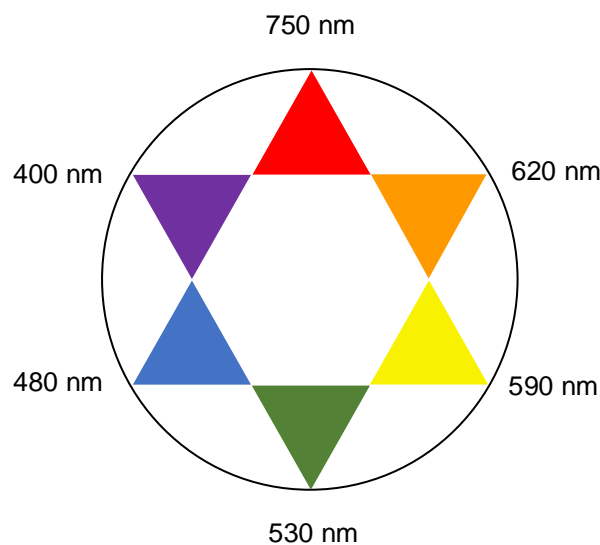


## General instructions

- This practical exam booklet contains **29** pages.
- You may begin working as soon as the **START** command is given.
- You have **5 hours** to complete the exam.
- All results and answers must be clearly written **with a pen into their respective boxes** on the exam papers. **Answers written outside the answer boxes will not be graded.**
- Do not use a pencil or a marker to write the answers. These results will not also be graded.
- You are allowed to use a calculator.
- You are provided with 3 sheets of draft paper. If you need more, use the backside of the exam sheets.
- **The official English version** of the exam booklet is available upon request and serves for clarification only.
- If you need to leave the exam room (to use the toilet or have a drink or a snack), tell the supervisor assistant. He or she will come to accompany you.
- The supervisor will announce when the last 30 minutes are left.
- You must stop your work immediately when the **STOP** command is announced. Failure to stop working or writing will lead to the nullification of your practical exam.
- After the **STOP** command has been given, the supervisor will come to sign your answer sheet. After you and lab assistant has signed the booklet, put it back to the envelope and leave it to your work area.

## Visible light

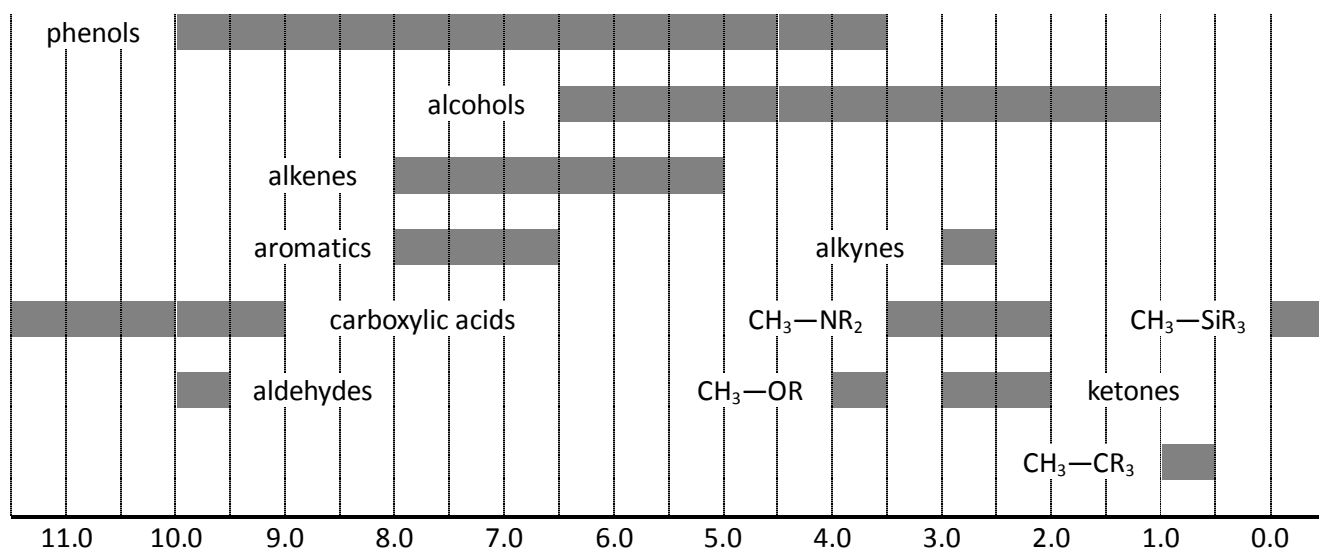


## Periodic table

1 H 1.008																	18 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	3	4	5	6	7	8	9	10	11	12	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 -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

## $^1\text{H}$ NMR chemical shifts (in ppm/TMS)





## Physical constants and equations

Avogadro's constant:  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Universal gas constant:  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Speed of light:  $c = 2.998 \times 10^8 \text{ m s}^{-1}$

Planck's constant:  $h = 6.626 \times 10^{-34} \text{ J s}$

Faraday constant:  $F = 9.6485 \times 10^4 \text{ C mol}^{-1}$

Standard pressure:  $p = 1 \text{ bar} = 10^5 \text{ Pa}$

Normal (atmospheric) pressure:  $p_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa}$

Zero of the Celsius scale:  $273.15 \text{ K}$

Mass of electron:  $m_e = 9.109 \times 10^{-31} \text{ kg}$

Unified atomic mass unit:  $u = 1.6605 \times 10^{-27} \text{ kg}$

Ångström:  $1 \text{ Å} = 10^{-10} \text{ m}$

Electronvolt:  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

Watt:  $1 \text{ W} = 1 \text{ J s}^{-1}$

Ideal gas equation:  $pV = nRT$

The first law of thermodynamics:  $\Delta U = q + W$

Power input for electrical device:  $P = UI$

where  $U$  is voltage and  $I$  electric current

Enthalpy:  $H = U + pV$

Gibbs free energy:  $G = H - TS$

$$\Delta G^\circ = -RT \ln K = -zFE_{\text{cell}}^\circ$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Reaction quotient  $Q$

for a reaction  $a A + b B \rightleftharpoons c C + d D$ :

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Entropy change:

