25th Baltic Chemistry Olympiad

Vilnius 2017

Theoretical Exam

		Student code:				
1	2	3	4	5	6	

April 30, 2017
Vilnius, Lithuania

Periodic Table

Key:
Atomic number → 1
Atomic weight → 1.00794
Atomic symbol → H
Covalent radius, Å → 0.28

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.00794 0.28																	2 He 4.00260 1.40
2	3 Li 6.941	4 Be 9.01218											5 B 10.811 0.89	6 C 12.011 0.77	7 N 14.0067 0.70	8 O 15.9994 0.66	9 F 18.9984 0.64	10 Ne 20.1797 1.50
3	11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815 1.17	14 Si 28.0855 1.10	15 P 30.9738 1.04	16 S 32.066	17 Cl 35.4527 0.99	18 Ar 39.948 1.80
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.867 1.46	23 V 50.9415 1.33	24 Cr 51.9961 1.25	25 Mn 54.9381 1.37	26 Fe 55.845 1.24	27 Co 58.9332 1.25	28 Ni 58.6934 1.24	29 Cu 63.546 1.28	30 Zn 65.39 1.33	31 Ga 69.723 1.35	32 Ge 72.61 1.22	33 As 74.9216 1.20	34 Se 78.96 1.18	35 Br 79.904 1.14	36 Kr 83.80 1.90
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224 1.60	41 Nb 92.9064 1.43	42 Mo 95.94 1.37	43 Tc (97.905) 1.36	44 Ru 101.07 1.34	45 Rh 102.906 1.34	46 Pd 106.42 1.37	47 Ag 107.868 1.44	48 Cd 112.41 1.49	49 In 114.818 1.67	50 Sn 118.710 1.40	51 Sb 121.760 1.45	52 Te 127.60 1.37	53 I 126.904 1.33	54 Xe 131.29 2.10
6	55 Cs 132.905	56 Ba 137.327	57-71 La-Lu	72 Hf 178.49 1.59	73 Ta 180.948 1.43	74 W 183.84 1.37	75 Re 186.207 1.37	76 Os 190.23 1.35	77 Ir 192.217 1.36	78 Pt 195.08 1.38	79 Au 196.967 1.44	80 Hg 200.59 1.50	81 Tl 204.383 1.70	82 Pb 207.2 1.76	83 Bi 208.980 1.55	84 Po (208.98) 1.67	85 At (210)	86 Rn (222.02) 2.20
7	87 Fr (223)	88 Ra (226.03) 2.25	89-103 Ac-Lr	104 Rf (261.11)	105 Db (262.11)	106 Sg (263.12)	107 Bh (262.12)	108 Hs (265)	109 Mt (266)	110 Ds (271)	111 Rg (272)	112 Cn (285)	113 Nh (284)	114 Fl (289)	115 Mc (288)	116 Lv (293)	117 Ts (294)	118 Og (294)

Lanthanides:

57 La 138.906 1.87	58 Ce 140.115 1.83	59 Pr 140.908 1.82	60 Nd 144.24 1.81	61 Pm (144.91) 1.83	62 Sm 150.36 1.80	63 Eu 151.965 2.04	64 Gd 157.25 1.79	65 Tb 158.925 1.76	66 Dy 162.50 1.75	67 Ho 164.930 1.74	68 Er 167.26 1.73	69 Tm 168.934 1.72	70 Yb 173.04 1.94	71 Lu 174.04 1.72

Actinides:

89 Ac (227.03) 1.88	90 Th 232.038 1.80	91 Pa 231.036 1.56	92 U 238.029 1.38	93 Np (237.05) 1.55	94 Pu (244) 1.59	95 Am (243.06) 1.73	96 Cm (247.07) 1.74	97 Bk (247.07) 1.72	98 Cf (251.08) 1.99	99 Es (252.08) 2.03	100 Fm (257.10)	101 Md (258.10)	102 No (259.1)	103 Lr (260.1)

Constants and Formulae

Avogadro's constant, $N_A = 6.0221 \times 10^{23}$ mol^{-1}

Boltzmann constant, $k_B = 1.3807 \times 10^{-23}$ J K^{-1}

Universal gas constant, $R = 8.3145$ J K^{-1} mol^{-1} = 0.08205 atm L K^{-1} mol^{-1}

Speed of light, $c = 2.9979 \times 10^8$ m s^{-1}

Planck's constant, $h = 6.6261 \times 10^{-34}$ J s

Faraday constant, $F = 9.64853399 \times 10^4$ C

Mass of electron, $m_e = 9.10938215 \times 10^{-31}$ kg

Standard pressure, $P = 1$ bar $= 10^5$ Pa

Atmospheric pressure, $P_{atm} = 1.01325 \times 10^5$ Pa $= 760$ mmHg $= 760$ torr

Zero of the Celsius scale, 273.15 K

1 picometer (pm) $= 10^{-12}$ m; 1 Å $= 10^{-10}$ m; nanometer (nm) $= 10^{-9}$ m

1 eV $= 1.6 \times 10^{-19}$ J

1 amu $= 1.66053904 \times 10^{-27}$ kg

Ideal gas equation: $PV = nRT$

Enthalpy: $H = U - PV$

Gibbs free energy: $G = H - TS$ $\Delta G = \Delta G^o + RT \ln Q$

$$\Delta G^o = -RT \ln K = -nFE^o_{cell}$$

Entropy change: $\Delta S = \dfrac{q_{rev}}{T}$, where q_{rev} is heat for the reversible process

$$\Delta S = nR \ln \frac{V_2}{V_1} \text{ (for isothermal expansion of an ideal gas)}$$

Nernst equation: $E = E^O + \dfrac{RT}{nF} \ln \dfrac{C_{ox}}{C_{red}}$

Energy of a photon: $E = \dfrac{hc}{\lambda}$ Lambert-Beer law: $A = \log \dfrac{I_0}{I} = \varepsilon bC$

Integrated rate law

Zero order $[A] = [A]_0 - kt$ First order $\ln[A] = \ln[A]_0 - kt$

Second order $\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$

 Arrhenius equation

$$k = Ae^{-E_a/RT}$$

General Directions

- Write your name and student code on each page of the answer sheets.

- You have 5 hours to work on the exam problems. **Begin** only when the **START** command is given.

- You must **stop** working when the **STOP** command is given.

