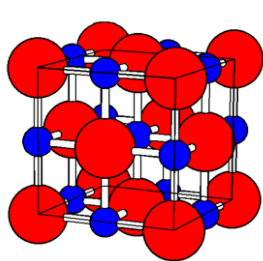


25th BChO 2017, Vilnius, Lithuania

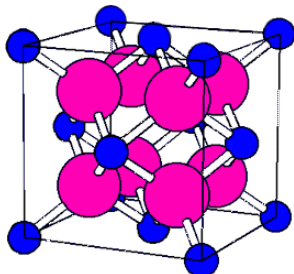
Problem 1 - CRYSTAL - Crystal packing



AB

$$3.34 \text{ g cm}^{-3}$$

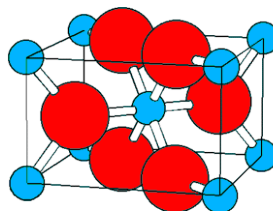
$$a = 4.81 \text{ \AA}$$



AC₂

$$3.18 \text{ g cm}^{-3}$$

$$a = 5.46 \text{ \AA}$$

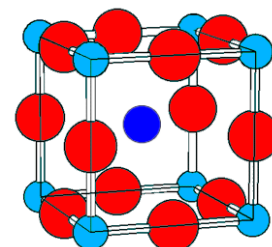


DB₂

$$4.25 \text{ g cm}^{-3}$$

$$a = b = 4.59 \text{ \AA}$$

$$c = 2.96 \text{ \AA}$$



ADB₃

$$3.98 \text{ g cm}^{-3}$$

$$a = 3.84 \text{ \AA}$$

Unit cells, densities, and lattice parameters of four crystals are given in the Figure.

- Determine the number of each ion in each unit cell (**AB**, **AC₂**, **DB₂**, **ADB₃**).
- Determine the coordination number of **A** and **D** in all crystals (**AB**, **AC₂**, **DB₂**, **ADB₃**).
- Calculate the molar mass of each compound (**AB**, **AC₂**, **DB₂**, **ADB₃**).
- Determine the elements **A-D**.

Problem 2 - CRYSTAL, EQUIL, THERMO - Solubility

In the table below are ionic radii and standard reduction potentials (Me^{n+}/Me) for a set of metals:

	Fe ³⁺	Fe ²⁺	Cu ²⁺	Cu ⁺	Zn ²⁺	Hg ²⁺	Pb ²⁺	Ag ⁺	Hg ⁺
r_+ [Å]	0.55	0.61	0.73	0.77	0.74	1.14	1.19	1.15	1.19
$E^\circ(\text{Me}^{n+}/\text{Me})$ [V]	-0.04	-0.45	+0.34	+0.52	-0.76	+0.85	-0.13	+0.80	+0.80

Enthalpy change of the metal-iodide solvation ($\text{MeI}_n(\text{s}) \rightarrow \text{Me}^{n+}(\text{aq}) + n\text{I}^-(\text{aq})$) can be roughly estimated using Latimer and Kapustinskii equations:

$$\Delta H_{\text{solv}} = A \cdot \frac{|z_+|^2}{r_+ + r_0} + n\Delta H_{\text{hyd}}(\text{I}^-) - B \cdot \frac{v \cdot |z_+| \cdot |z_-|}{r_+ + r_-}$$

where $A = -610 \text{ kJ \AA mol}^{-1}$, $B = -1080 \text{ kJ \AA mol}^{-1}$, $r_0 = 0.50 \text{ \AA}$, v is the number of ions in the empirical formula, z_+ and z_- are the charges on the cation and anion, respectively, in elementary charges, and r_+ and r_- are the radii of the cation and anion, respectively, in Å, $\Delta H_{\text{hyd}}(\text{I}^-) = -308 \text{ kJ mol}^{-1}$. The radius of the iodide is 2.06 \AA .

The entropy change of the metal-iodide solvation can be estimated using Sackur-Tedore and Powell-Latimer equations:

$$\Delta S_{\text{solv}} = C + n\Delta S_{\text{hyd}}(\text{I}^-) - D \cdot \frac{|z_+|}{(r_+ + r_{\text{dip}})^2} - E \cdot \ln M_+$$

where $C = 88 \text{ J mol}^{-1} \text{ K}^{-1}$, $D = 644 \text{ J \AA}^2 \text{ mol}^{-1} \text{ K}^{-1}$, $r_{\text{dip}} = 1.30 \text{ \AA}$, $E = 12.5 \text{ J mol}^{-1} \text{ K}^{-1}$, M is the molar mass of the cation, $\Delta S_{\text{hyd}}(\text{I}^-) = -58.1 \text{ J mol}^{-1} \text{ K}^{-1}$.