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

Heat change

where  $q_{\text{rev}}$  is heat for the reversible processfor temperature-independent  $c_m$ :

$$\Delta q = n c_m \Delta T$$

where  $c_m$  is molar heat capacity

Van 't Hoff equation:

$$\frac{d \ln K}{dT} = \frac{\Delta_r H_m}{RT^2} \Rightarrow \ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta_r H_m}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Nernst–Peterson equation:

$$E = E^\circ - \frac{RT}{zF} \ln Q$$

Energy of a photon:

$$E = \frac{hc}{\lambda}$$

Relation between  $E$  in eV and in J:

$$E/\text{eV} = \frac{E/\text{J}}{q_e/\text{C}}$$

Lambert–Beer law:

$$A = \log \frac{I_0}{I} = \epsilon l c$$

Wavenumber:

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

Reduced mass  $\mu$  for a molecule AX:

$$\mu = \frac{m_A m_X}{m_A + m_X}$$

Energy of harmonic oscillator:

$$E_n = h\nu \left( n + \frac{1}{2} \right)$$

Arrhenius equation:

$$k = A e^{-\frac{E_a}{RT}}$$

Rate laws in integrated form:

Zero order:

$$[\text{A}] = [\text{A}]_0 - kt$$

First order:

$$\ln[\text{A}] = \ln[\text{A}]_0 - kt$$

Second order:

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt$$

## Problem 1. Iron complexes (9%)

Iron – element that makes up the greatest part of Earth by mass ((34.6 %), also constitutes 4.65 % of Earth's crust. It has been used in the production of various tools. Also, iron complex compounds have been used as pigments. Depending on the pH of the aqueous solution,  $\text{Fe}^{3+}$  ions can form octahedral complexes which differ in colour. Iron(III) ions containing salt was dissolved in concentrated acid, and the pH of the solution was slowly increased by adding NaOH solution dropwise. During adding of NaOH solution, there was a gradual changing in the colour of the solutions as shown in the table below:

pH	The colour of the solution	Complex
Increase ↓	Pale violet	<b>A</b>
	Yellow	<b>B</b>
	Green	<b>C</b>

- a) Write the formulas of the complexes **A**, **B** and **C**. If **A**, **B**, **C** isomers exist, provide their structures.

<b>A</b>	<b>B</b>	<b>C</b>
Isomers		

- b) Provide the equations of formation of **B** from complex **A** and **C** from complex **B**.

<b>B</b>
<b>C</b>

- c) At high pH value,  $\text{Fe}^{3+}$  ions almost could not be found in solution, because brown solid substance **D** is formed. Provide formula of substance **D**.

<b>D</b>
----------



According to the magnetic measurements, it was stated that  $[\text{Fe}(\text{CN})_6]^{3-}$  ion has one unpaired electron, while  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  more than one.

d) Draw crystal field diagrams for both complexes.

$[\text{Fe}(\text{CN})_6]^{3-}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
---------------------------------	--

e) Circle the correct answer:

i)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is      A) Paramagnetic      B) Diamagnetic

ii)  $[\text{Fe}(\text{CN})_6]^{3-}$  is      A) Paramagnetic      B) Diamagnetic

It is very common, that iron ions interfere analysis of the other ions. In order to prevent interference of  $\text{Fe}^{2+}$  ions, sodium oxalate is added to the solution.  $\text{Fe}^{2+}$ , combined with oxalate ions, make a very stable octahedral complex (stability constant  $K = 1.7 \cdot 10^5$ ). Equal volumes of solution, where the concentration of  $\text{Fe}^{2+}$  ions is  $0.20 \text{ g/dm}^3$ , and solution of  $0.20 \text{ mol/dm}^3 \text{ Na}_2\text{C}_2\text{O}_4$  were mixed.

f) Find pH of the  $0.20 \text{ mol/dm}^3$  concentration sodium oxalate solution (oxalic acid's  $\text{p}K_{a1} = 1.27$ ;  $\text{p}K_{a2} = 4.27$ ).



- g) Calculate the percentage of free  $\text{Fe}^{2+}$  ions remaining in the solution after mixing equal volumes of  $0.20 \text{ g/dm}^3 \text{ Fe}^{2+}$  and  $0.20 \text{ mol/dm}^3 \text{ Na}_2\text{C}_2\text{O}_4$  solutions.

**Hint:** because  $\text{C}_2\text{O}_4^{2-}$  concentration is relatively high, you can assume, that complex formation does not affect it.

$[\text{Fe}(\text{SCN})_6]^{3-}$  solution shows strong absorbance at  $\lambda = 490 \text{ nm}$ . This characteristic is used for iron concentration's determination by absorption spectrophotometry in white wine.  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ , and  $\text{KSCN}$  are added into wine. Then absorption is measured.

- h) Provide a Lewis dot structure for  $\text{SCN}^-$  ion. If resonance structures exist, provide them as well.

- i) What colour the solution of  $[\text{Fe}(\text{SCN})_6]^{3-}$  will be? Circle the correct answer.  
A) bluish purple;      B) greenish blue;  
C) colourless;      D) yellowish orange.
- j) Why are  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  added into wine? Answer by writing net ionic equation/equations for appropriate reaction/reactions.



It was determined that 100,0 g of compound  $X_y[Fe(CN)_6]_z$  contain 45.50 g of iron.

- k)** Find the element **X** and write down the formula of the compound. Show your calculation.



## Problem 2. $\text{CaCO}_3$ in nature and laboratory (10%)

When solving this problem, you will need thermodynamic data from the table below. Assume that all gases and solutions are ideal, and enthalpy change of all reactions are temperature independent.

Thermodynamic data at 298 K temperature and 1 bar pressure.

	$\Delta_f H^\circ / \text{kJ/mol}$	$\Delta_f G^\circ / \text{kJ/mol}$	$S^\circ / \text{J}/(\text{mol}\cdot\text{K})$
$\text{CaO(s)}$	-635.1	-604.0	39.7
$\text{Ca}^{2+}(\text{aq})$	-542.8	-553.6	-53.1
$\text{Ca(OH)}_2(\text{s})$	-986.1	-898.5	83.4
$\text{CaCO}_3(\text{s, calcite})$	-1206.9	-1128.8	92.9
$\text{CaCO}_3(\text{s, aragonite})$	-1207.1	-1127.7	88.7
$\text{CO}_2(\text{g})$	-393.5	-394.4	213.7
$\text{H}_2\text{O(l)}$	-285.8	-237.2	69.9
$\text{OH}^-(\text{aq})$	-230.0	-157.2	-10.7

Calcium carbonate is found in nature in the form of several polymorphs: calcite, aragonite, vaterite, ikaite. First three polymorphs are anhydrous calcium carbonate. Ikaite is hydrated calcium carbonate – mineral, that is found in cold waters of Ikka Fjord in Greenland.

