
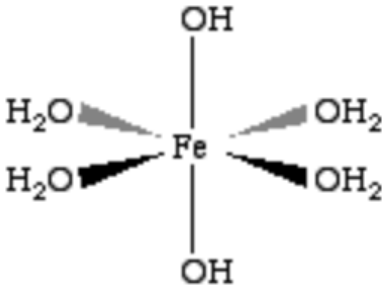
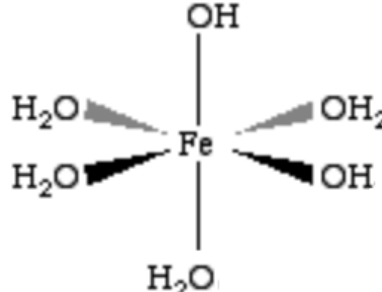


Problem 1. Iron complexes (9%)

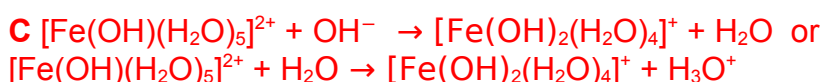
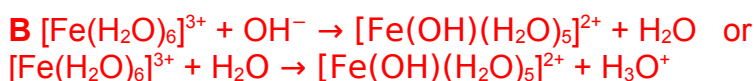
Iron – element that makes up the greatest part of Earth by mass ((34.6 %), also constitutes 4.65 % of Earth's crust. It has been used in the production of various tools. Also, iron complex compounds have been used as pigments. Depending on the pH of the aqueous solution, Fe^{3+} ions can form octahedral 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	A
	Yellow	B
	Green	C

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

A $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	B $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$	C $[\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4]^+$
Isomers <div style="display: flex; justify-content: space-around; align-items: center;">   </div>		

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

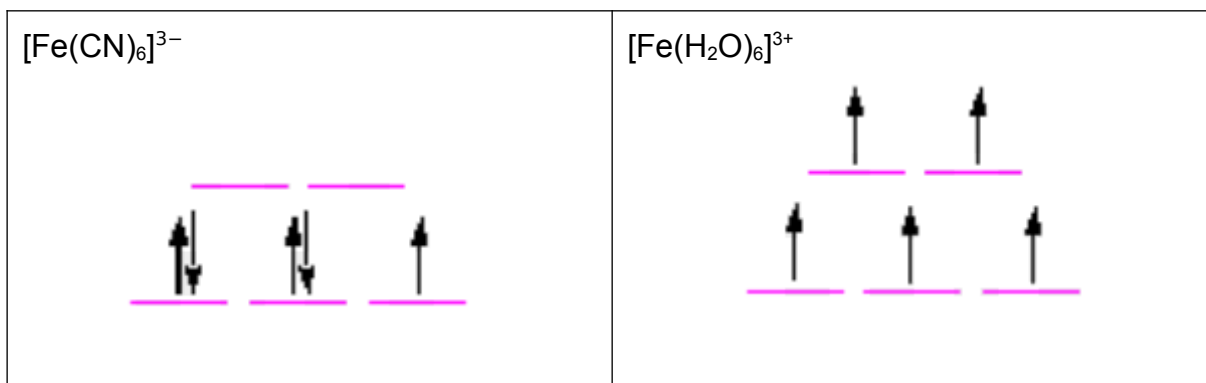


c) At high pH value, Fe^{3+} ions almost could not be found in solution, because brown solid substance **D** is formed. Provide formula of substance **D**.



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.



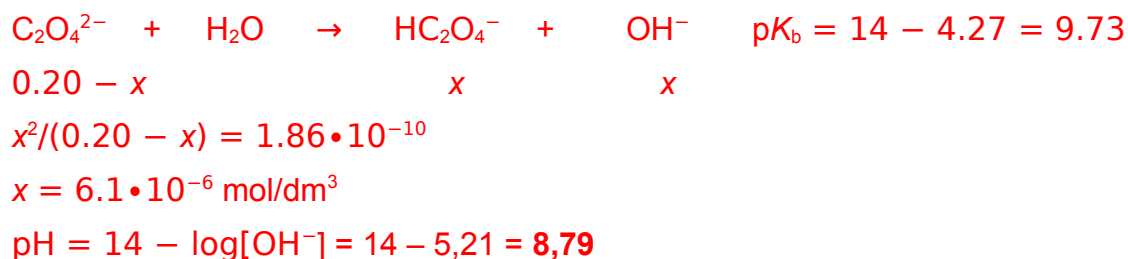
e) Circle the correct answer:

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

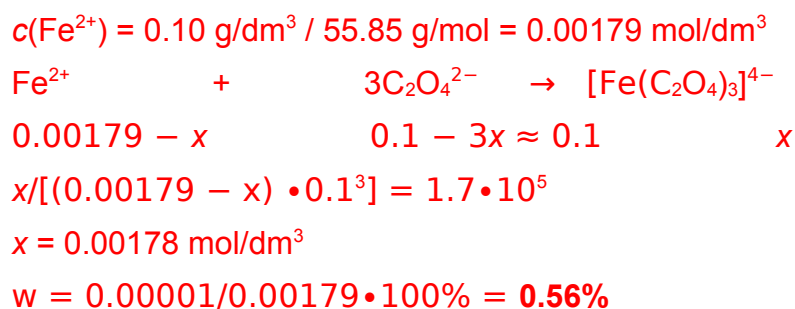
It is very common, that iron ions interfere analysis of the other ions. In order to prevent interference of Fe^{2+} ions, sodium oxalate is added to the solution. Fe^{2+} , combined with oxalate ions, make a very stable octahedral complex (stability constant $K = 1.7 \cdot 10^5$). Equal volumes of solution, where the concentration of Fe^{2+} ions is 0.20 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 mol/dm^3 concentration sodium oxalate solution (oxalic acid's $\text{pK}_{a1} = 1.27$; $\text{pK}_{a2} = 4.27$).



g) Calculate the percentage of free 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.

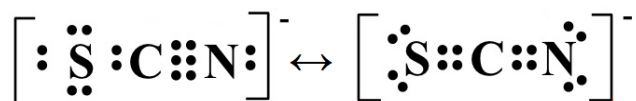
Hint: because $\text{C}_2\text{O}_4^{2-}$ concentration is relatively high, you can assume, that complex formation does not affect it.



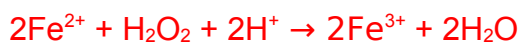
$[\text{Fe}(\text{SCN})_6]^{3-}$ solution shows strong absorbance at $\lambda = 490 \text{ nm}$. This characteristic is

used for iron concentration's determination by absorption spectrophotometry in white wine. H_2O_2 , HNO_3 , and KSCN are added into wine. Then absorption is measured.

- h) Provide a Lewis dot structure for 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 H_2O_2 and 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 $\text{X}_y[\text{Fe}(\text{CN})_6]_z$ contain 45.50 g of iron.

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

$$n(\text{Fe}) = 45.50 \text{ g} / 55.845 \text{ g/mol} = 0.8148 \text{ mol}$$

$$\text{If all Fe is in inner coordination sphere, then } n(\text{CN}) = 6 \cdot 0.8148 = 4.889 \text{ mol}$$

$$m(\text{CN}) = 4.889 \text{ mol} \cdot 26.02 \text{ g/mol} = 127.21 \text{ g}$$

That means that assumption that all Fe is in the inner coordination sphere is wrong. So element **X** can only be **iron**.