- The official English version of this examination is available on request only for clarification.
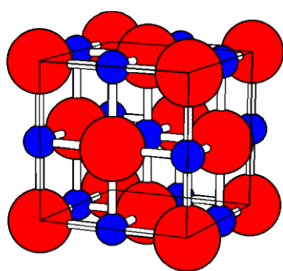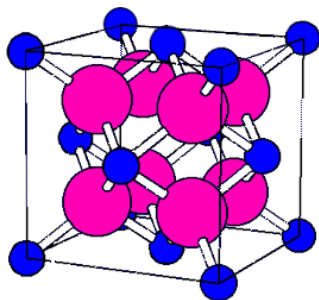
Name_____   **Code**

Problem1. Crystals

8 points

AB	AC$_2$	DB$_2$	ADB$_3$
3,34 g/cm^3	3,18 g/cm^3	4,25 g/cm^3	3,98 g/cm^3
$a = 4,81$ Å	$a = 5,46$ Å	$a = b = 4,59$ Å	$a = 3,84$ Å
		$c = 2,96$ Å	
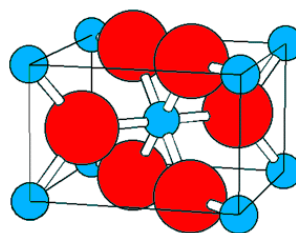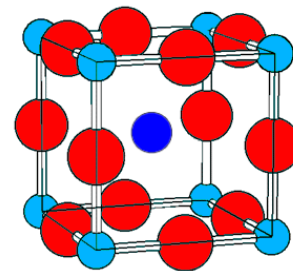
Unit cell, density, and lattice parameter(s) of four crystals are given in picture. Picture with colours will be presented separately.

a) Determine the number of each ion in each unit cell.

	AB	**AC$_2$**	**DB$_2$**	**ADB$_3$**
$n(\mathbf{A})$			–	
$n(\mathbf{B})$		–		
$n(\mathbf{C})$	–		–	–
$n(\mathbf{D})$	–	–		

b) Determine the coordination number (CN) of **A** and **D** in all crystals.

	AB	**AC$_2$**	**DB$_2$**	**ADB$_3$**
CN(**A**)			–	
CN(**D**)	–	–		

c) Calculate the molar mass of each compound.

AB	
AC$_2$	
DB$_2$	
ADB$_3$	

d) Determine elements **A**–**D**.

A	B	C	D

Problem2: Solubility

10 points

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
$E°(Me^{n+}$/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 ($MeI_n(s) \rightarrow Me^{n+}(aq) + nI^-(aq)$) can be roughly estimated using Latimer and Kapustinskii equations:

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

where $A = -610$ kJ Å/mol, $B = -1080$ kJ Å/mol, $r_O = 0,50$ Å, 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, $\Delta H_{hyd}(I^-) = -308$ kJ/mol. Radius of the iodide is 2,06 Å.

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

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

where $C = 88$ J/(mol K), $D = 644$ J Å²/(mol K), $r_{dip} = 1,30$ Å, $E = 12,5$ J/(mol K), M is the molar mass of the cation, $\Delta S_{hyd}(I^-) = -58,1$ J/(mol K).

a) Show with calculations that for CuI $\Delta G_{solv} > 0$, while for CuI_2 $\Delta G_{solv} < 0$.

CuI	
CuI_2	

b) Mark with an X 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. $E°(I_2/I^-) = 0,535$ V.

c) Calculate the standard reduction potential for Fe^{3+}/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 Cu^{2+}/Cu^+ and show that the reduction of I^- to I_2 by Cu^{2+} is spontaneous. $K_{sp}(CuI) = 1,1·10^{-12}$.

Five test tubes **A**–**E** contain 0,1 M aqueous solutions of one of the following substances: $AgNO_3$, $CuSO_4$, $FeCl_3$, $Hg(NO_3)_2$, KI. The results of identification of the particular test tubes by mutual reactions are shown in 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 the tubes **A**–**E** and write balanced chemical equations of the reactions marked in the table (P = precipitate, S = solution).

A	**B**	**C**	**D**	**E**

orange-red P formation	
yellow P and brown S formation	
brown S formation	
yellowish P formation	
white P formation	

Problem 3. Analeptics

9 points

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 centre depression in human brain. Analeptics (breathing stimulators) such as Doxapram could help in such critical situation when injected. Following you will find two synthesis schemes of main components used in Doxapram manufacture.

1) Please complete synthesis schemes by filling in missing parts:

$$A \xrightarrow[\text{light}]{Br_2} \quad \text{(PhCH}_2\text{Br)} \xrightarrow[\text{DMF}]{KCN} B \xrightarrow[110°C]{Br_2} C \xrightarrow[\text{AlCl}_3]{\substack{\text{benzene} \\ \text{DCM}}} \quad \text{(Ph}_2\text{CH-CN)} \quad \text{DMF}$$

A	B	C

$$D \xrightarrow{EtNH_2} E \xrightarrow{SOCl_2} \quad \textbf{E1}$$
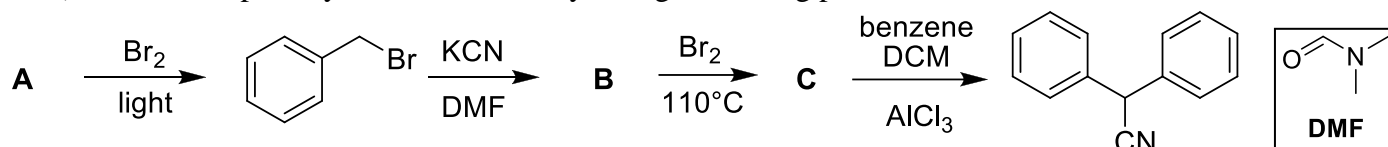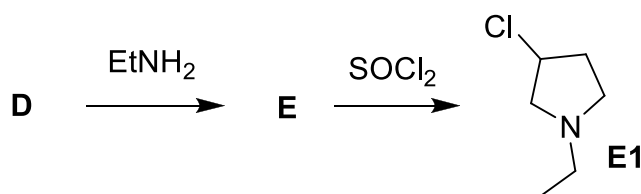
D	E

2) Why is light so important in the first reaction?
   a) Reaction performs faster.
   b) Light generates radicals.
   c) Light makes no influence to the reaction.
   d) a and b correct.
   e) All correct.