- a) When heated ikaite  $\text{CaCO}_3 \cdot x\text{H}_2\text{O}$  readily loses approximately 52% of its initial mass. Under the strong heating (1000 °C) it additionally loses approximately 21% of its initial mass. Determine number  $x$  in formula  $\text{CaCO}_3 \cdot x\text{H}_2\text{O}$ . Show your calculations.



- b)** Which polymorph – calcite or aragonite – is more stable at 298 K temperature and 1 bar pressure? Circle the correct answer.
- A) Calcite  
B) Aragonite
- c)** Calcium carbonate minerals are abundant in nature and cause the forming of hard water. Write the chemical equation that shows what is happening with calcium carbonate when hard water is formed.

- d)** Calculate equilibrium constant of the reactions  $\text{CaCO}_3(\text{s, calcite}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  at 25 °C.



- e) Calculate equilibrium constant of the reactions  $\text{CaCO}_3(\text{s, calcite}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  at 1070 K.

In the laboratory special tightly closed reactor with the possibility to heat samples of substance was constructed. This reactor was equipped with a special mechanism that gives the possibility to input samples of solid without any gas leakage. The volume of the reactor is  $5,0 \text{ dm}^3$ . In the beginning, the reactor was filled with argon ( $25 \text{ }^\circ\text{C}$ ,  $p=1.0 \text{ bar}$ ).

- f) Calculate pressure (in bars) in the reactor, when the temperature was increased till 1070 K

- g) Than five samples of calcite in consecutive order was introduces into the reactor. Mass of each sample was 1.0 g. Temperature all the time remains 1070 K. New sample of calcite was introduced only after establishing constant pressure in the reactor. Calculate final total gas pressure in the reactor after the introduction of each sample of calcite. Fill the table below and show your calculations.

	After 1 <sup>st</sup> 1.0 g sample	After 2 <sup>nd</sup> 1.0 g sample	After 3 <sup>rd</sup> 1.0 g sample	After 4 <sup>th</sup> 1.0 g sample	After 5 <sup>th</sup> 1.0 g sample
The total gas pressure in the reactor (in bars)					

Calculations

- i) Finally, the reactor was quickly cooled down to temperature 25 °C and flushed by argon gas to expel all carbon dioxide. A mixture of solid compounds from the reactor was transferred into the water. The final volume of the solution is 0.60 dm<sup>3</sup>. Calculate the pH of this solution (at 25 °C). Show your calculations.



A large empty rectangular box for writing answers.

### Problem 3. Colourful kinetics (10%)

Reactions between iodide ion and iron(III) ion as well as iodine and thiosulfate ion in aqueous solution are known to occur spontaneously.

- a)** Examine the given standard potentials and predict the products of the reactions
- i)** between  $\text{Fe}^{3+}$  and  $\text{I}^-$  as well as **ii)** between  $\text{I}_2$  and  $\text{S}_2\text{O}_3^{2-}$ . Show your calculations. Write and balance feasible reactions.  $E^\circ(\text{Fe}^{3+}/\text{Fe}) = -0.04 \text{ V}$ ;  $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}$ ;  $E^\circ(\text{FeO}_4^{2-}/\text{Fe}^{3+}) = +2.20 \text{ V}$ ;  $E^\circ(\frac{1}{2}\text{I}_2/\text{I}^-) = +0.54 \text{ V}$ ;  $E^\circ(\text{IO}_3^-/\frac{1}{2}\text{I}_2) = +1.20 \text{ V}$ ;  $E^\circ(\text{HOI}/\frac{1}{2}\text{I}_2) = +1.44 \text{ V}$ ;  $E^\circ(\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}) = +0.08 \text{ V}$ .

**i)**

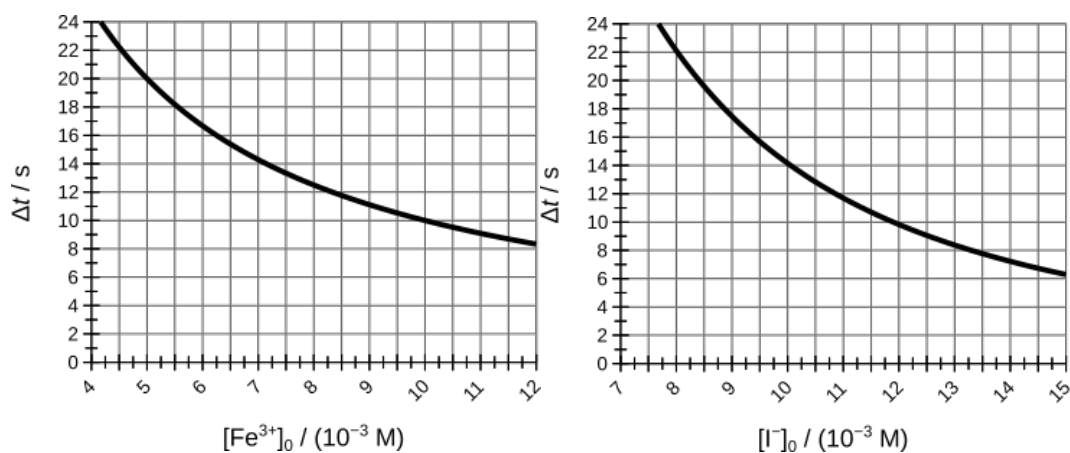
Reaction(s):

**ii)**

Reaction(s):

Oxidation of iodide by iron(III) ions in the presence of  $\text{S}_2\text{O}_3^{2-}$  ions and starch can run like a clock reaction. The reaction is started by mixing a solution of iron(III) nitrate with a solution containing thiosulfate, iodide, and starch. The solution immediately turns purple due to the formation of  $\text{Fe}(\text{S}_2\text{O}_3)^+$  complex. The colour gradually fades until the solution becomes colourless and then suddenly turns dark blue due to the formation of starch–pentaiodide complexes. The kinetics of the reaction between iodide and iron(III) can be studied by the initial rates method by measuring the time ( $\Delta t$ ) elapsed from the mixing of the two solutions to a sudden colour change. Under certain conditions, the initial reaction rate is inversely proportional to the measured

time:  $v_0 = [\text{S}_2\text{O}_3^{2-}]_0 / \Delta t$ . Two graphs given below were obtained measuring  $\Delta t$  after mixing solutions with different initial  $[\text{Fe}^{3+}]_0$  or  $[\text{I}^-]_0$  concentrations while keeping the concentration of all other components constant.