- a) Show with calculations that for CuI $\Delta G_{\text{solv}} > 0$, while for CuI_2 $\Delta G_{\text{solv}} < 0$.
- b) Which of the following iodides are insoluble in water: FeI_2 , CuI , ZnI_2 , HgI_2 , PbI_2 , AgI , HgI .
In aqueous solution, Cu^{2+} and Fe^{3+} reduce I^- to I_2 . $E^\circ(\text{I}_2/\text{I}^-) = 0.535 \text{ V}$.
- c) Calculate the standard reduction potential for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and show that the reduction of I^- to I_2 by Fe^{3+} is spontaneous under standard conditions.
- d) Calculate the standard reduction potential for $\text{Cu}^{2+}/\text{Cu}^+$ and show that the reduction of I^- to I_2 by Cu^{2+} is spontaneous. $K_{\text{sp}}(\text{CuI}) = 1.1 \cdot 10^{-12}$.

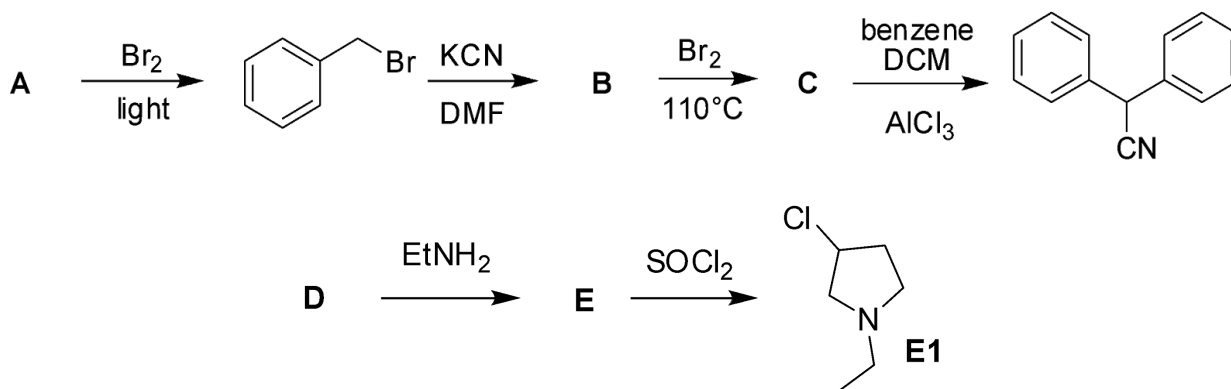
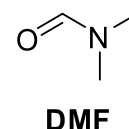
Five test tubes **A–E** contain 0,1 M aqueous solutions of one of the following substances: AgNO_3 , CuSO_4 , FeCl_3 , $\text{Hg}(\text{NO}_3)_2$, KI . The results of the identification of the particular test tubes by mutual reactions are shown in the following table:

	A	B	C	D	E
A	-				
B	Orange-red P	-			
C	Yellow P, brown S	-	-		
D	Brown S	-	-	-	
E	Yellowish P	-	-	White P	-

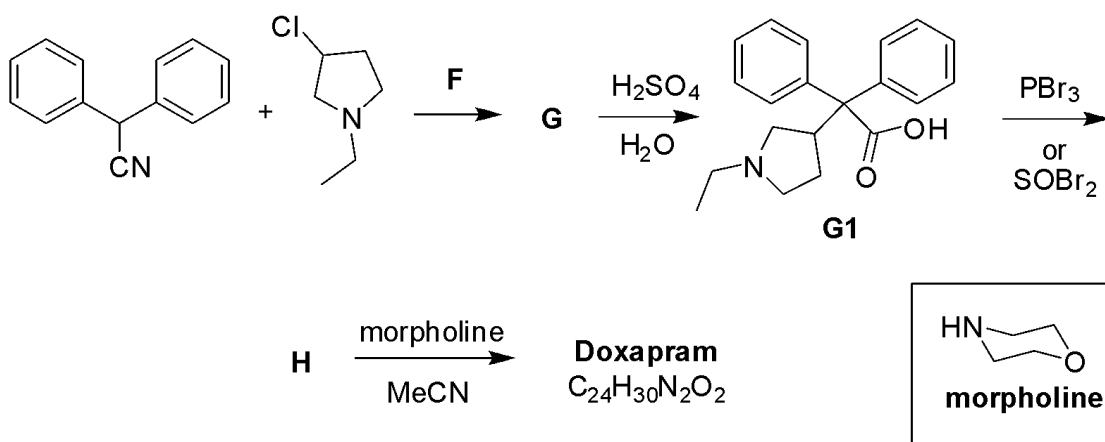
- e) Determine the content of tubes **A–E** and write chemical equations of the reactions marked in the table (P – precipitate, S – solution).