So the substance is $\text{Fe}_A(\text{CN})_B$

$$m(\text{CN}) = 100 - 45.50 = 54.50 \text{ g}$$

$$n(\text{CN}) = 54.50 \text{ g} / 26.02 \text{ g/mol} = 2.095 \text{ mol}$$

$$n(\text{Fe}) : n(\text{CN}) = 0.8148 : 2.095 = 1 : 2.571 = 7 : 18$$

In complex $\text{Fe}_y[\text{Fe}(\text{CN})_6]_z$, $z = 3$, $y = 4$.



Problem 2. 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.

	$\Delta_f H^\circ / \text{kJ/mol}$	$\Delta_f G^\circ / \text{kJ/mol}$	$S^\circ / \text{J/(mol}\cdot\text{K)}$
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.

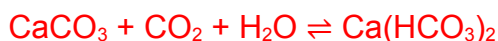
$100 \text{ g CaCO}_3 \cdot x\text{H}_2\text{O} - 52 \text{ g of water} \rightarrow 48 \text{ g CaCO}_3 - 21 \text{ g of CO}_2 \rightarrow 27 \text{ g CaO}$
 $n(\text{CaCO}_3) = 48 \text{ g} / 100 \text{ g/mol} = 0,48 \text{ mol}$
 $M(\text{CaCO}_3 \cdot x\text{H}_2\text{O}) = 100 \text{ g} / 0,48 \text{ g/mol} \approx 208 \text{ g/mol}$
 $m(\text{H}_2\text{O}) = 208 \text{ g} - 100 \text{ g} = 108 \text{ g}$
 $x = 108 \text{ g} / 18 \text{ g/mol} = 6 \text{ mol}$
 $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$

- 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.

$$\Delta G^\circ = [-394.4 - 604,0 + 1128,8] \text{ kJ/mol} = 130,4 \text{ kJ/mol}$$

$$K_{298} = \exp(-\Delta G^\circ/RT) = 1.39 \cdot 10^{-23}$$

- 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.

$$\Delta H^\circ = [-393.5 - 635,1 + 1206.9] \text{ kJ/mol} = 178,3 \text{ kJ/mol}$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$K_{1070} = 0.50$$

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 dm³. In the beginning, the reactor was filled with argon (25 °C, $p = 1.0$ bar).

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

$$p_1/T_1 = p_2/T_2$$

$$p_2 = 1 \text{ bar} \cdot 1070 \text{ K} / 298 \text{ K} = 3.59 \text{ bar}$$

- 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 st 1.0 g sample	After 2 nd 1.0 g sample	After 3 rd 1.0 g sample	After 4 th 1.0 g sample	After 5 th 1.0 g sample
The total gas pressure in the reactor (in bars)	3.77	3.95	4.09	4.09	4.09



$$a(\text{CaCO}_3) = 1 \text{ and } a(\text{CaO}) = 1$$

$$K = p(\text{CO}_2)$$

Max pressure of CO_2 in the reactor can be $0.50 \text{ bar} = 5.0 \cdot 10^4 \text{ Pa}$

$n(\text{CO}_2)$ necessary for establishing this pressure is:

$$pV = nRT \Rightarrow n = 5.0 \cdot 10^4 \text{ Pa} \cdot 0.0050 \text{ m}^3 / 8.314 \text{ J/(mol} \cdot \text{K)} \cdot 1070 \text{ K} = 0.0281 \text{ mol}$$

Max amount of CaCO_3 that could decompose in the reactor is 0.0281 mol. Mass of this amount is 2,81 g.

1st and 2nd samples decompose completely. After introduction 3rd, 4th and 5th samples partial pressure of CO_2 will be 0,50 bar.

Total pressure of gases will be $0.50 \text{ bar} (\text{CO}_2) + 3.59 \text{ bar} (\text{Ar}) = \mathbf{4.09 \text{ bar}}$

1st sample decomposes completely and gives 0.010 mol of CO_2 .

$$p = nRT/V = 0.010 \text{ mol} \cdot 8.314 \text{ J/(mol} \cdot \text{K)} \cdot 1070 \text{ K} / 0,0050 \text{ m}^3 = 1.78 \cdot 10^4 \text{ Pa}$$

$$p = 0.178 \text{ bar}$$

Total pressure of gases will be $0.178 \text{ bar} (\text{CO}_2) + 3.59 \text{ bar} (\text{Ar}) = \mathbf{3.77 \text{ bar}}$

2nd sample also decomposes completely and creates $2 \cdot 0.178 \text{ bar} = 0.356 \text{ bar}$

Total pressure of gases will be $0.356 \text{ bar} (\text{CO}_2) + 3.59 \text{ bar} (\text{Ar}) = \mathbf{3.95 \text{ bar}}$

- 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^3 . Calculate the pH of this solution (at 25°C). Show your calculations.

Amount of CaCO_3 that was decomposed (and amount of CaO that was formed) is 0.0281 mol



Ca(OH)_2 is moderately soluble. We need to check if all Ca(OH)_2 was able to dissolve.

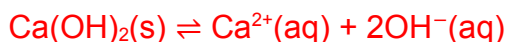
For this we need to calculate equilibrium constant for the reaction:



$$\Delta G^\circ = [-157.4 \cdot -553.6 + 898.5] \text{ kJ/mol} = 30.4 \text{ kJ/mol}$$

$$K = \exp(-\Delta G^\circ/RT) = \mathbf{4.65 \cdot 10^{-6}}$$

$$K = [\text{Ca}^{2+}][\text{OH}^{-}]^2$$



$$\begin{array}{ccc} -x & +x & +2x \end{array}$$

$$K = x \cdot 2x^2 = 4.65 \cdot 10^{-6}$$

$x = 0.0105 \text{ mol/dm}^3$ (max concentration)

$0.0105 \text{ mol/dm}^3 \cdot 0.60 \text{ dm}^3 = 0.00631 \text{ mol}$ of Ca(OH)_2 could be dissolved.

$0.00631 \text{ mol} < 0.0281 \text{ mol}$

So, the solution is saturated. Not all Ca(OH)_2 could be dissolved

$c(\text{OH}^-) = 2 \cdot 0.0105 \text{ mol} = 0.0210 \text{ mol/dm}^3$

$\text{pOH} = 1.677$

$\text{pH} = \mathbf{12.32}$

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 Fe^{3+} and I^- as well as ii) between I_2 and $\text{S}_2\text{O}_3^{2-}$. Show your calculations. Write and balance feasible reactions. $E^\circ(\text{Fe}^{3+}/\text{Fe}) = -0.04 \text{ V}$; $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}$; $E^\circ(\text{FeO}_4^{2-}/\text{Fe}^{3+}) = +2.20 \text{ V}$; $E^\circ(\frac{1}{2}\text{I}_2/\text{I}^-) = +0.54 \text{ V}$; $E^\circ(\text{IO}_3^-/\frac{1}{2}\text{I}_2) = +1.20 \text{ V}$; $E^\circ(\text{HOI}/\frac{1}{2}\text{I}_2) = +1.44 \text{ V}$; $E^\circ(\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}) = +0.08 \text{ V}$.

$$\text{i) } E^\circ(\text{Fe}^{3+}/\text{Fe}) - E^\circ(\frac{1}{2}\text{I}_2/\text{I}^-) = -0.58 \text{ V}$$

$$E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) - E^\circ(\frac{1}{2}\text{I}_2/\text{I}^-) = +0.23 \text{ V (positive)}$$

$$-E^\circ(\text{FeO}_4^{2-}/\text{Fe}^{3+}) - E^\circ(\frac{1}{2}\text{I}_2/\text{I}^-) = -2.74 \text{ V}$$