3) Would compound **E1** be racemic or not if we used enantiomerically pure **D**?
   a) Yes
   b) No
   c) Compound **E1** has no stereocenters

4) Please complete Doxapram synthesis scheme by filling in missing parts:
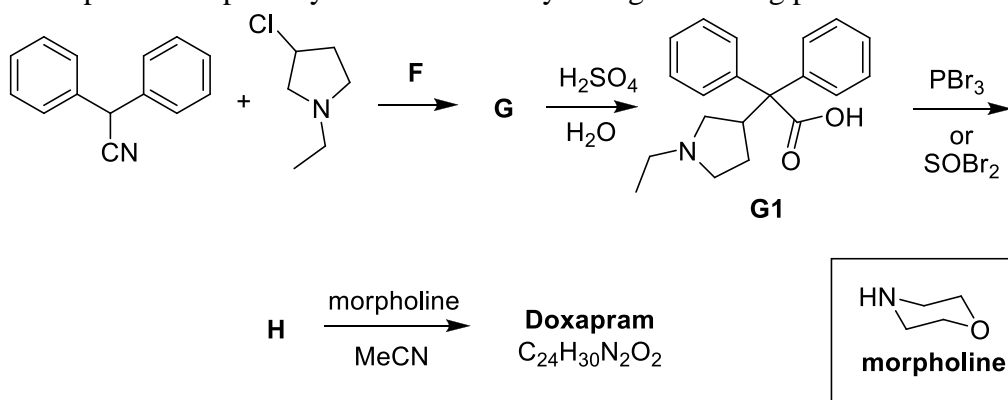
*Compound **H** is not **acidic** and not **basic**.

*In doxapram all carbons attached to N of morpholine are Sp^3.

G	H	Doxapram

5) What are the most suitable conditions **F**:
   a) HCl/MeOH
   b) KOtBu/THF
   c) bees wax and naphtha
   d) BF$_3$·Et$_2$O

6) Draw reaction mechanism **G1 → H**

7) What side products would we get if SOBr$_2$ would be used in **G1 → H** step?

8) Is Doxapram **acidic**, **basic** or **amphoteric** by Lewis (underline correct answer)

9) What type of reaction is **H → Doxapram**?
   a) Sn2
   b) Sn1
   c) E1Cb
   d) SnAr

10) Mark chiral centres with asterisks (if there are any) in all compounds (tasks and your answers).

Problem 4. Nickel knickknackery

<div align="right">**11 points**</div>

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 $NiCl_2 \cdot 6H_2O$. It might be due to 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 odour of which might wake even the heaviest sleeper from the deepest winter hibernation. A colourful metal-ammine complex is formed when the reaction is taking place.

$$NiCl_2 \cdot 6H_2O + 5\,NH_3 \rightarrow [Ni(NH_3)_5(H_2O)]Cl_2 + 5H_2O$$

Several colourful crystals have formed, were filtered, dissolved in 5 mL of water, poured into spectrophotometrical cuvette and placed into 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 colourful crystals in 10,0 mL water and poured this solution into photometric cuvette with 5,00 cm optical pathlength. The device showed, that the solution transmitted only 0,7 % of light. By knowing, that the device is not very accurate at this part of the scale, he transferred the solution from the cuvette into volumetric flask, diluted it to 25,0 mL and again transferred 10,0 mL of this solution to the same photometric cuvette. This time the device showed that 13,5 % of light was transmitted.

4.1. Calculate the molar absorption coefficient of this material:
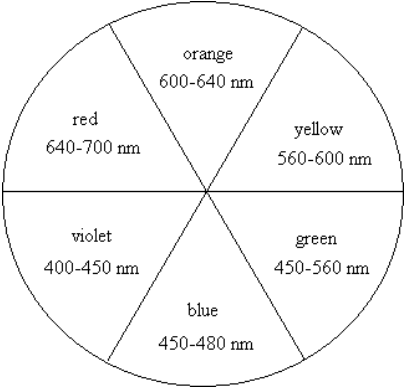
Colour wheel is a simplified, but effective and visual tool to predict the absorbance bands without having to use a spectrophotometer.

<u>4.2.Take a look at Fig 1. Determine and mark the colours of substances A, B and C.</u>

Colour	Substance A	Substance B	Substance C
Red (Red)	◯	◯	◯
Orange (Orange)	◯	◯	◯
Yellow (Yellow)	◯	◯	◯
Green (Green)	◯	◯	◯
Blue (Blue)	◯	◯	◯
Violet (Violet)	◯	◯	◯

Fig. 1 Absorbance spectra of octahedral Ni(II) coordination compounds: A - $[Ni(en)_3]^{2+}$(en – ethylenediamine), B -$[Ni(NH_3)_6]^{2+}$, C - $[Ni(H_2O)_6]^{2+}$,

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

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

Later on, Cheminykas heated the NiCl$_2$ · 6H$_2$O salt to remove water and treated it with dry dimethylammonium chloride to synthesize another compound - ((CH$_3$)$_2$-NH$_2$)$_2$[NiCl$_4$] - bis(dimethylammonium) tetrachloronickelate (II), 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 colour 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 colour if it changed again from blue to yellow (substance F). Even more so, in two weeks it came back to original red colour while being stored at room temperature.

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

4.4. Which of the following statements best describe the colour change of $((CH_3)_2\text{-}NH_2)_2[NiCl_4]$ upon heating?

a) With an increasing temperature, enough energy is passed to material to surpass the activation energy of reforming crystal lattice and formation of more thermodynamically stable $((CH_3)_2\text{-}NH_2)_2[NiCl_4]$ stereoisomer.
b) A decomposition reaction of organic ligands is taking place followed by the change of chemical composition of coordination compound.
c) Because of the increased temperature, hydrogen bonds are weakenend and infinite two-dimensional structure is destroyed, accompanied by the shift from octahedral to tetrahedric coordination geometry.
d) The temperature excites the electrons in Ni^{2+} d orbitals, enabling the electronic transitions within the semiconductor bandgap.

4.5. Draw all possible coordination stereoisomers of $((CH_3)_2\text{-}NH_2)_2[NiCl_4]$. If there are any optically active stereoisomers (enantiomers) – mark them.

