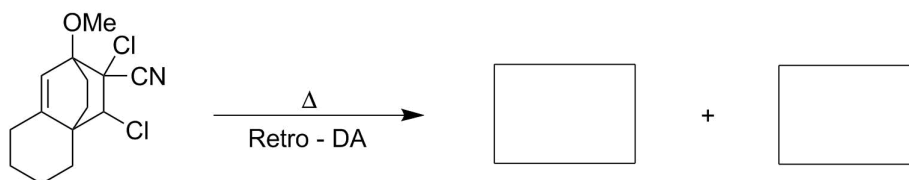
   a) Give the product of the following reaction.

   b) Draw the FMO diagrams for the reacion in a.)

   c) Give the product of the following reaction.

   d) In c.), one of the two possible regioisomers of the product is formed preferentially. Give a possible explanation for this.

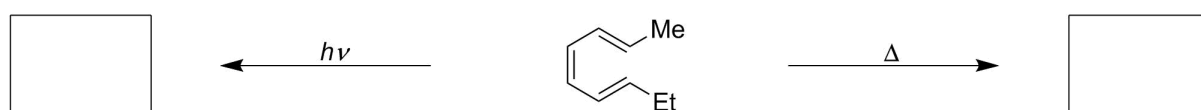   e) Give both products that are formed during this retro - Diels Alder reaction.

Part II - Electrocyclisations
Include the relevant stereochemistry in your answers for the following questions !
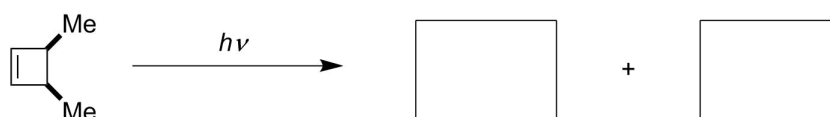
f) Give the products obtained under thermal and under photochemical conditions.
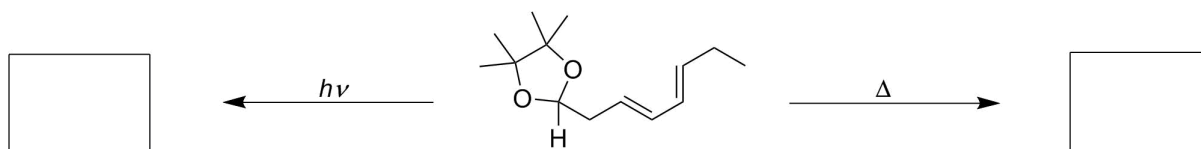
g) Give the products obtained under thermal and under photochemical conditions.

h) Give the products obtained under photochemical conditions.

i) in h.) one of the two possible products is formed preferentially. Suggest a possible explanation for this phenomenon.

PROBLEM 10 - TOTAL SYNTHESIS OF VARENICLIN   **15 POINTS**

Vareniclin is a drug used as an aid to quit smoking. It works by acting on the same receptors as nicotine. As a partial agonist of these nicotine-receptors it partially stimulates the receptors, resulting in fewer withdrawal symptoms. Vareniclin furthermore lowers the effects of externally added nicotine.
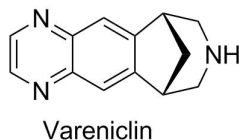
Vareniclin

The synthesis of Vareniclin starts with commercially available 1,2-dibromobenzene:
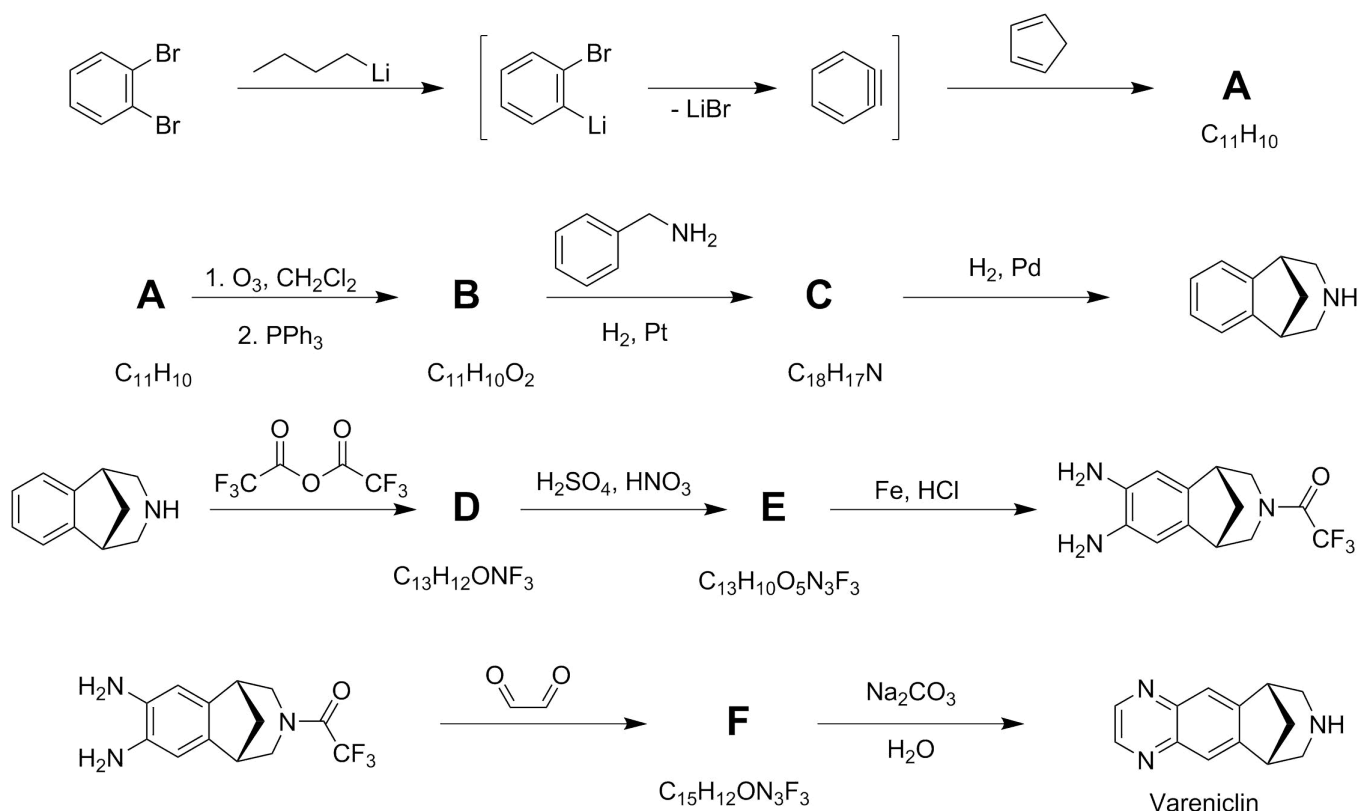
a) Draw the structures of the missing intermediates **A, B, C, D, E** and **F**.

b) How is the reaction called, that leads to molecule **A**?

c) What type of reaction leads to **E** from **D**?

d) Is one of the carbon atoms in Vareniclin optically active (chiral)? If yes mark it with an asterisk.