Problem 3 – SYNTH – Analeptics

It is known that when people are highly intoxicated with depressants, they tend to stop breathing and could even die. It happens because of breathing center depression in the human brain. Analeptics (breathing stimulators) such as Doxapram could help in such critical situations when injected. Following, you will find two synthesis schemes of the main components used in Doxapram manufacture.



- a) Draw the structural formula of compounds **A–E**.
- b) Why is light so important in the first reaction?
- c) Would compound **E1** be racemic or not if we used enantiomerically pure **D**?



- Compound **H** is neither **acidic** nor **basic**.
- In Doxapram, all carbons attached to the N atom (from morpholine) are sp^3 .

- d)** Draw the structural formula of compounds **F–H** and Doxapram.
- e)** What are the most suitable conditions **F**: **i)** HCl/MeOH; **ii)** *t*-BuOK/THF; **iii)** beeswax and naphtha; **iv)** $\text{Et}_2\text{O} \cdot \text{BF}_3$.
- f)** Draw reaction mechanism **G1** \rightarrow **H**.

Problem 4 – CALC, SPECTRA, STRUCT – Nickel knickknackery

By exploring the deepest corners of his table drawers, a student Dominykas (respectfully called Cheminykas by his friends) found a bottle containing a green crystalline substance with a writing $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. It might be due to the never-coming spring, mesmerized by the greenery of this substance, Cheminykas decided to carry out a few experiments with this material.

After dissolving it in water, he treated the solution with concentrated ammonia solution, the odor of which might wake even the heaviest sleeper from the deepest winter hibernation. A colorful metal-ammine complex is formed when the reaction takes place.



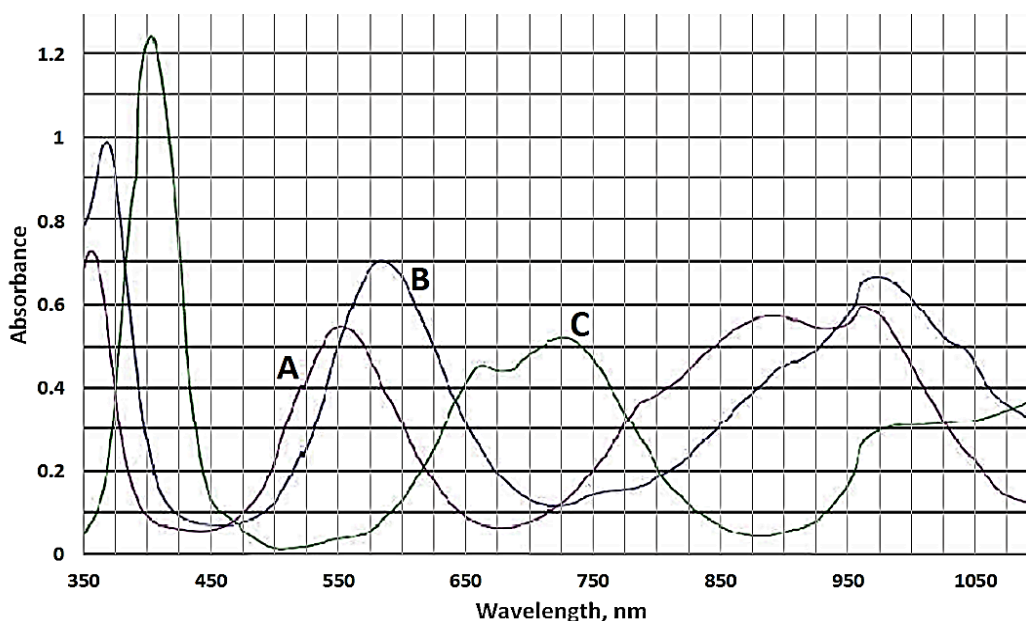
Several colorful crystals have formed, were filtered, dissolved in 5 cm^3 of water, poured into the spectrophotometric cuvette and placed into the spectrophotometer. After registering the UV-Vis spectrum, Cheminykas observed that the most intense absorbance occurred at 394 nm wavelength. Wanting to explore this material more thoroughly, he decided to carry out a photometric analysis.