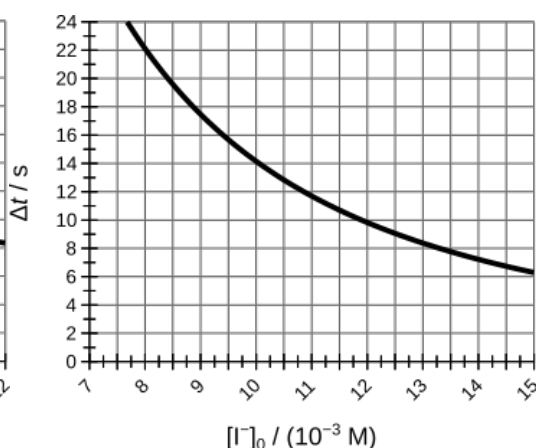
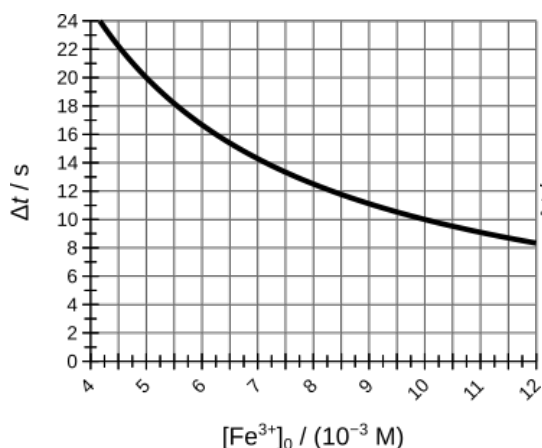
$$\text{ii) } -E^\circ(\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}) + E^\circ(\frac{1}{2}\text{I}_2/\text{I}^-) = +0.46 \text{ V (positive)}$$

$$-E^\circ(\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}) - E^\circ(\text{HOI}/\frac{1}{2}\text{I}_2) = -1.52 \text{ V}$$

$$-E^\circ(\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}) - E^\circ(\text{IO}_3^-/\frac{1}{2}\text{I}_2) = -1.28 \text{ V}$$



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 (Δt) 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 Δt 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) Fe^{3+} and ii) I^- , then calculate the half-life of $[\text{Fe}^{3+}]$ in solution at experimental conditions.

i) $v_0 = k[\text{Fe}^{3+}]^x[\text{I}^-]^y$, when $[\text{I}^-] = \text{const}$, $v_0 = [\text{S}_2\text{O}_3^{2-}]_0/\Delta t = k'[\text{Fe}^{3+}]^x$

$\log(1/\Delta t) = \text{const} + x \cdot \log[\text{Fe}^{3+}]$

$x = \Delta \log(1/\Delta t) / \Delta \log[\text{Fe}^{3+}]$

Data were taken from the graph:

$x = [\log(1/10) - \log(1/20)] / [\log(10) - \log(5)] = 1.0$

Order in respect to Fe^{3+} : **1**

Half-life: as can be seen in the graph, $[\text{Fe}^{3+}]$ decreases twice every **10 s**

ii) $v_0 = k[\text{Fe}^{3+}]^x[\text{I}^-]^y$, when $[\text{Fe}^{3+}] = \text{const}$, $v_0 = [\text{S}_2\text{O}_3^{2-}]_0/\Delta t = k''[\text{I}^-]^y$

$\log(1/\Delta t) = \text{const} + y \cdot \log[\text{I}^-]$

$y = \Delta \log(1/\Delta t) / \Delta \log[\text{I}^-]$

Data taken from the graph:

$x = [\log(1/9) - \log(1/22.3)] / [\log(12.5) - \log(8)] = 2.0$

Order in respect to I^- : **2**

Some experimental results are summarised in the table below:

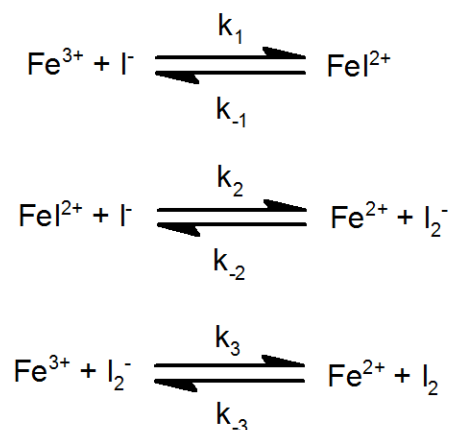
#	$[\text{Fe}^{3+}]_0$	$[\text{I}^-]_0$	$v_0 [\text{M s}^{-1}]$
1	0.09900	0.0744	0.008836
2	0.09900	0.0431	0.002978
3	0.04945	0.0960	0.007319
4	0.00118	0.0960	0.000175
5	0.00118	0.0607	0.000070
6	0.00118	0.0431	0.000035

c) Calculate the rate constant of the reaction.

$k = v_0 / \{[\text{Fe}^{3+}][\text{I}^-]^2\}$

$k = 16 \text{ M}^{-2} \text{ s}^{-1}$

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



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

(1) Let $\text{d}[\text{I}_2^-]/\text{d}t = 0$

$$\text{d}[\text{I}_2^-]/\text{d}t = k_2[\text{FeI}_2^+][\text{I}^-] + k_{-3}[\text{Fe}^{2+}][\text{I}_2] - \{k_3[\text{Fe}^{3+}] + k_{-2}[\text{Fe}^{2+}]\}[\text{I}_2^-]$$

$$[\text{I}_2^-] = \{k_2[\text{FeI}_2^+][\text{I}^-] + k_{-3}[\text{Fe}^{2+}][\text{I}_2]\} / \{k_3[\text{Fe}^{3+}] + k_{-2}[\text{Fe}^{2+}]\}$$

$$[\text{I}_2^-] \approx k_2[\text{FeI}_2^+][\text{I}^-] / \{k_3[\text{Fe}^{3+}] + k_{-2}[\text{Fe}^{2+}]\}, \text{ i.e. } k_2[\text{FeI}_2^+][\text{I}^-] \gg k_{-3}[\text{Fe}^{2+}][\text{I}_2]$$

(2) Let $k_{-1}[\text{FeI}_2^+] = k_1[\text{Fe}^{3+}][\text{I}^-]$

$$\text{Then } [\text{I}_2^-] \approx k_2K[\text{Fe}^{3+}][\text{I}^-]^2 / \{k_3[\text{Fe}^{3+}] + k_{-2}[\text{Fe}^{2+}]\}$$

(3) $-\text{d}[\text{Fe}^{3+}]/\text{d}t = \frac{1}{2}\text{d}[\text{I}_2]/\text{d}t = k_3[\text{Fe}^{3+}][\text{I}_2^-]$

$$-\text{d}[\text{Fe}^{3+}]/\text{d}t \approx k_2K[\text{Fe}^{3+}][\text{I}^-]^2 / \{1 + k_{-2}/k_3 \cdot [\text{Fe}^{2+}]/[\text{Fe}^{3+}]\}$$

$$-\text{d}[\text{Fe}^{3+}]/\text{d}t \approx k_2K[\text{Fe}^{3+}][\text{I}^-]^2$$

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

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 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 $p(\text{CO}_2) = 4.9\text{ kPa}$.