4.6. 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 absorbtion band per material is required to draw.
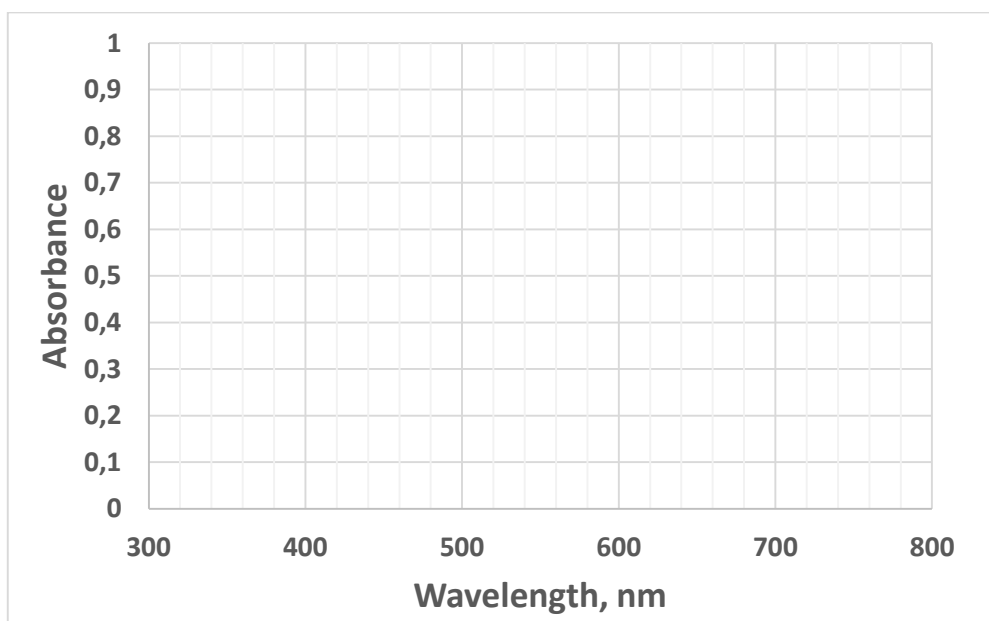
4.7. Which conclusion can we draw from the absorbance spectra above?

Compared with the $((CH_3)_2-NH_2)_2[NiCl_4]$ at thermochromic shift temperature, after cooling to room temperature, the required energy for *d-d* electronic transitions is:

a) Lower than at thermochromic shift temperature
b) Higher than at thermochromic shift temperature
c) Same as at thermochromic shift temperature

Finally Cheminykas decided to treat the thermochromic nickel complex with some bromine and ethylenediamine (H2N-CH2-CH2-NH2, en) which is common bidentate ligand in coordination chemistry. He obtained a compound $[NiBrCl(en)_2]$, coordination number of which is 6.

4.8. Draw all possible coordination stereoisomers of $[NiBrCl(en)_2]$. If there are any optically active stereoisomers (enantiomers) – mark their pairs.

Problem 5. Cleaning oil pipes

11 points

As oil wells are drilled further offshore in deeper water, the phenomenon of paraffin, asphaltene, and hydrate deposition becomes more severe and extensive due to the extremely low temperature of the ocean floor. Removal of wax from wells and pipelines has accounted for significant additional operating costs for example using using deep-sea divers with special equipment who can cut and remove paraffin blockage from a pipeline.

One of the more feasible solutions to the paraffin deposition problem is to melt it. The reaction between ammonium chloride and sodium nitrite has been proposed to design reaction systems.

1. Complete reaction equation (reaction 1):
   $NaNO_2 + NH_4Cl \rightarrow NaCl + H_2O +$ __ ____
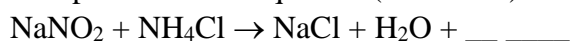
   and calculate standard enthalpy change for reaction, enthalpies of formation are: -359.4 kJ · mol^{-1} for sodium nitrite, -314.43 kJ · mol^{-1} for ammonium chloride, -411.12 kJ · mol^{-1} for sodium chloride and -285.8 kJ · mol^{-1} for water.

2. It is known that reaction 1 equilibrium constant is approximately $K = 10^{60}$. Based on this information and calculations before what can be stated about reaction 1, choose one most correct answer:
   a. reaction is endothermic and reversible;
   b. reaction is exothermic and irreversible;
   c. reaction is endothermic and irreversible;
   d. reaction is exothermic and reversible.

If reaction 1 is planned to use in oil industry, then reaction rate and reaction mechanism should be known. Scientists proposed different mechanisms for this reaction, for example, scientist group I proposed that reaction is second order and rate determining step is the reaction of nitrosyl ion (NO^+) with molecular ammonia (NH_3) while other scientist group II proposed that reaction is a third order with rate determining step attack of N_2O_3, derived from HNO_2, on NH_3.

3. Draw Lewis structures for all compounds or particles mentioned:

NH_3	NO^+	HNO_2	N_2O_3

One more scientist group (abbreviated as scientist group III) repeated and modified experiments done by scientist groups I and II. They took 150 mL of sodium nitrite solution and 150 mL of ammonium chloride solution and mixed both solutions at various temperatures and pH levels (adjusted by adding HCl solution or NaOH solution to reaction mixture). Before reaction apparatus was swept with nitrogen gas to minimize side reactions. Experimental setup for investigation reaction 1 kinetics is shown in figure 1.

Figure 1.

4. Which reactions can be as side reactions in experiment if pH values were in interval from 3 to 7. Choose one or more answers.
   a. $NO + \frac{1}{2} O_2 \rightarrow NO_2$
   b. $2HNO_2 \Leftrightarrow NO_2 + NO + H_2O$
   c. $NH_4Cl + NaOH \rightarrow NH_3 + H_2O + NaCl$ ($pK_a(NH_4^+) = 9{,}25$)
   d. $NaNO_2 + O_2 \rightarrow NaNO_3$

If side reactions are eliminated then reaction 1 rate can be determined from gas formed this reaction volume.

5. Obtain or give rate expression for reaction 1 as function of gas volume, use standard abbreviations for variables.

$$\frac{dC}{dt} = \text{reaction rate} = \ldots$$

Calculated reaction rates at various concentrations of nitrite and ammonium ions were plotted, graph obtained is shown in figure 2 (at 25°C temperature, pH = 5). Use graph provided and determine reaction orders with respect to both reactants.