**b)** Show how to determine the reaction order in respect to **i)  $\text{Fe}^{3+}$**  and **ii)  $\text{I}^-$** , then calculate the half-life of  $[\text{Fe}^{3+}]$  in solution at experimental conditions.

**i)**

Order in respect to  $\text{Fe}^{3+}$ : \_\_\_\_\_

Half-life: \_\_\_\_\_

**ii)**

Order in respect to  $\text{I}^-$ : \_\_\_\_\_

Some experimental results are summarised in the table below:

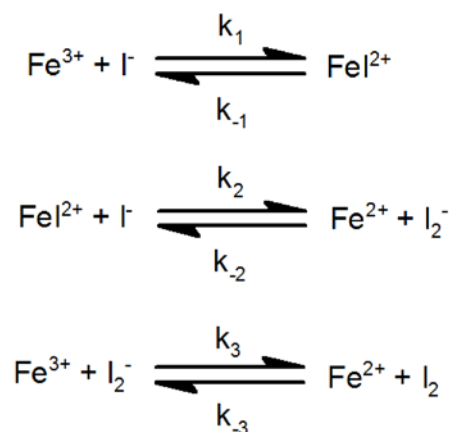
#	$[\text{Fe}^{3+}]_0$	$[\text{I}^-]_0$	$v_0 [\text{M s}^{-1}]$
1	0.09900	0.0744	0.008836



2	0.09900	0.0431	0.002978
3	0.04945	0.0960	0.007319
4	0.00118	0.0960	0.000175
5	0.00118	0.0607	0.000070
6	0.00118	0.0431	0.000035

c) Calculate the rate constant of the reaction.

The following reaction scheme was proposed to explain the mechanism of  $\text{Fe}^{3+}$  reduction by  $\text{I}^-$ :



d) Derive a rate equation for consumption of  $\text{Fe}^{3+}$  ( $-\text{d}[\text{Fe}^{3+}]/\text{d}t$ ) from the provided scheme, stating any reasonable assumptions made.



A large empty rectangular box for writing answers.



e) Conclude whether the provided experimental data confirm the proposed mechanism or not. Circle the correct answer:

A) Confirm

B) Do not confirm

## Problem 4. Some penguin chemistry (10%)

While in the rookery, Antarctic Adélie penguins may encounter intense solar radiation. Panting during severe heat stress can result in alternations of gas composition and acid-base balance in the blood of brooding adults. Let us examine how the temperature influences the pH by altering the  $\text{HCO}_3^-/\text{CO}_2(\text{aq})/\text{CO}_2(\text{g})$  equilibrium in which the level of  $\text{CO}_2$  is adjusted by respiration. The following data is available:  $\text{p}K_{\text{a}1}(38.5\text{ }^\circ\text{C}) = 6.07$ ,  $\text{p}K_{\text{a}1}(25\text{ }^\circ\text{C}) = 6.35$ ,  $\Delta H_{\text{vap}}(\text{CO}_2, \text{blood}) = 19.95\text{ kJ mol}^{-1}$  (enthalpy of vaporization),  $K_{\text{H}}(\text{CO}_2, 38.5\text{ }^\circ\text{C}) = 2.2 \cdot 10^{-4}\text{ mol m}^{-3}\text{Pa}^{-1}$  (solubility constant).



- a) Using the Henderson–Hasselbalch equation, calculate pH of the Adélie penguin blood at normal body temperature of  $38.5\text{ }^\circ\text{C}$  if  $[\text{HCO}_3^-] = 29,4\text{ mM}$  and  $p(\text{CO}_2) = 4.9\text{ kPa}$ .

pH =

- b) Calculate the values of  $\text{p}K_{\text{a}1}(40.7\text{ }^\circ\text{C})$  and  $K_{\text{H}}(\text{CO}_2, 40.7\text{ }^\circ\text{C})$ .

$\text{p}K_{\text{a}1}(40.7\text{ }^\circ\text{C}) =$



$$K_H(\text{CO}_2, 40.7 \text{ }^\circ\text{C}) =$$

- c) Estimate the pH of the Adélie penguin blood at critical body temperature of 40.7 °C assuming that the CO<sub>2</sub> pressure remains the same, and the concentration of HCO<sub>3</sub><sup>-</sup> depends on the pH as [HCO<sub>3</sub><sup>-</sup>] = (302.4 – 36.4·pH) mM.

pH =

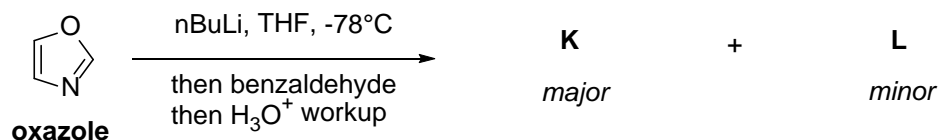
- d) Estimate the pH of the Adélie penguin blood at critical body temperature of 40.7 °C taking into account that due to hyperventilation  $p(\text{CO}_2)$  decreases to 1.5 kPa.