$$\begin{aligned}\text{pH} &= \text{p}K_{\text{a}1} + \log\{[\text{HCO}_3^-]/[\text{CO}_2(\text{aq})]\} \\ \text{pH} &= 6.07 + \log\{0.0294\text{ M}/(2.2 \cdot 10^{-4}\text{ mol m}^{-3}\text{ Pa}^{-1} \cdot 4.9\text{ kPa})\} \\ \text{pH} &= 7.5\end{aligned}$$

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

$$\begin{aligned}\ln\left(\frac{K_2}{K_1}\right) &= -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ \Delta H^\circ &= -8.314\text{ J/mol} \cdot \ln(10^{-6.07}/10^{-6.35})/(1/311.65 - 1/298.15) \\ \Delta H^\circ &= 36894\text{ J/mol} \\ K_{\text{a}1}(40.7\text{ }^\circ\text{C}) &= 10^{-6.35} \cdot \exp(-36894/8.314 \cdot (1/313.85 - 1/298.15)) = 9.40 \cdot 10^{-7} \\ \text{p}K_{\text{a}1}(40.7\text{ }^\circ\text{C}) &= 6.03\end{aligned}$$

$$\begin{aligned}K_{\text{H}}(\text{CO}_2, 40.7\text{ }^\circ\text{C}) &= K_{\text{H}}(\text{CO}_2, 38.5\text{ }^\circ\text{C}) \cdot \exp[\Delta H_{\text{vap}}/R \cdot (T_2^{-1} - T_1^{-1})] \\ K_{\text{H}}(\text{CO}_2, 40.7\text{ }^\circ\text{C}) &= 2.2 \cdot 10^{-4}\text{ mol m}^{-3}\text{ Pa}^{-1} \cdot \exp(19950/8.314 \cdot (1/313.85 - 1/311.65)) \\ K_{\text{H}}(\text{CO}_2, 40.7\text{ }^\circ\text{C}) &= 2.1 \cdot 10^{-4}\text{ mol m}^{-3}\text{ Pa}^{-1}\end{aligned}$$

- c) Estimate the pH of the Adélie penguin blood at critical body temperature of $40.7\text{ }^\circ\text{C}$ assuming that the CO_2 pressure remains the same, and the concentration of HCO_3^- depends on the pH as $[\text{HCO}_3^-] = (302.4 - 36.4 \cdot \text{pH})\text{ mM}$.

$$\text{pH} = 6.03 + \log\{(0.3024 - 0.0364 \cdot \text{pH})\text{ M}/(2.1 \cdot 10^{-4}\text{ mol m}^{-3}\text{ Pa}^{-1} \cdot 4.9\text{ kPa})\}$$

$$\text{pH} = 6.03 + \log\{294 - 35.3 \cdot \text{pH}'\} \text{ (try } \text{pH}' = 7.5 \text{ on the right side)}$$

$$\text{pH} = 7.5 \text{ (the pH changes insignificantly)}$$

- 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.

$$\text{pH} = 6.03 + \log\{(0.3024 - 0.0364 \cdot \text{pH}) \text{ M} / (2.1 \cdot 10^{-4} \text{ mol m}^{-3} \text{ Pa}^{-1} \cdot 1.5 \text{ kPa})\}$$

$$\text{pH} = 6.03 + \log(960 - 115.6 \cdot \text{pH}') \text{ (try } \text{pH}' = 7.5 \text{ on the right side)}$$

$$\text{pH} = 8.0 \text{ (new value for } \text{pH}')$$

$$\text{pH} = 6.03 + \log(960 - 115.6 \cdot \text{pH}') \text{ (try again with } \text{pH}' = 8.0 \text{ on the right side)}$$

$$\text{pH} = 7.6 \text{ (new value for } \text{pH}')$$

$$\dots \text{ the pH converges at } 7.8 \text{ (the pH changes significantly)}$$

- 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 answer:

A) Alkalosis

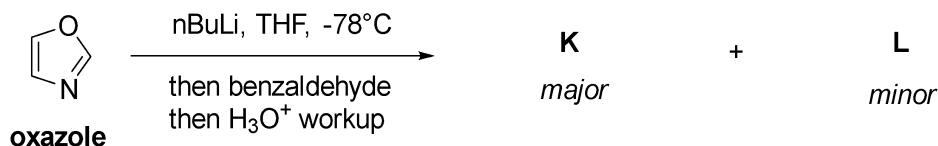
C) Acidosis

B) Hypocarbica

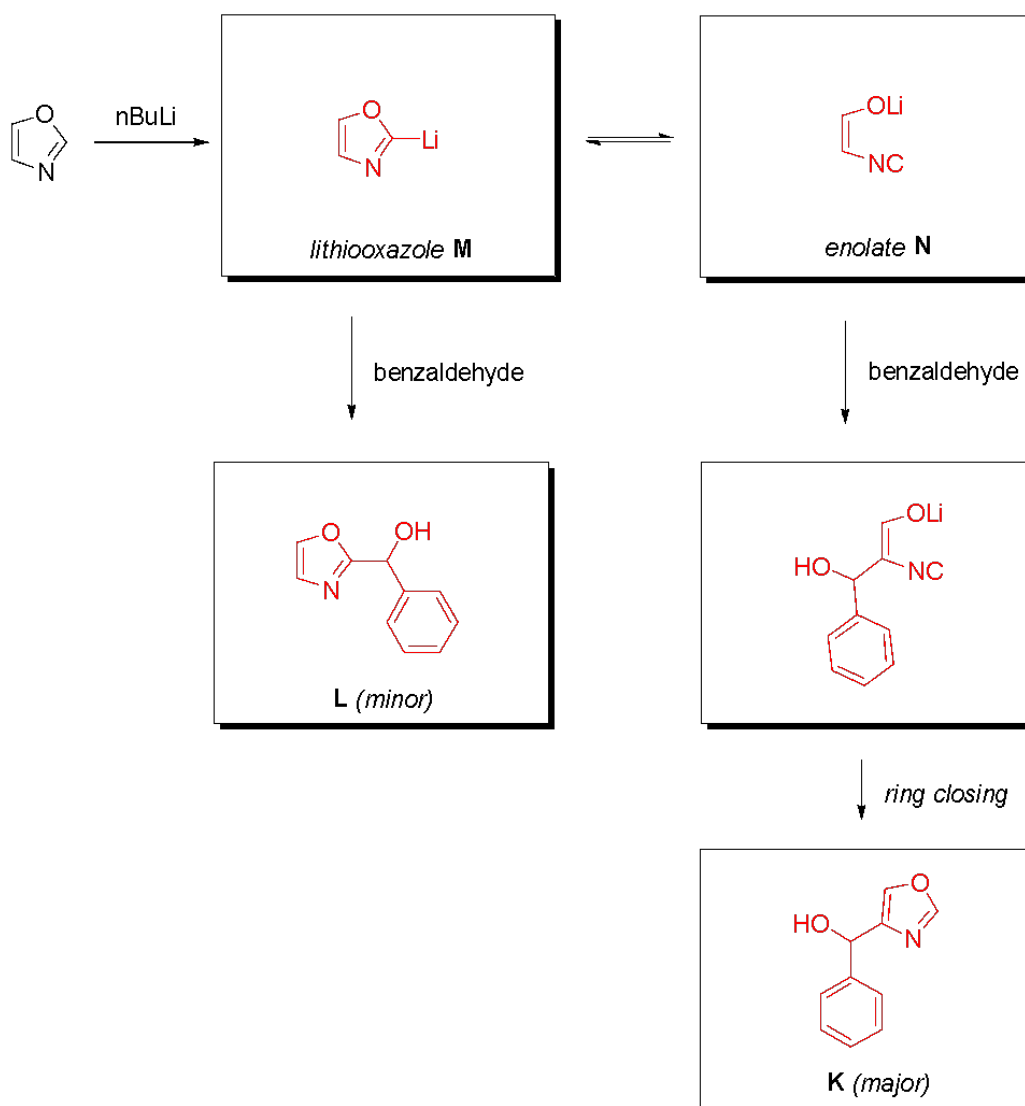
D) Hypercarbica

Problem 5. Lithiation and alkylation

One of the most popular methods for introducing substituents in heterocyclic compounds is lithiation and then subsequential 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.