Consequently, he dissolved 0.2017 g of obtained colorful crystals in 10.0 cm^3 water and poured this solution into a photometric cuvette with a 5.00 cm optical path length. The device showed that the solution transmitted only 0.7% of light. Knowing that the device is not very accurate at this part of the scale, he transferred the solution from the cuvette into a volumetric flask, diluted it to 25.0 cm^3 , and again transferred 10.0 cm^3 of this solution to the same photometric cuvette. This time, the device showed that 13.5% of light was transmitted.

- a)** Calculate the molar absorption coefficient of this material.

The color wheel is a simplified but effective visual tool to predict the absorbance bands without having to use a spectrophotometer.

- b)** Determine the colors of substances **A**, **B**, and **C**.



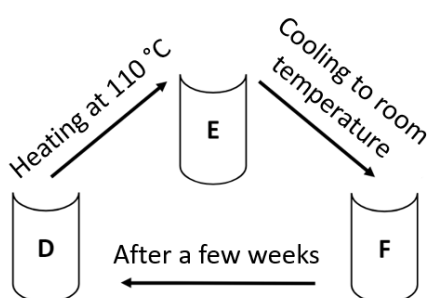
Three absorption bands in the UV-VIS spectrum are usually observed for the coordination compounds of octahedral geometry, given in the descending order of transition energy: ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$, ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and $T_{2g} \leftarrow {}^3A_{2g}$.

c) Calculate the difference between ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transition energies of $[\text{Ni}(\text{en})_3]^{2+}$ (en – ethylenediamine) (substance A) and $[\text{Ni}(\text{NH}_3)_6]^{2+}$ (substance B), providing an answer in electronvolts (eV).

Later on, Cheminykas heated the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ salt to remove water and treated it with dry dimethylammonium chloride to synthesize another compound $((\text{CH}_3)_2\text{-NH}_2)_2[\text{NiCl}_4]$ bis(dimethylammonium) tetrachloronickelate(II), the coordination number of which is 6.

Having completed the synthesis, he took some of the material for characterization but carelessly left the remaining material on the heating plate. When the temperature rose to 110 °C, the color of the substance changed from red (substance D) to deep blue (substance E). Cheminykas quickly noticed that and turned off the heating plate. He further noticed that while the substance was cooling down to room temperature, the color of it changed again from blue to yellow (substance F). Even more so, in two weeks, it returned to its original red color while being stored at room temperature.

Genuinely interested in this phenomenon, Cheminykas carried out literature research and found out that materials that possess an ability to reversibly change their color according to their temperature are called thermochromic, and the phenomenon itself is called thermochromism. He raised a few hypotheses to explain the thermochromic behavior of $((\text{CH}_3)_2\text{-NH}_2)_2[\text{NiCl}_4]$.



- d)** Which of the following statements best describes the color change of $((\text{CH}_3)_2\text{-NH}_2)_2[\text{NiCl}_4]$ upon heating?
- With an increasing temperature, enough energy is passed to the material to surpass the activation energy of reforming crystal lattice and formation of a more thermodynamically stable $((\text{CH}_3)_2\text{-NH}_2)_2[\text{NiCl}_4]$ stereoisomer.
 - A decomposition reaction of organic ligands is taking place, followed by a change in the chemical composition of the coordination compound.
 - Because of the increased temperature, hydrogen bonds are weakened, and an infinite two-dimensional structure is destroyed, accompanied by the shift from octahedral to tetrahedral coordination geometry.
 - The temperature excites the electrons in Ni^{2+} *d*-orbitals, enabling the electronic transitions within the semiconductor bandgap.
- e)** Draw all possible coordination stereoisomers of $((\text{CH}_3)_2\text{-NH}_2)_2[\text{NiCl}_4]$. If there are any optically active stereoisomers (enantiomers) – mark them.
- f)** Schematically depict the absorbance spectra of thermochromic nickel coordination compound before heating (substance **D**), at thermochromic shift temperature (substance **E**) and after cooling back to room temperature (substance **F**). Only one absorption band per material is required to draw.
- g)** Compared with the $((\text{CH}_3)_2\text{-NH}_2)_2[\text{NiCl}_4]$ at thermochromic shift temperature, after cooling to room temperature, the required energy for *d-d* electronic transitions is:
- Lower than at thermochromic shift temperature.
 - Higher than at thermochromic shift temperature.
 - Same as at thermochromic shift temperature.