pH =

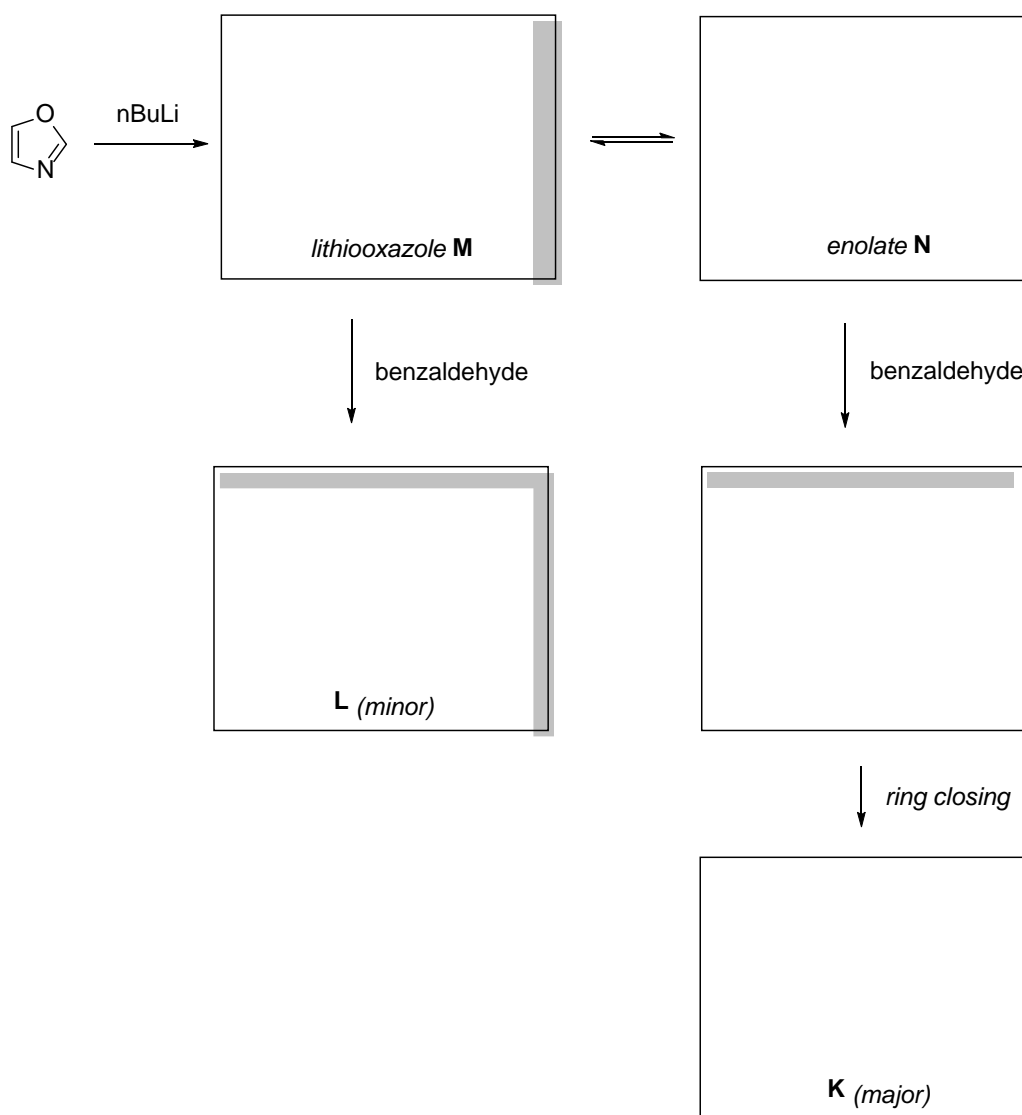
- e) Would you expect the described overheating to cause some of the following conditions? **Hint:** “hypo” and “hyper” originate from the Greek words meaning “below” and “above”, respectively. Circle the correct answers:
- A) Alkalosis                      C) Acidosis  
B) Hypocarbica                  D) Hypercarbica

## Problem 5. Lithiation gone wrong (11%)

One of the most popular methods for introducing substituents in heterocyclic compounds is lithiation and then subsequent alkylations, acylations, additions etc. The lithiation of oxazole is harder and produces two regioisomers after addition of benzaldehyde and sequential aqueous workup, where the minor isomer is the needed.



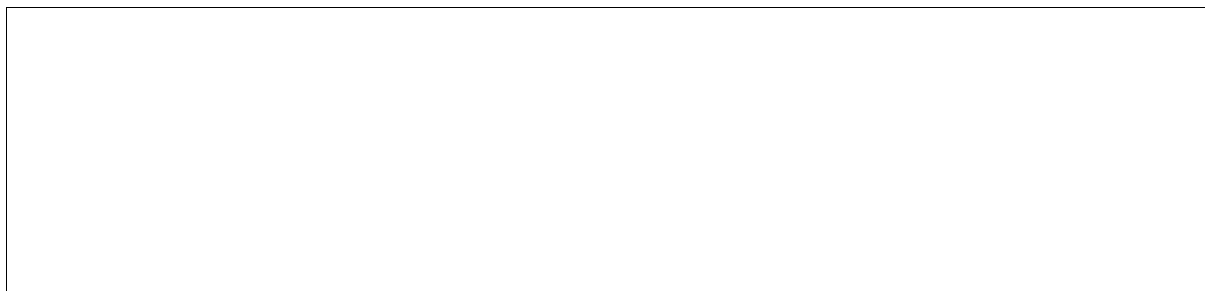
The reason for that is, when the oxazole has been lithiated in the most acidic position, the obtained lithiooxazole **M** is not stable and is in equilibrium with enolate **N**. Enolate **N** can attack benzaldehyde and after closing the ring, create the major addition product **K**.