6. Reaction order with respect to ammonium ions (ammonium chloride) _____
7. Reaction order with respect to ammonium ions (ammonium chloride) _____

8. Determine value and units for reaction rate constant (at 25°C temperature, pH = 5).
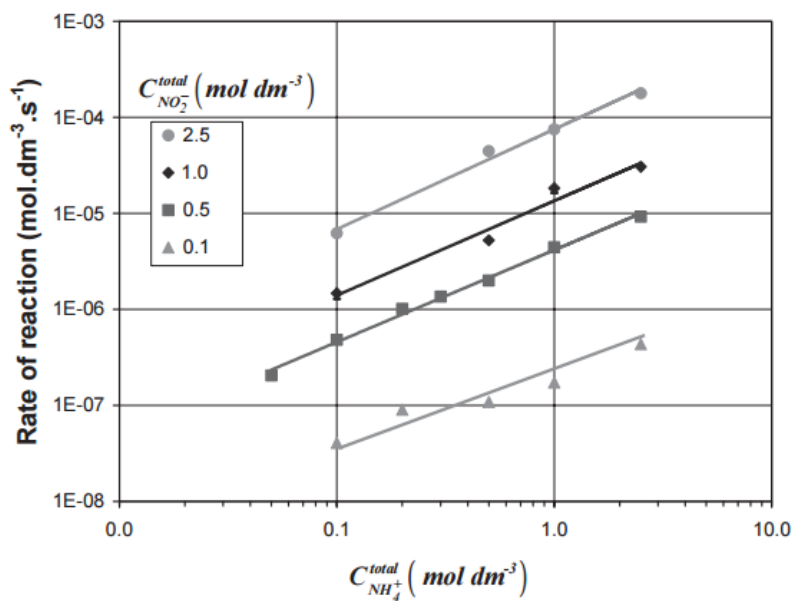
Figure 2.

A temperature range of 4–50°C was used to study the reaction of ammonium chloride with sodium nitrite at an initial concentration of each reactant of 0.5 mol dm^{-3} and pH 4, 5, and 6 as a function of temperature. As expected, the reaction rate follows the Arrhenius equation, corresponding data are provided in figure 3
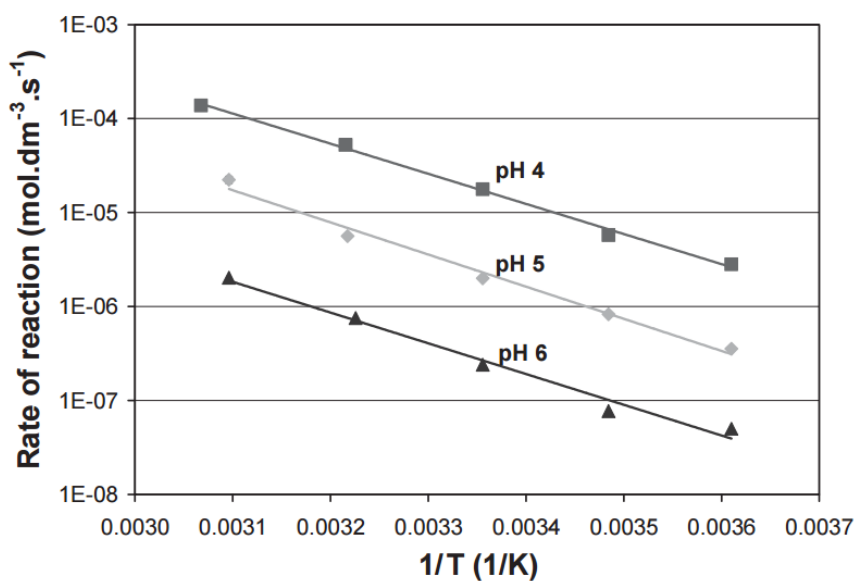
Figure 3.

9. Determine activation energy form data provided.

Scientist group III continued their studies with aim to determine reaction mechanism. They firstly postulated that an intermediate that can form the two final products N_2 and H_2O in the fast step, then propose different reaction pathways to form the intermediate from the two true reactants, NH_3 and HNO_2 or its derivatives. It is believed that nitrosamine $H_2N-N=O$ is the most plausible intermediate which proceeds to the final two products.

10. Propose mechanism for decomposition of nitrosamine

There are several ways for formation of nitrosamine from initial reactants. One way to investigate the feasibility of a possible formation pathway is to compare its intrinsic Arrhenius (E^*) activation energy with the experimental Arrhenius activation energy (E) obtained from kinetics study.

The intrinsic Arrhenius activation energy can be obtained from molecular modelling

$$E^* = \Delta H^* + RT$$

where ΔH^*- enthalpy change in the slowest step.

If you did not calculate activation energy in 9 part, assume it is 60 kJ·mol^{-1}.

11. There has been proved that $HNO_{2(aq)}$ are in equilibrium with N_2O_3, NO and NO_2. Write reaction equations shoving equilibrium existing.

Scientists proposed multiple mechanisms for production of nitrosamine. Three of them are shown below in table:
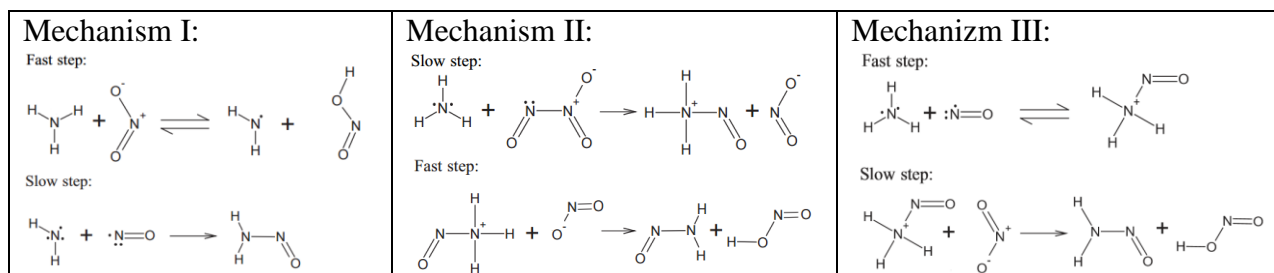
Mechanism I:	Mechanism II:	Mechanizm III:
Fast step:	Slow step:	Fast step:
Slow step:	Fast step:	Slow step:

12. Write rate expression for each mechanism in terms of concentrations of HNO_2 and NH_3. Show your calculations. Comment on mechanism – does it correspond to reaction.