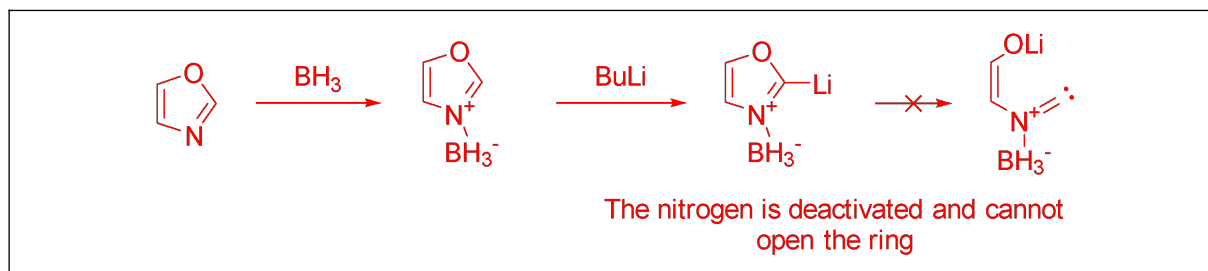
The reason for that is, when the oxazole has been lithiated in the most acidic position, the obtained lithiooxazole **M** is not stable and is in equilibrium with enolate **N**. Enolate **N** can attack benzaldehyde and after closing the ring, create the major addition product **K**.



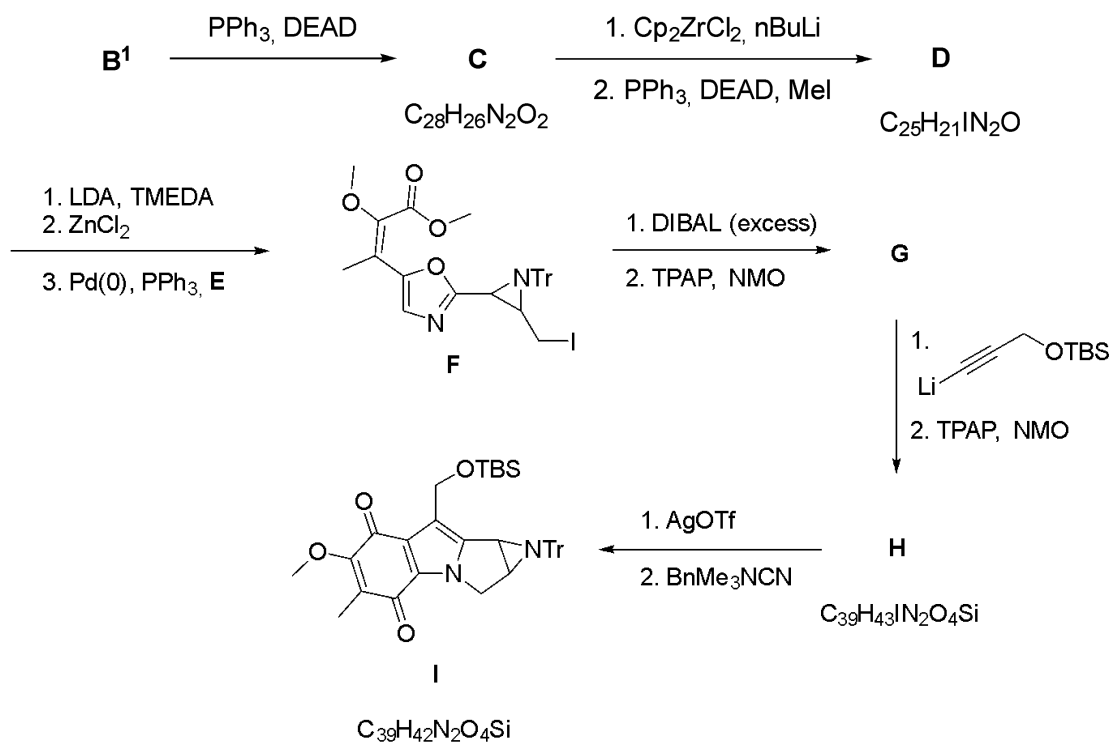
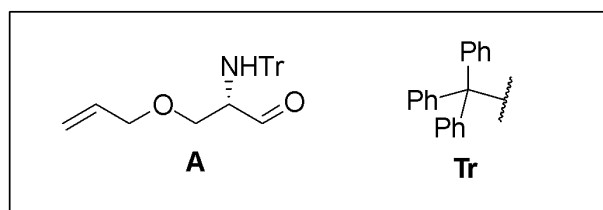
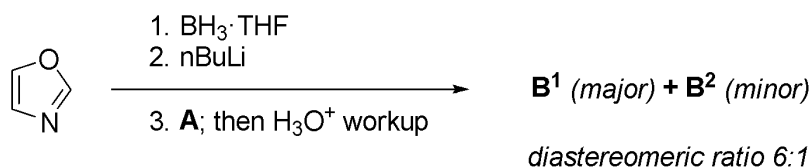
a) Draw all the structures in the empty boxes given above.

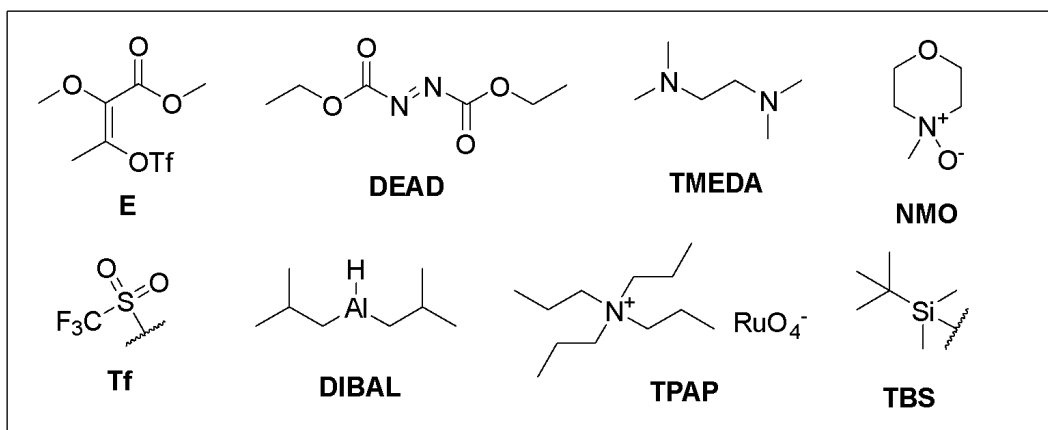
To overcome the unwanted selectivity, the addition of 1 equivalent of BH_3 before lithiation is used.

b) Explain, drawing mechanism or structures, how BH_3 might change the selectivity.