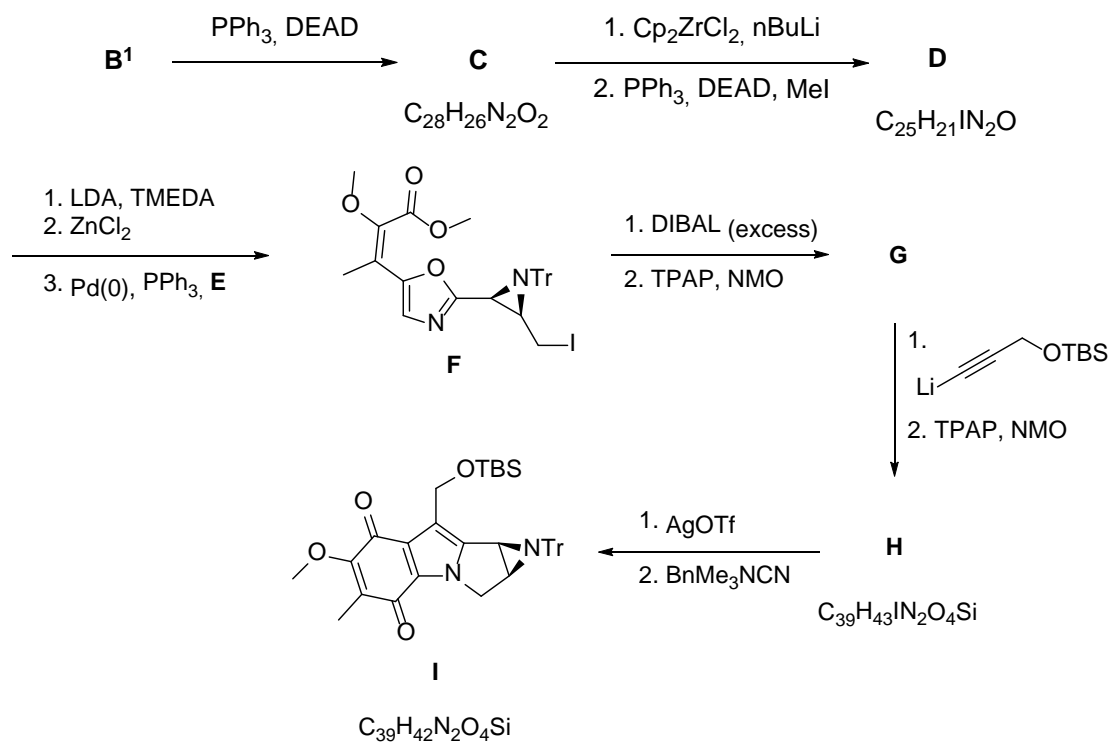
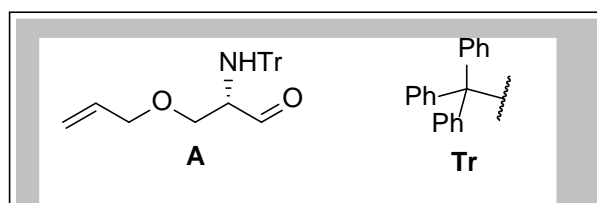
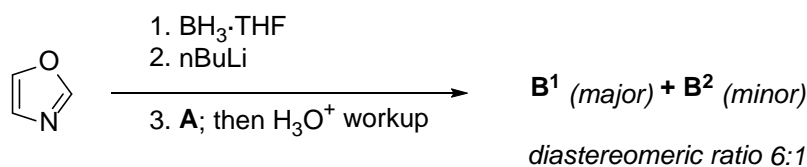
a) Draw all the structures in the empty boxes given above.

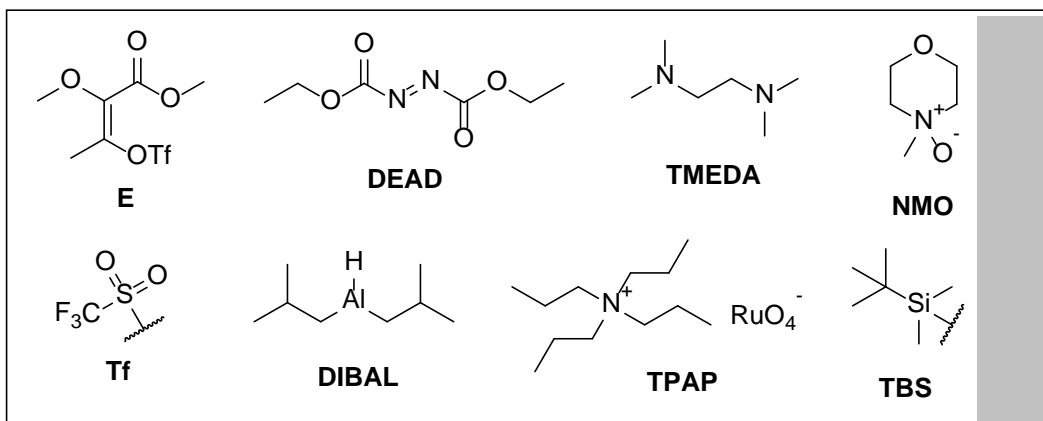
To overcome the unwanted selectivity, the addition of 1 equivalent of  $\text{BH}_3$  before lithiation is used.

b) Explain, drawing mechanism or structures, how  $\text{BH}_3$  might change the selectivity.



This method was used in an attempted synthesis of a synthetic product Aziridinomitosenone **A**, which has the same core structure as Mytomycins, natural compounds that possess interesting structure and antitumor activity. The synthesis starts with selective oxazole lithiation.





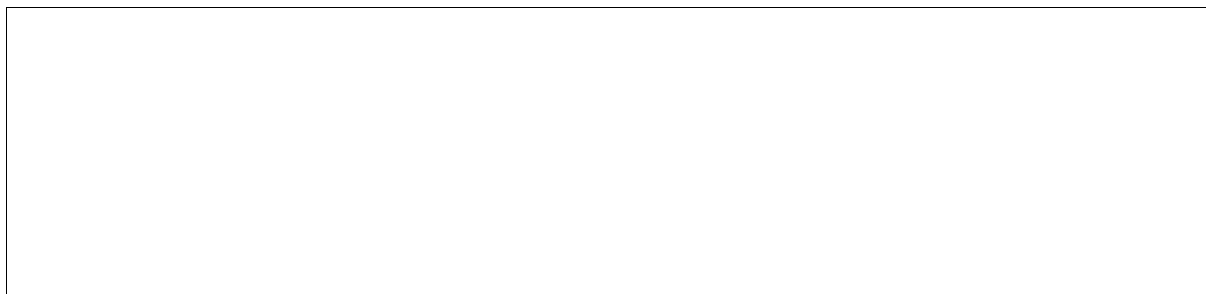
Note:  $\text{Cp}_2\text{ZrCl}_2$ , BuLi are allyl group deprotection conditions.

c) Draw structures **B<sup>1</sup>**, **B<sup>2</sup>**, **C**, **D**, **G**, **H** and indicate the stereochemistry.