Mechanizm I

Mechanizm II

Mechanizm III

13. Which of these mechanisms could be the correct one comparing intrinsic Arrhenius activation
energies at standard conditions (25°C)?

Bond enthalpies:

N-H	391 kJ · mol^{-1}	H-H	432 kJ · mol^{-1}	N-N	163 kJ · mol^{-1}
N-O	201 kJ · mol^{-1}	N=N	418 kJ · mol^{-1}	N=O	607 kJ · mol^{-1}
O=O	495 kJ · mol^{-1}	O-H	467 kJ · mol^{-1}	N≡N	941 kJ· mol^{-1}

Problem 6. The synthesis of Stagonolide D

11 points

During the last decade there has been a singificant interest in 10-membered cyclic macrolides. One such macrolide is the Stagonolide D, which in 2007 was isolated from 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.
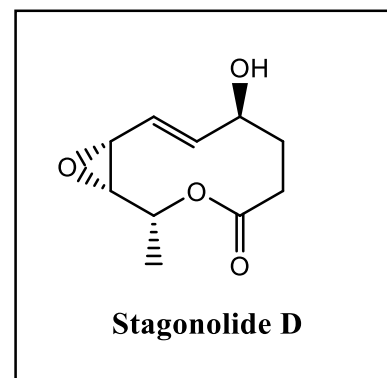
Stagonolide D

In order to make Stagonolide D, we first have to make the fragment **X**, the synthesis of which is shown below.
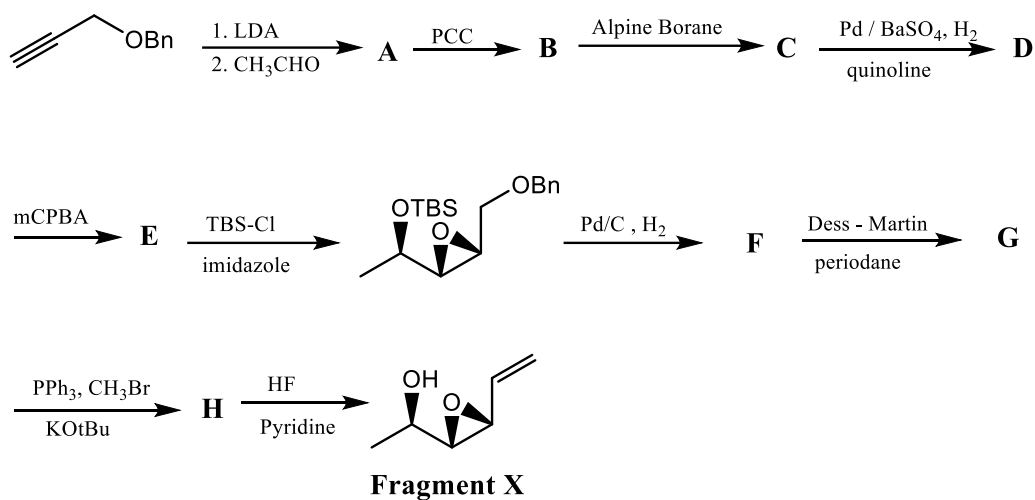
Fragment X

The obtained fragment is further used for the synthesis of the Stagonolide D, as shown below and employs Ring Closing Methathesis as the key step.
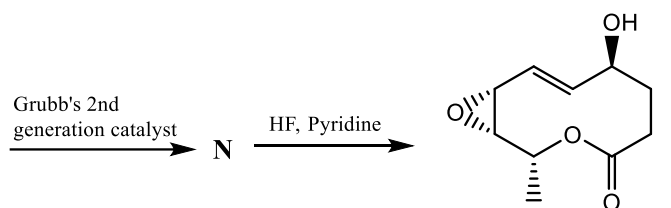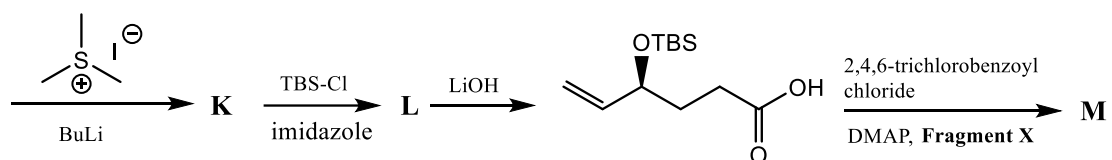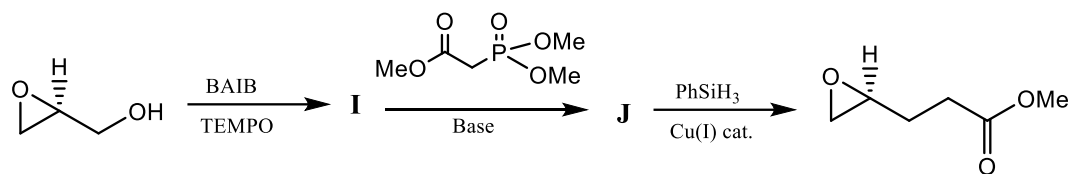
Stagonolide D

Reagents and abreviations

Dess - Martin periodane ≡

Alpine Borane ≡
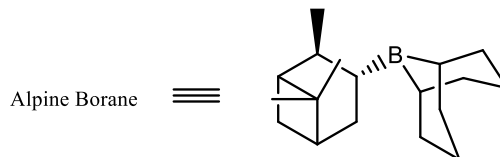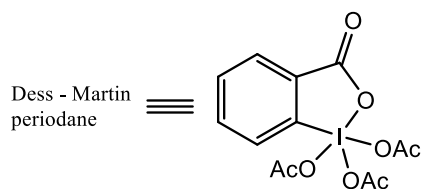
PCC - pyridinium chlorochromate
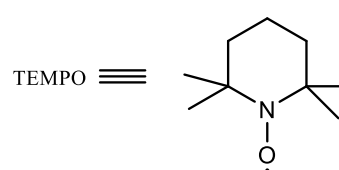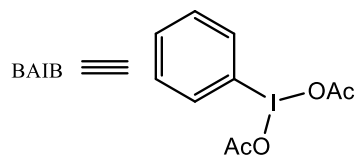
BAIB ≡

TEMPO ≡

1. Deduce the structures **A – N**. Show the appropriate stereochemistry, where necessary.

A	B	C
D	E	F
G	H	I
J	K	L

M	N

2. Provide a mechanism for the transformation leading to **K**.

$$\text{epoxide-CH}_2\text{CH}_2\text{-C(=O)-OMe} \xrightarrow[\text{BuLi}]{\text{(CH}_3)_2\text{S}^{+}\text{-CH}_2^{-}} \textbf{K}$$
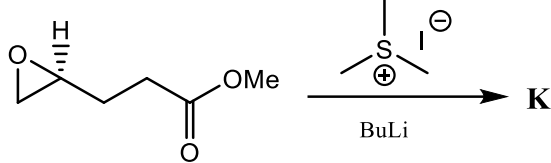
3. Provide a mechanism for the transformation **F -> G**.