Finally, Cheminykas decided to treat the thermochromic nickel complex with some bromine and ethylenediamine ($\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_2$, en) which is a common bidentate ligand in coordination chemistry. He obtained a compound $[\text{NiBrCl}(\text{en})_2]$, the coordination number of which is 6.

- h)** Draw all possible coordination stereoisomers of $[\text{NiBrCl}(\text{en})_2]$. If there are any optically active stereoisomers (enantiomers) – mark their pairs.

Problem 5 – INORG, KINETICS, THERMO – Cleaning oil pipes

As wells are drilled in deeper and deeper waters, the accumulation of paraffin, asphaltene and hydrates is increasing due to the extremely low temperatures on the ocean floor. Removing the wax from wells and pipelines will entail additional costs such as the use of deep-water divers and special equipment to cut and remove paraffin build-up from the pipelines.

One simpler solution is to melt paraffin. A reaction between ammonium chloride and sodium nitrite has been proposed to achieve this (**reaction 1**).

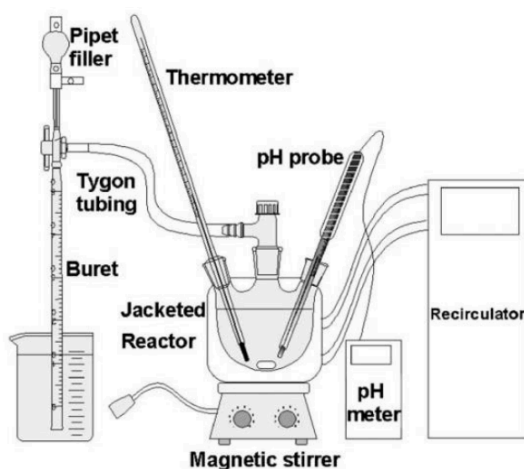
- a)** Calculate the standard enthalpy of the reaction if the enthalpies of formation are:
 $\Delta H_f(\text{NaNO}_2) = -359.4 \text{ kJ mol}^{-1}$; $\Delta H_f(\text{NH}_4\text{Cl}) = -314.43 \text{ kJ mol}^{-1}$; $\Delta H_f(\text{NaCl}) = -411.12 \text{ kJ mol}^{-1}$; $\Delta H_f(\text{H}_2\text{O}) = -285.8 \text{ kJ mol}^{-1}$.
- b)** We know that the equilibrium constant of **reaction 1** is $K \approx 10^{60}$. What can we say about reaction 1 based on this information and the previous calculations? Choose which of the following statements is the most correct.
- The reaction is endothermic and reversible.

- ii) The reaction is exothermic and irreversible.
- iii) The reaction is endothermic and irreversible.
- iv) The reaction is exothermic and reversible.

To use **reaction 1** in the oil industry, it is necessary to know the reaction rate and mechanism. Research Group I thought that the reaction was of the second order and that the rate-limiting step was the reaction of nitrosyl ion (NO^+) with molecular ammonia. Group II, on the other hand, was convinced that the reaction was of the third order and that the rate-limiting step was the reaction of N_2O_3 (from HNO_2) with NH_3 .

- c) Draw the Lewis structures of the compounds and particles mentioned above and, where appropriate, also the resonance structure.

Research Group III replicated and adapted the experiments of the previous two groups. They mixed, at different temperatures and pH values, 150 cm^3 sodium nitrite solution and 150 cm^3 ammonium chloride solution. pH was adjusted by adding HCl or NaOH solution to the reaction mixture. Before the experiment, the reaction vessel was cleaned with nitrogen gas to minimize the occurrence of side reactions. The tools used to study the kinetics of reaction 1 are shown.



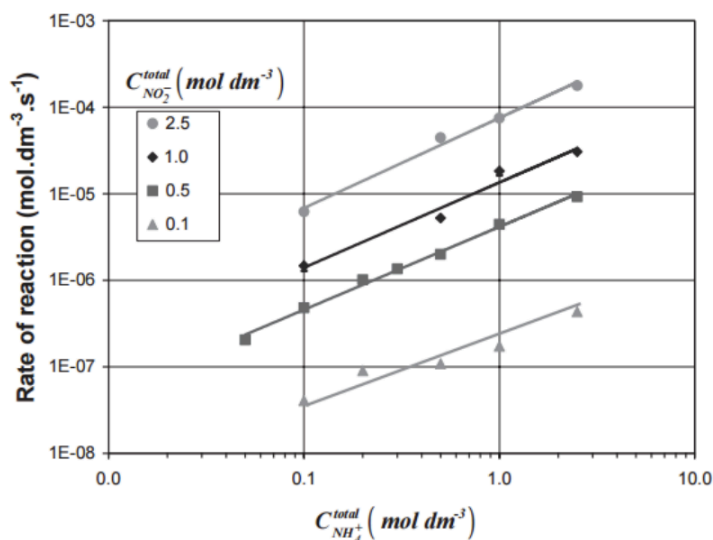
- d) What are the possible adverse reactions if the test was carried out at pH 3–7? Choose one or several answers.