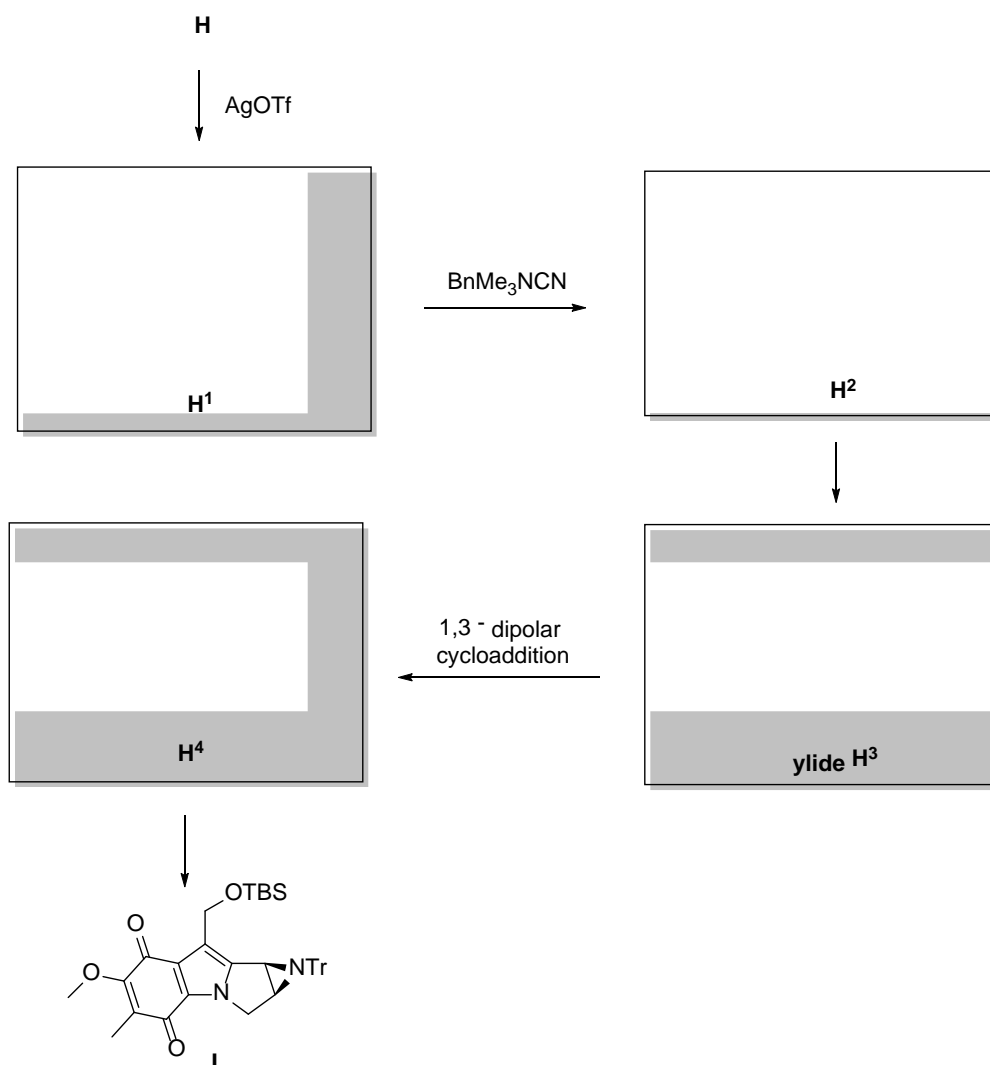
<b>B<sup>1</sup></b>	<b>B<sup>2</sup></b>
<b>C</b>	<b>D</b>
<b>G</b>	<b>H</b>



- d) Draw the mechanism for the transformation  $\mathbf{B}^1 \rightarrow \mathbf{C}$ . Feel free to use abbreviations and denote parts of the molecule, that do not participate in the mechanism.



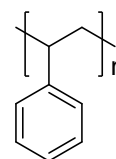
The reaction  $\mathbf{H} \rightarrow \mathbf{I}$  is a complex multi-step transformation. First AgOTf is added to  $\mathbf{H}$ , which creates ionic compound  $\mathbf{H}^1$  and a yellow salt. To  $\mathbf{H}^1$   $\text{BnMe}_3\text{NCN}$  is added, which is a source of cyanide anions and addition product  $\mathbf{H}^2$  is obtained, which reorganises to azomethine ylide  $\mathbf{H}^3$ . Ylide  $\mathbf{H}^3$  undergoes an intramolecular 1,3-dipolar cycloaddition reaction, forming  $\mathbf{H}^4$ , which subsequently gives  $\mathbf{I}$ .



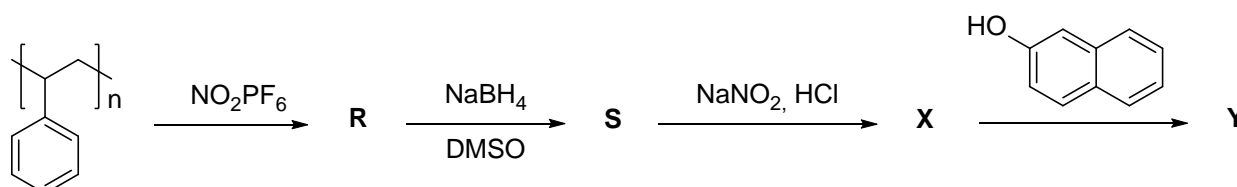
- e) Draw all the structures in the empty boxes given above.

## Problem 6. Deformed polymers (10%)

In order to change the colour of polystyrene (in a picture on the right side) one may use so-called polymer-analogous reactions, that alter only functional groups but leave alkyl chains unaffected. These sorts of reactions may also be useful in the synthesis of polymers that are impossible to make from monomers.

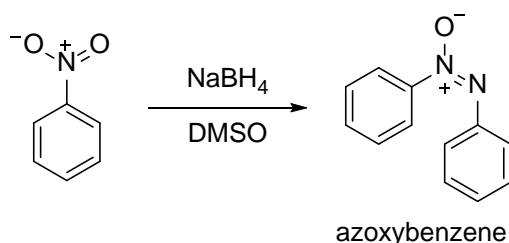


Let us look at one of the modifications that could be made with the polymer (scheme below).



a) Identify product **R** considering that not all benzenes are nitrated.

$\text{NaBH}_4$  is not good for reduction of aromatic nitro compounds, because of the formation of various side products, such as azoxybenzene:



Side products form due to the fact that reduction happens stepwise.

b) Identify product **S** and four other possible intermediates (**S**<sup>1</sup>, **S**<sup>2</sup>, **S**<sup>3</sup> and **S**<sup>4</sup>), knowing that **S** is fully reduced.