Problem1. Crystals (solutions)

a)

		AB	**AC$_2$**	**DB$_2$**	**ADB$_3$**
$n(\mathbf{A})$		4	4	–	1
$n(\mathbf{B})$		4	–	4	3
$n(\mathbf{C})$		–	8	–	–
$n(\mathbf{D})$		–	–	2	1

b)

	AB	**AC$_2$**	**DB$_2$**	**ADB$_3$**
CN($\mathbf{A}$)	6	8	–	X
CN($\mathbf{D}$)	–	–	6	6

c) $M(\text{AB}) = \frac{1}{4} \cdot 3{,}34 \text{ g/cm}^3 \cdot 6{,}022 \cdot 10^{23} \text{ mol}^{-1} \cdot \left(4{,}81 \cdot 10^{-8} \text{ cm}\right)^3 = 56{,}0 \text{ g/mol}$

$M(\text{AC}_2) = \frac{1}{4} \cdot 3{,}18 \text{ g/cm}^3 \cdot 6{,}022 \cdot 10^{23} \text{ mol}^{-1} \cdot \left(5{,}46 \cdot 10^{-8} \text{ cm}\right)^3 = 78{,}0 \text{ g/mol}$

$M(\text{DB}_2) = \frac{1}{2} \cdot 4{,}24 \text{ g/cm}^3 \cdot 6{,}022 \cdot 10^{23} \text{ mol}^{-1} \cdot \left(4{,}59 \cdot 10^{-8} \text{ cm}\right)^2 \cdot 2{,}96 \cdot 10^{-8} \text{ cm}$

$M(\text{DB}_2) = 79{,}9 \text{ g/mol}$

$M(\text{ADB}_3) = 3{,}98 \text{ g/cm}^3 \cdot 6{,}022 \cdot 10^{23} \text{ mol}^{-1} \cdot \left(3{,}84 \cdot 10^{-8} \text{ cm}\right)^3 = 136 \text{ g/mol}$

d) $\mathbf{A} = \text{Ca}$
$\mathbf{B} = \text{O}$
$\mathbf{C} = \text{F}$
$\mathbf{D} = \text{Ti}$

Problem2: Solubility (solutions)

a) **CuI**

$$\Delta H_{solv}\left(Cu^+\right) = -610 \cdot \frac{1^2}{0,77+0,50} + 1080 \cdot \frac{2 \cdot 1 \cdot 1}{0,77+2,06} - 308 = -25 \text{ kJ/mol}$$

$$\Delta S_{solv}\left(Cu^+\right) = 88 - 644 \cdot \frac{1}{(0,77+1,30)^2} - 12,5 \cdot ln63,5 - 58,1 = -172 \text{ J/(mol K)}$$

$$\Delta G_{solv}\left(Cu^+\right) = -25 \text{ kJ/mol} + 298 \text{ K} \cdot 0,172 \text{ kJ/(mol K)} = 26 \text{ kJ/mol} > 0$$

CuI₂

$$\Delta H_{solv}(CuI_2) = -610 \cdot \frac{2^2}{0,73+0,50} + 1080 \cdot \frac{3 \cdot 2 \cdot 1}{0,73+2,06} - 308 \cdot 2 = -277 \text{ kJ/mol}$$

$$\Delta S_{solv}(CuI_2) = 88 - 644 \cdot \frac{2}{(0,73+1,30)^2} - 12,5 \cdot ln63,5 - 58,1 \cdot 2 = -393 \text{ J/(mol K)}$$

$$\Delta G_{solv}(CuI_2) = -277 \text{ kJ/mol} + 298 \text{ K} \cdot 0,393 \text{ kJ/(mol K)} = -160 \text{ kJ/mol} < 0$$

b) **HgI₂**
PbI₂
AgI
HgI

Solvation entropy change is negative for all studied iodides. We may assume that solvation enthalpy change is negative. Thus, for salts insoluble in water, $\Delta H_{solv} - T\Delta S_{solv} > 0$ and $|\Delta H_{solv}| < T\Delta S_{solv}$. Taking into account that $\Delta H_{solv} = \Delta H_{hyd} - \Delta H_{lat}$, where $\Delta H_{hyd} \sim -A/(r_+ + r_O)$, $\Delta H_{latt} \sim -B/(r_+ + r_-)$, $r_- > r_O$, and $|B| > |A|$ we may conclude that ΔH_{solv} decreases with increasing r_+. Therefore, AgI and HgI are less soluble than CuI as Ag^+ and Hg^+ have larger radii. Similarly, Hg^{2+} and Pb^{2+} have much larger radii than other divalent metal ions. Note that $|\Delta S_{solv}| \sim 1/r_+^2$, yet the decrease in absolute entropy change is compensated by the $E \cdot lnM$ term which is larger for heavier Hg^{2+} and Pb^{2+} ions. Estimated ΔH_{solv}, ΔS_{solv} and ΔG_{solv} are:

	Fe^{3+}	Fe^{2+}	Cu^{2+}	Cu^+	Zn^{2+}	Hg^{2+}	Pb^{2+}	Ag^+	Hg^+
ΔH_{solv}	−1187	−387	−277	−25	−269	−79	−66	−5	−4
ΔS_{solv}	−701	−432	−393	−172	−390	−311	−303	−136	−140
ΔG_{solv}	−978	−259	−160	**26**	−153	**14**	**24**	**36**	**37**

c) $E°(Fe^{3+}/Fe^{2+}) = [3E°(Fe^{3+}/Fe^0) − 2E°(Fe^{2+}/Fe^0)]/(3 − 2) = \mathbf{0{,}78 \text{ V}}$