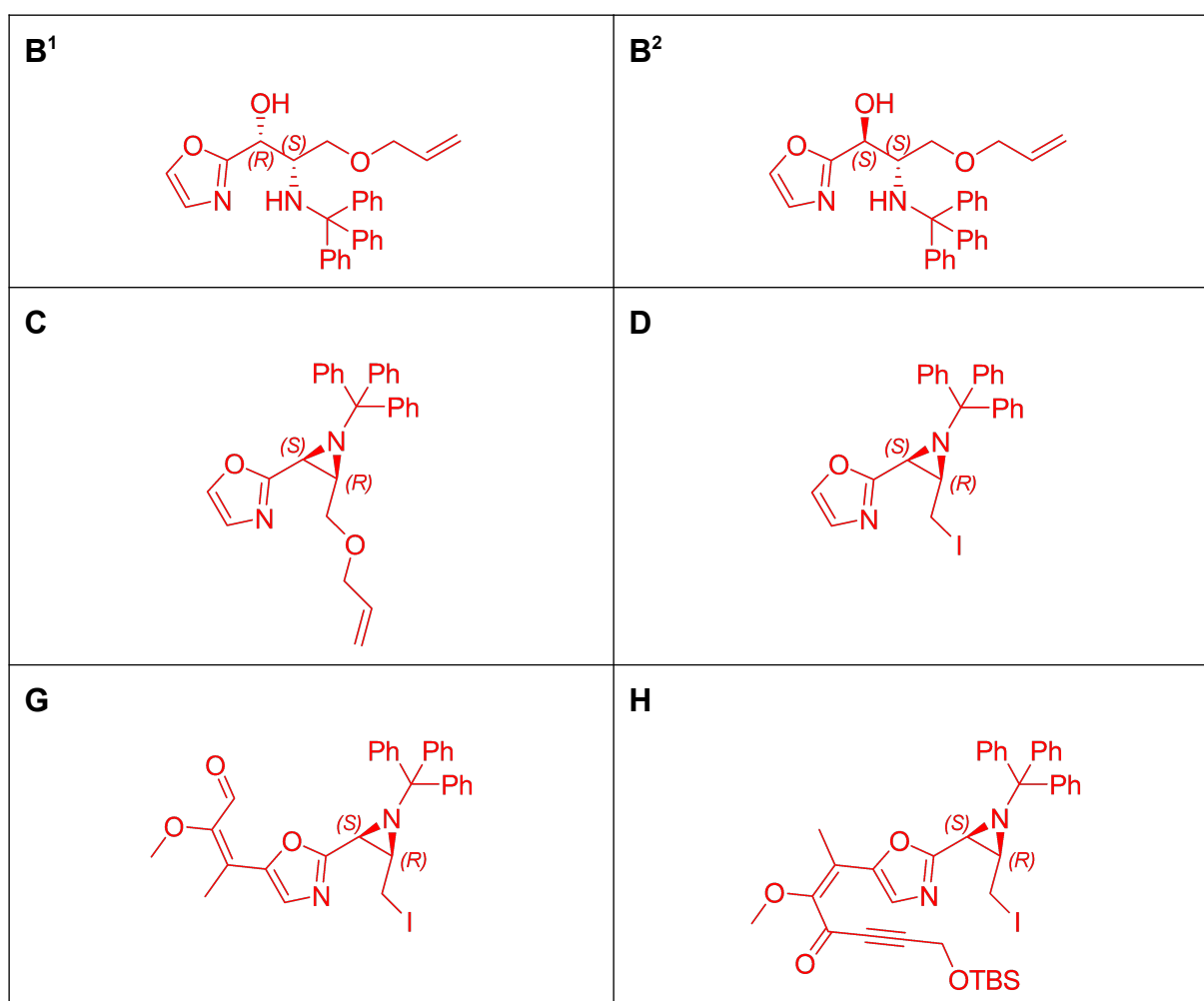
This method was used in an attempted synthesis of a synthetic product Aziridinomitosen A, which has the same core structure as Mytomycins, natural compounds that possess interesting structure and antitumor activity. The synthesis starts with selective oxazoline lithiation.



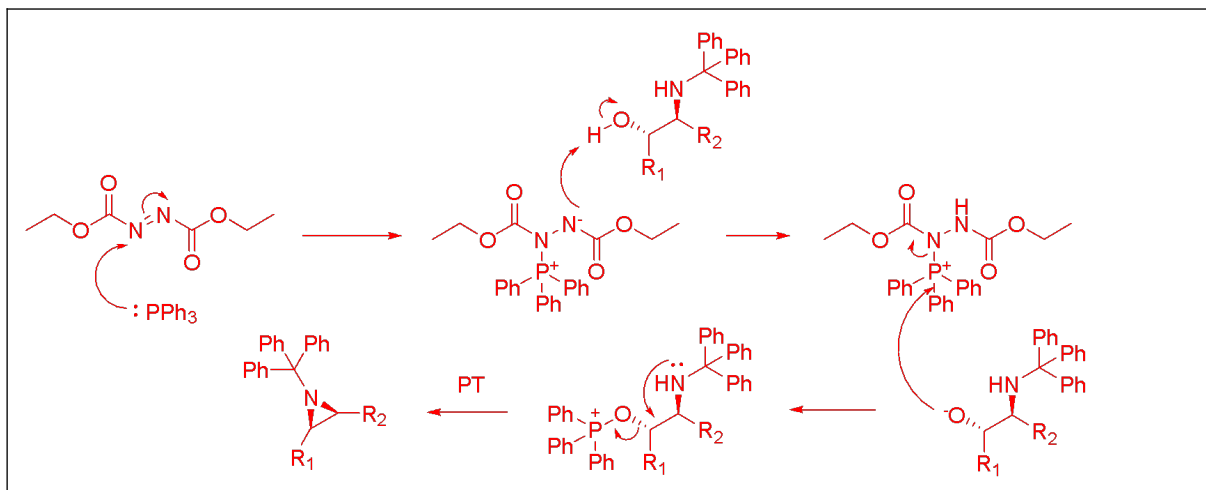


Note: Cp_2ZrCl_2 , BuLi are allyl group deprotection conditions.