<b>S</b>	<b>S</b> <sup>1</sup>
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<b>S<sup>2</sup></b>	<b>S<sup>3</sup></b>
<b>S<sup>4</sup></b>	Free space

c) Which two intermediates lead to the formation of azoxybenzene? Circle the correct answers:

- A) **S<sup>1</sup>**      B) **S<sup>2</sup>**      C) **S<sup>3</sup>**      D) **S<sup>4</sup>**

d) What product is also formed in the reaction of azoxybenzene formation?

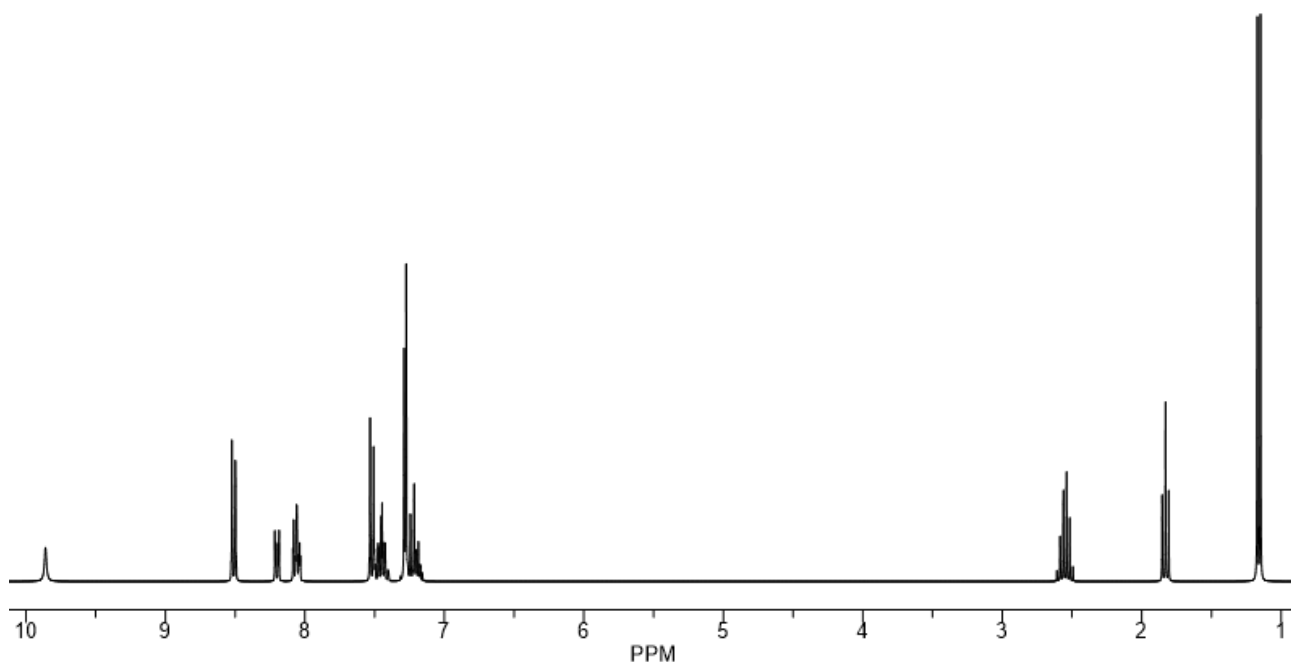
e) Azoxy-product is going to form at (circle the correct answer):

- A) high polystyrene concentrations  
B) low polystyrene concentrations

In case of a more convenient reduction of **R** (with hydrogen), polymer **P** was obtained. Titration of 1.000 g of **P** required 1.920 mL of 0.2000 M HCl.

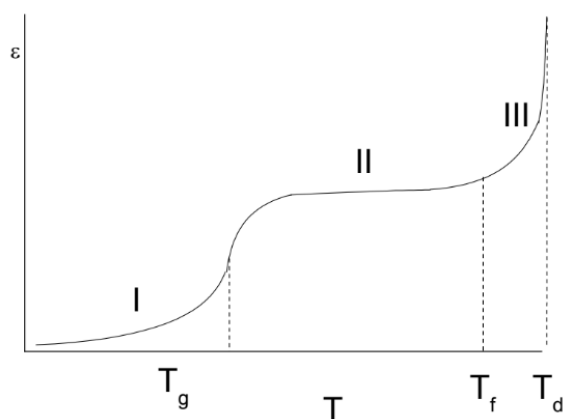
f) Calculate the percentage of nitrated benzene rings, considering that all reactions are quantitative.

g) Give the structures of **X** and **Y**, considering the  $^1\text{H}$  NMR spectrum of **Y**:



**Y**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.86 ppm (s), 8.51 (d), 8.20-8.05 (m), 7.52-7.43 (m), 7.27-7.19 (m), 2.58-2.53 (m), 1.89-1.83 (m), 1.16 (d)

<b>X</b>	<b>Y</b>



An important characteristic of mechanical properties of polymers is the dependence of equilibrium deformation  $\varepsilon$  on temperature  $T$ .  $\varepsilon$  describes straightening of polymer chains under calibrated stress. If polymer chains are mobile, then the sample has more developed equilibrium deformations. On the left, you can see the thermomechanical curve for polystyrene. At low temperatures polymer has small deformations (I). At the temperatures higher than  $T_g$  polymer becomes highly-elastic in which deformations are determined by the movement of segments of macromolecules (II), higher than  $T_f$  polymer becomes liquid and at the temperature  $T_d$  is decomposes.



- h)** Sketch thermomechanical curves and denote temperature for phase change on the same graph:
- i)** For nitrated polystyrene, reduced with excess  $\text{NaBH}_4$  at low polymer concentration (nitrated/non-nitrated = **5%**).
  - ii)** For nitrated polystyrene, reduced with excess  $\text{NaBH}_4$  at high polymer concentration (nitrated/non-nitrated = **5%**).
  - iii)** For nitrated polystyrene, reduced with excess  $\text{NaBH}_4$  at high polymer concentration (nitrated/non-nitrated = **15%**).

**Hint:**remember your answer to question **d**).