- i) $\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2$
- ii) $2\text{HNO}_2 \rightleftharpoons \text{NO}_2 + \text{NO} + \text{H}_2\text{O}$
- iii) $\text{NH}_4\text{Cl} + \text{NaOH} \rightarrow \text{NH}_3 + \text{H}_2\text{O} + \text{NaCl}$, $\text{p}K_a(\text{NH}_4^+) = 9.25$
- iv) $\text{NaNO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{NaNO}_3$

Once the side reactions have been eliminated, the rate of **reaction 1** can be differentiated from the volume of the gas produced.

- e) Differentiate the rate equation for **reaction 1** via the volume of the gas using the commonly used variables (symbols).

Reaction rates at different concentrations of nitrite and ammonium ions were calculated and plotted on the graph shown in Figure 2 ($T = 25\text{ }^\circ\text{C}$, $\text{pH} = 5$). Determine the reaction order for both of the two reactants on the basis of the graph below.

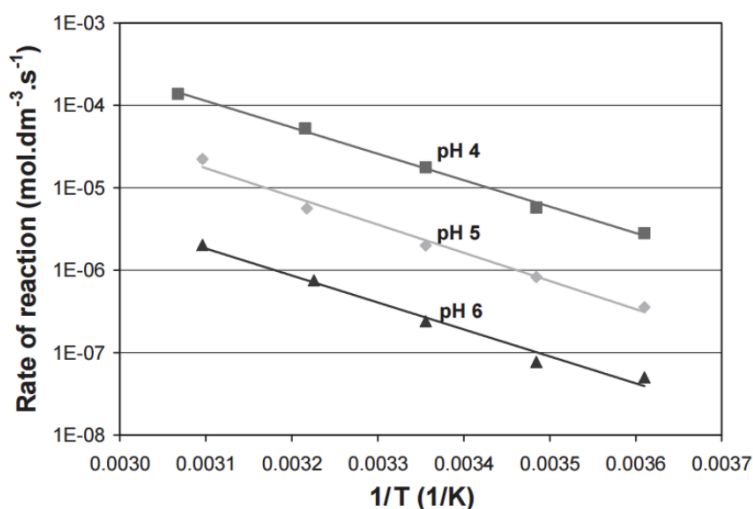


f) Determine the reaction order for ammonium ions (ammonium chloride).

g) Determine the reaction order for nitrite ions (HNO₂).

h) Give the value and unit of the rate constant of the reaction ($T = 25\text{ }^{\circ}\text{C}$, pH = 5).

The temperature dependence of the reaction between ammonium chloride ($c_0 = 0.5\text{ M}$) and sodium nitrite ($c_0 = 0.5\text{ M}$) was investigated in the temperature range 4–50 °C at pH 4, 5 and 6. As expected, the reaction rate followed the Arrhenius equation.



i) Derive the activation energy from available data.

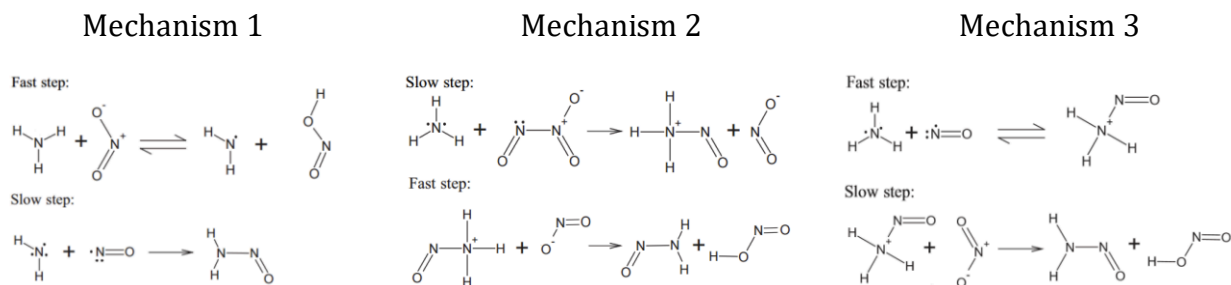
Research Group III continued its studies to determine the mechanism of the reaction. First, they assumed that there was an intermediate from which two end products (N₂ and H₂O) could be rapidly formed. They then proposed different reactions to obtain the intermediate from the two reactants originally used (NH₃ and HNO₂) or their derivatives. The most probable intermediate was thought to be nitrosamine (H₂N–N=O), yielding two final products.

j) Draw the mechanism of nitrosamine degradation.