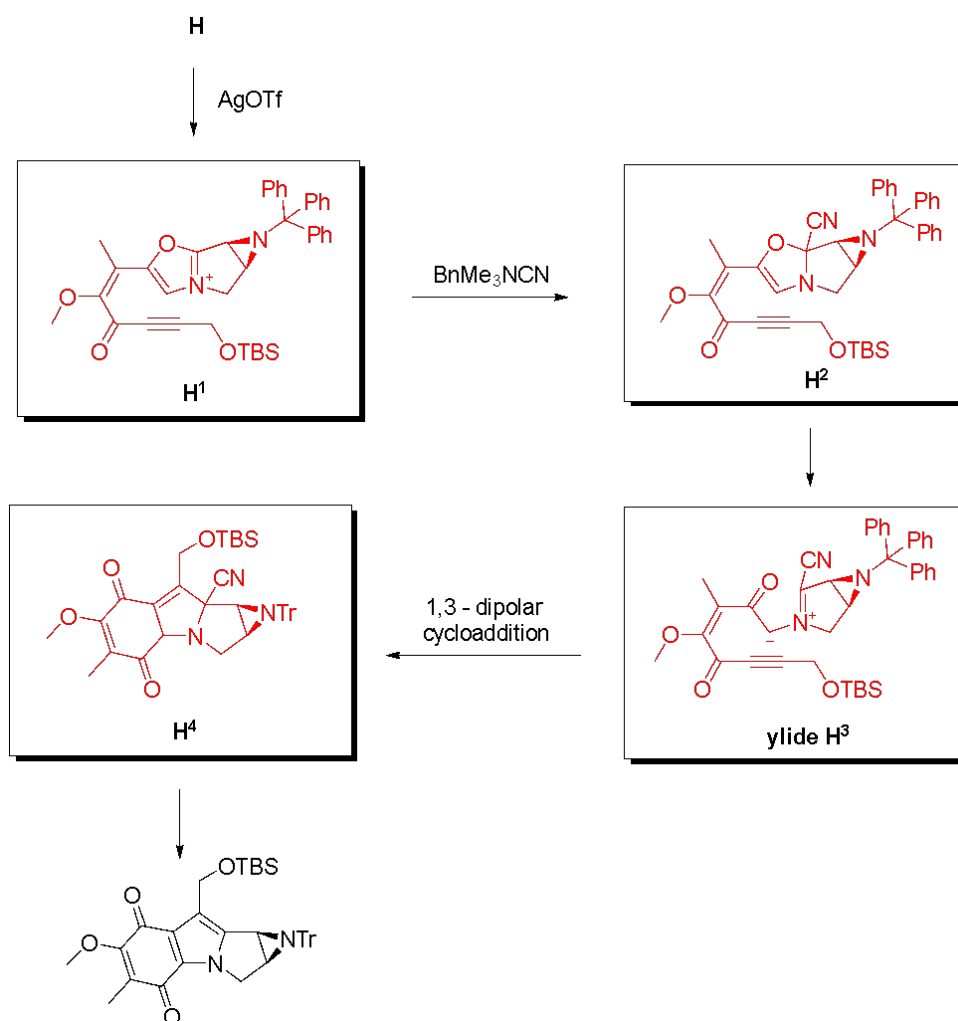
c) Draw structures **B¹**, **B²**, **C**, **D**, **G**, **H** and indicate the stereochemistry.



d) Draw the mechanism for the transformation **B¹** → **C**. Feel free to use abbreviations and denote parts of the molecule, that do not participate in the mechanism.



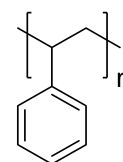
The reaction $\mathbf{H} \rightarrow \mathbf{I}$ is a complex multi-step transformation. First AgOTf is added to \mathbf{H} , which creates ionic compound \mathbf{H}^1 and a yellow salt. To \mathbf{H}^1 BnMe_3NCN is added, which is a source of cyanide anions and addition product \mathbf{H}^2 is obtained, 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} .



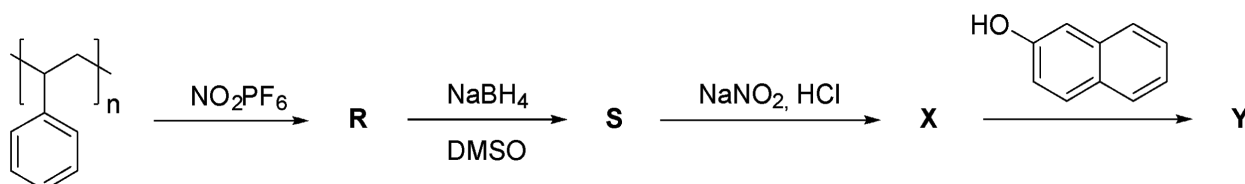
e) Draw all the structures in the empty boxes given above.

Problem 6. Deformed polymers (10%)

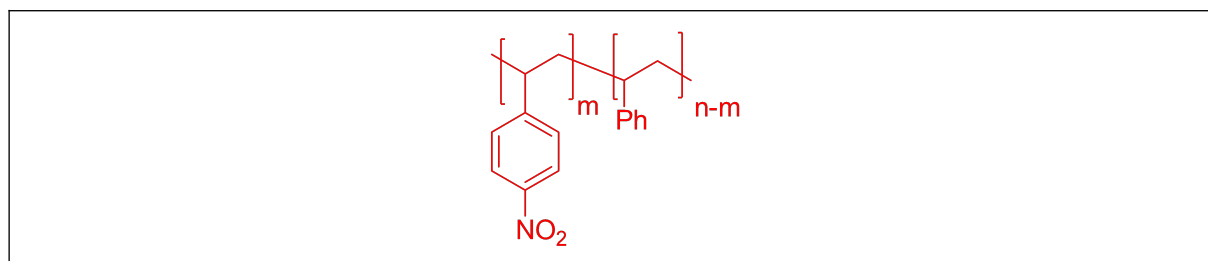
In order to change the colour of polystyrene (in a picture on the right side), one may use so-called polymer-analogous reactions, that alter only functional groups but leave alkyl chains unaffected. These sorts of reactions may also be useful in the synthesis of polymers that are impossible to make from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



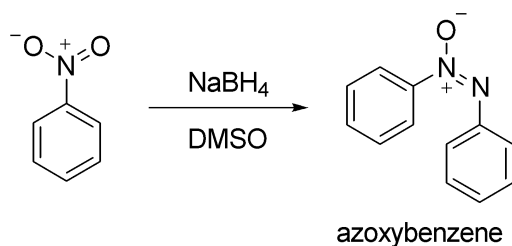
Let us look at one of the modifications that could be made with the polymer (scheme below).



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



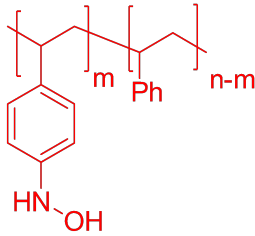
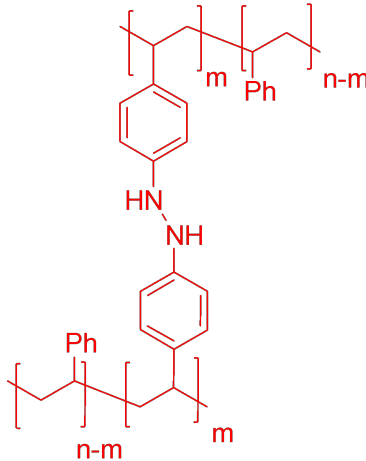
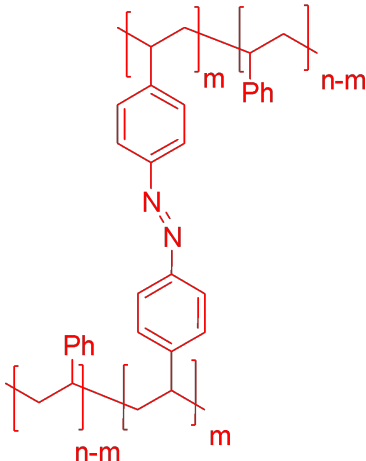
NaBH_4 is not good for reduction of aromatic nitro compounds, because of the formation of various side products, such as azoxybenzene:



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

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

<p>S</p>	<p>S¹</p>
<p>S²</p>	<p>S³</p>

	
<p>S⁴</p> 	<p>Free space</p>

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

A) S¹

B) S²

C) S³

D) S⁴

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

Water

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.

Nitro → amino.

Titrated $1.920/1000 \cdot 0.2000 = 3.840 \cdot 10^{-4}$ mol

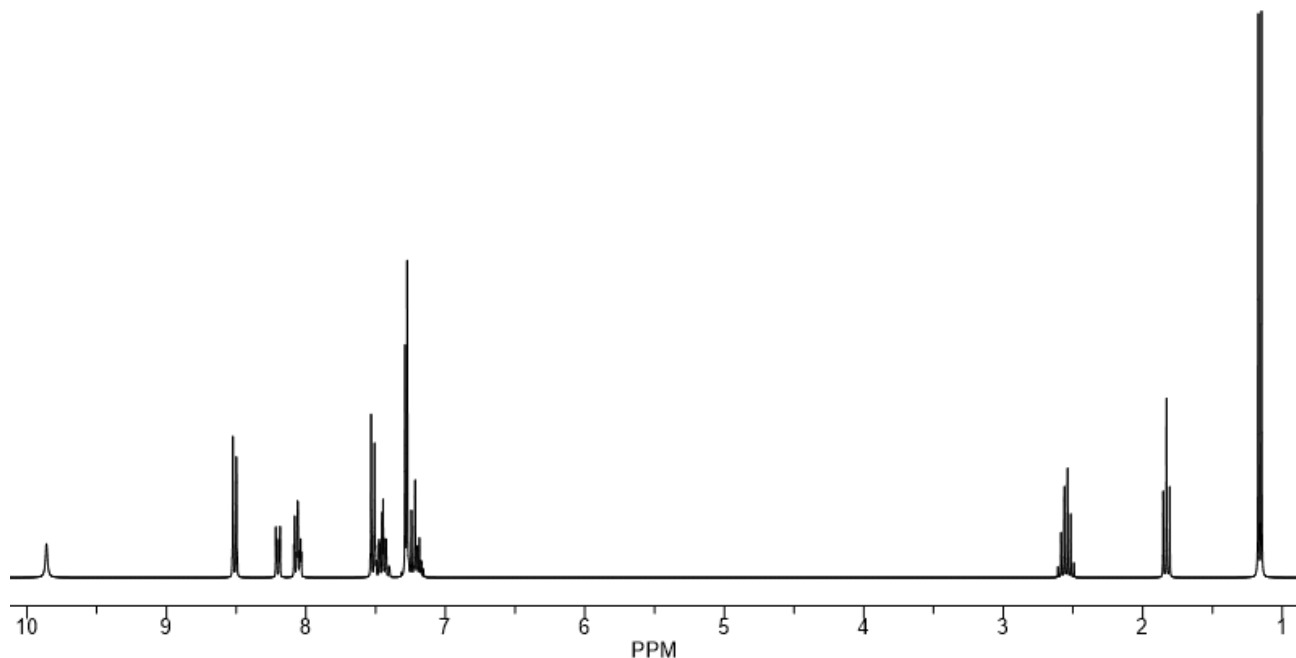
$$\text{mass} = 3.840 \cdot 10^{-4} \text{ mol} \cdot 119.6 \text{ g/mol} = 0.0458 \text{ g}$$

Other mass is non-nitrated benzene (0.9542 g)

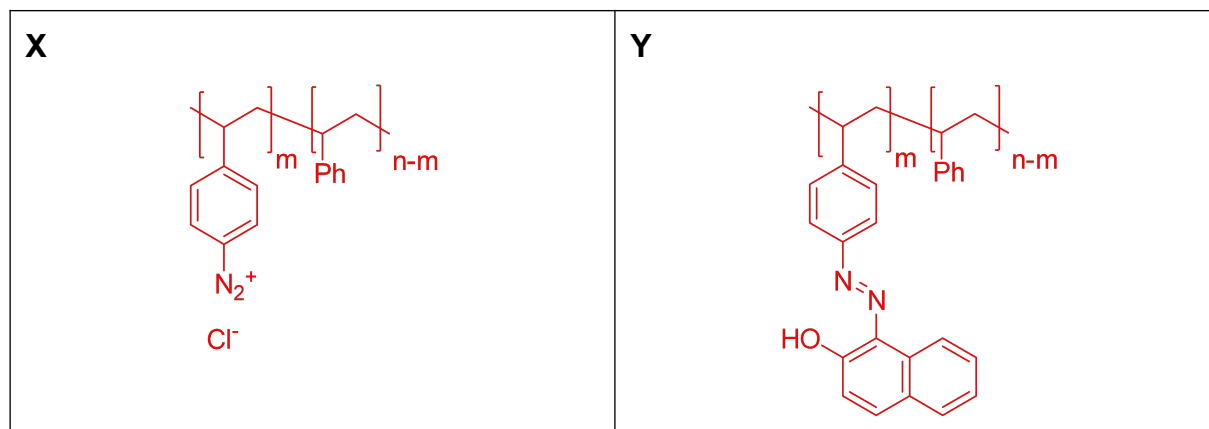
$$\text{amount (non-nitrated)} = 0.9542 \text{ g} / 104.5 \text{ g/mol} = 9.162 \cdot 10^{-4} \text{ mol}$$

Thus nitrated **4.0%**

g) Give the structures of **X and **Y**, considering the ^1H NMR spectrum of **Y**:**

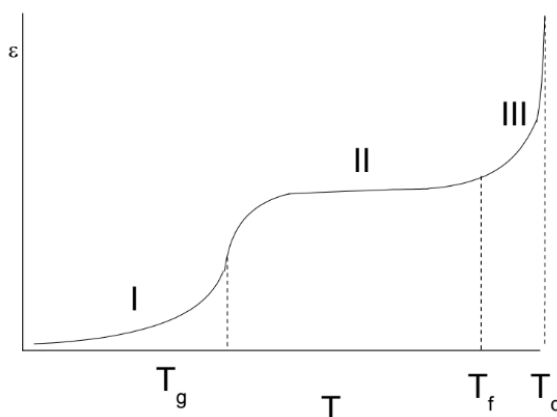


Y: ¹H NMR (300 MHz, CDCl₃): δ 9.86 ppm (s), 8.51 (d), 8.20-8.05 (m), 7.52-7.43 (m), 7.27-7.19 (m), 2.58-2.53 (m), 1.89-1.83 (m), 1.16 (d)



An important characteristic of mechanical properties of polymers is the dependence of equilibrium deformation ε on temperature T . ε 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.

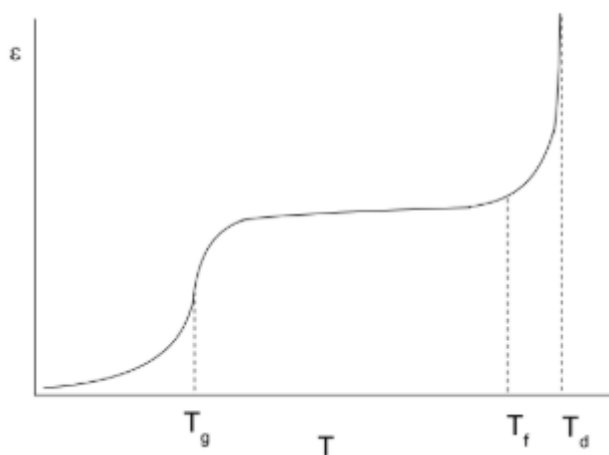


h) Sketch thermomechanical curves and denote temperature for phase change on the same graph:

- For nitrated polystyrene, reduced with excess NaBH_4 at low polymer concentration (nitrated/non-nitrated = **5%**).
- For nitrated polystyrene, reduced with excess NaBH_4 at high polymer concentration (nitrated/non-nitrated = **5%**).
- For nitrated polystyrene, reduced with excess NaBH_4 at high polymer concentration (nitrated/non-nitrated = **15%**).

Hint: remember your answer to question d).

i) nothing really changes, as there are no polymer-polymer interactions (azoxybond does not form)



ii) and **iii)** at high concentrations azoxy bond does form, hence 3D structure is unable to 'flow', be liquid, to T_f . The higher the concentration, the more stress the structure experiences.