There are several ways to obtain nitrosamine from the initial compounds. To investigate the possibility of an initiation reaction, one can compare its internal Arrhenius activation energy (E^*) with the Arrhenius activation energy (E) determined in a kinetics experiment. The internal Arrhenius activation energy is described by the equation $E^* = \Delta H^* + RT$, where ΔH^* is the enthalpy change of the slowest phase.

k) HNO_2 (aq) has been shown to be in equilibrium with N_2O_3 , NO and NO_2 . Write the equilibrium reaction equations for the reactions describing the equilibrium state.

Scientists proposed three following mechanisms for nitrosamine production:



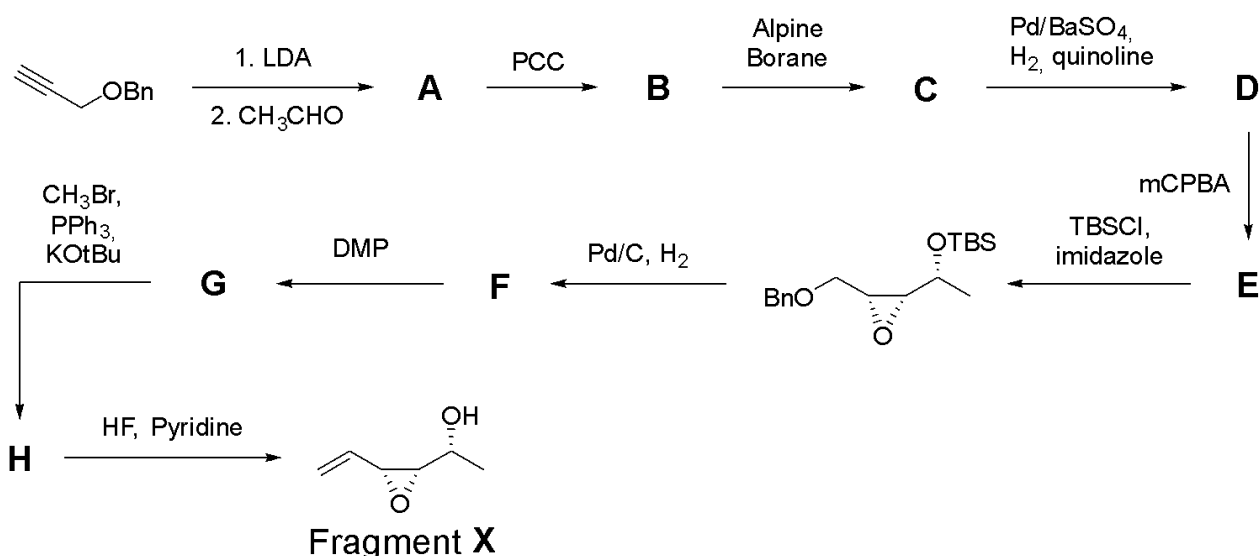
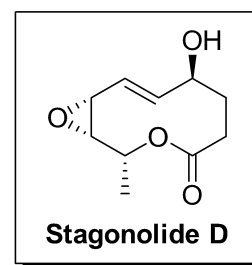
l) Write the expression for the reaction rate for all three mechanisms (using HNO_2 and NH_3 concentrations) and a derivation.

m) Compare the internal Arrhenius activation energies at standard conditions ($T = 25\text{ }^\circ\text{C}$) and decide which of these mechanisms could be correct. Bond dissociation energies:

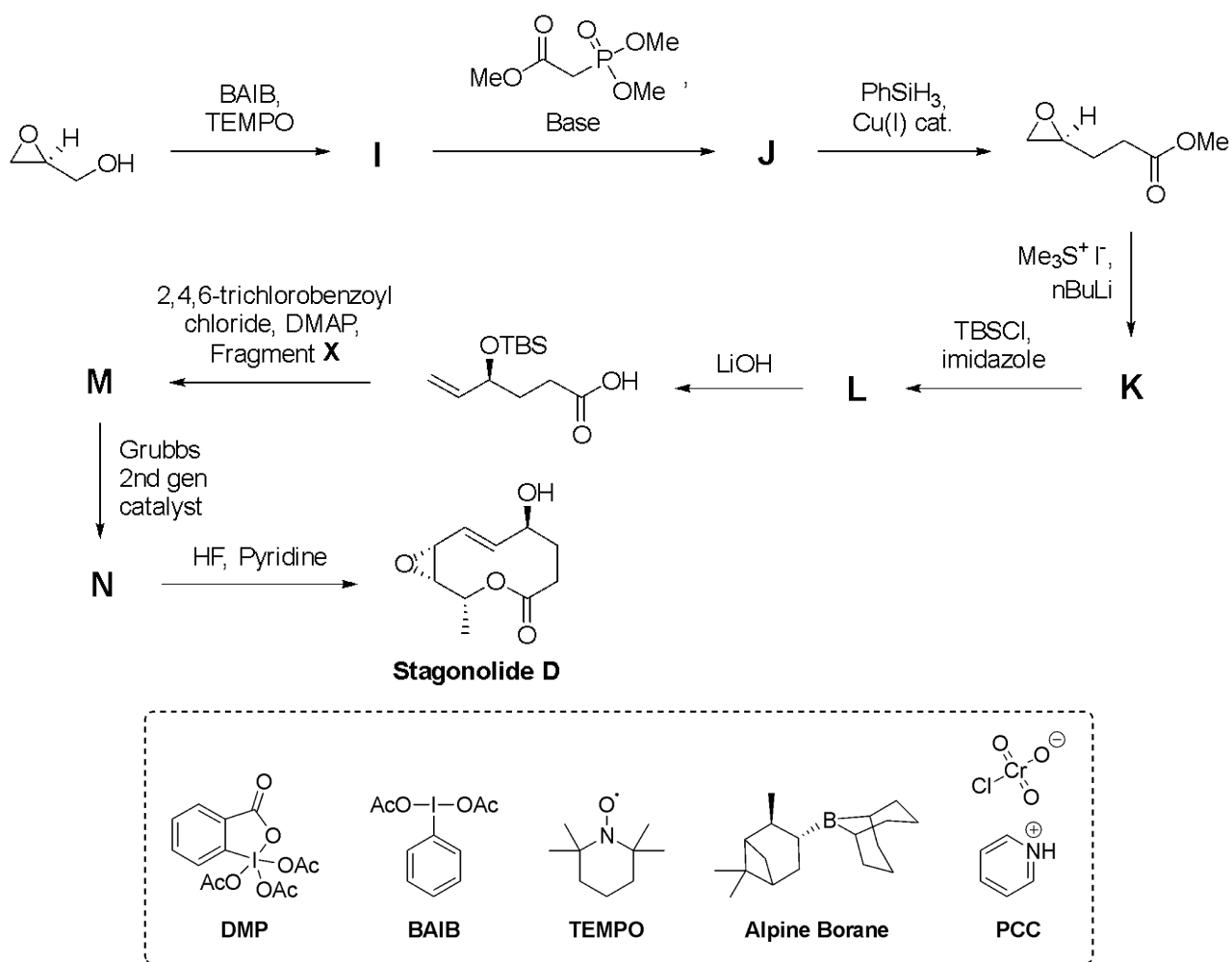
N-H	H-H	N-N	N-O	N=N
391 kJ mol^{-1}	432 kJ mol^{-1}	163 kJ mol^{-1}	201 kJ mol^{-1}	418 kJ mol^{-1}
N=O	O=O	O-H	$\text{N}\equiv\text{N}$	
607 kJ mol^{-1}	495 kJ mol^{-1}	467 kJ mol^{-1}	941 kJ mol^{-1}	

Problem 6 – SYNTH – The synthesis of Stagonolide D

During the last decade, there has been a significant interest in 10-membered cyclic macrolides. One such macrolide is Stagonolide D, which in 2007 was isolated from the fungus *Stagnospora Cirsii*. Stagonolide D produces necrotic lesions on leaves and has shown some herbicidal activity. In this problem, we will discuss the total synthesis of Stagonolide D. In order to make Stagonolide D, we first have to make the fragment X, the synthesis of which is shown below.



The obtained fragment X is further used for the synthesis of the Stagonolide D, as shown below and it employs ring-closing metathesis as the key step.



- Draw the structural formulas of compounds **A–N**. Show the appropriate stereochemistry, where necessary.
- Draw a mechanism for the transformation leading to **K**.
- Draw a mechanism for the transformation **F** → **G**.