$2Fe^{3+} + 2I^- = 2Fe^{2+} + I_2$
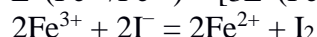
$\Delta E = E°(Fe^{3+}/Fe^{2+}) − E°(I_2/I^-) = 0{,}245 \text{ V}$

$\Delta G = −nF \cdot \Delta E < 0$, thus the reaction **is spontaneous**.

d) $E°(Cu^{2+}/Cu^+) = [2E°(Cu^{2+}/Cu^0) − E°(Cu^+/Cu^0)]/(2 − 1) = \mathbf{0{,}16 \text{ V}}$
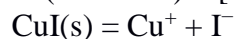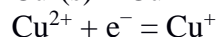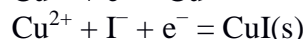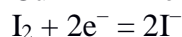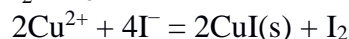
$CuI(s) = Cu^+ + I^-$	$\Delta G_1 = −RT \cdot lnK_{sp}$
$Cu^{2+} + e^- = Cu^+$	$\Delta G_2 = −FE°(Cu^{2+}/Cu^+)$
$Cu^{2+} + I^- + e^- = CuI(s)$	$\Delta G_3 = \Delta G_2 − \Delta G_1$
$I_2 + 2e^- = 2I^-$	$\Delta G_4 = −2FE°(I_2/I^-)$
$2Cu^{2+} + 4I^- = 2CuI(s) + I_2$	$\Delta G_5 = 2\Delta G_3 − \Delta G_4 = 2(\Delta G_2 − \Delta G_1) − \Delta G_4$

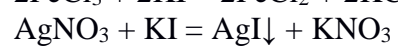$\Delta G_5 = −2FE°(Cu^{2+}/Cu^+) + 2RT \cdot lnK_{sp} + 2FE°(I_2/I^-) = \mathbf{−64 \text{ kJ/mol}}$
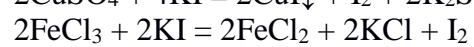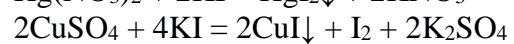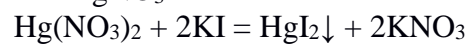
$\Delta G_5 = < 0$, thus the reaction **is spontaneous**. Precipitation of Cu^+ as CuI is the key step of the reaction as it practically removes the product Cu^+ from the solution, driving the reaction in the forward direction.

e) **A** = KI
B = Hg(NO₃)₂
C = CuSO₄
D = FeCl₃

E = $AgNO_3$

$Hg(NO_3)_2 + 2KI = HgI_2\downarrow + 2KNO_3$

$2CuSO_4 + 4KI = 2CuI\downarrow + I_2 + 2K_2SO_4$

$2FeCl_3 + 2KI = 2FeCl_2 + 2KCl + I_2$

$AgNO_3 + KI = AgI\downarrow + KNO_3$

$FeCl_3 + 3AgNO_3 = 3AgCl\downarrow + Fe(NO_3)_3$
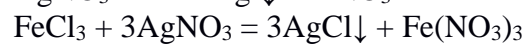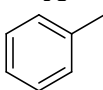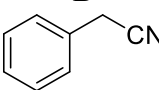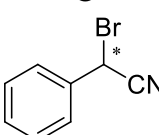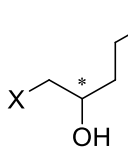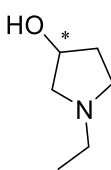
Problem 3. Analeptics (solutions)

1)

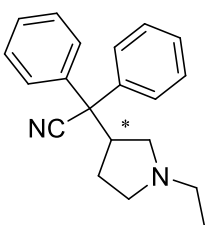| A	B	C
(toluene structure)	(benzyl cyanide, CN)	(Br, phenyl, *CN structure)
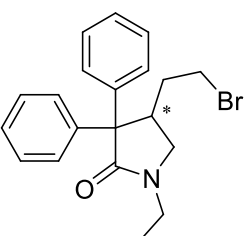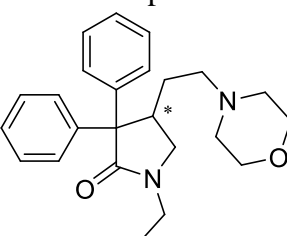
D	E	
X, X-Br or any good leaving group (OMs, OTf, I, etc.), *, OH structure	HO, *, N-ethyl pyrrolidine structure	

2) d

3) No

4)

G	H	Doxapram
(diphenyl, NC, *, N-ethyl pyrrolidine structure)	(diphenyl, *, Br, N-ethyl lactam structure)	(diphenyl, *, morpholine, N-ethyl lactam structure)

5) b

6)

7) SO₂ ir HBr

8) basic

9) a

10)

E   E1   D   **G1**
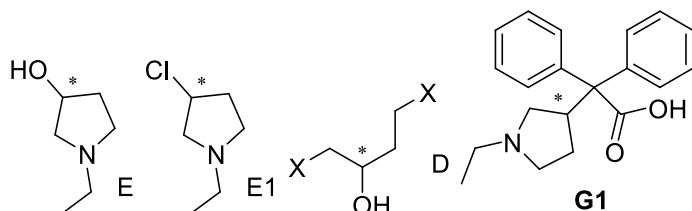
Problem 4. Nickel knickknackery (solutions)

1.1. <u>Calculate the molar absorption coefficient of this material:</u>

M ($[Ni(NH_3)_5H_2O]Cl_2$) = 232.77 g/mol
n = m / M = 0.2017 / 232.77 = 0.00086652 mol
A = -lg(T/100) = -lg(0.135) = 0.8697
$$\varepsilon = \frac{A}{c \times l} = \frac{A\,V}{l\,n} = \frac{0.8697 \times 25\ mL}{5\ cm \times 0.00086652\ mol} = \boxed{5.01\ \text{L mol}^{-1}\ \text{cm}^{-1}}\ (answer)$$

1.2. <u>Take a look at Fig 1. Determine and mark the colours of substances A, B and C.</u>

Colour	Substance A	Substance B	Substance C
Red (Red)	○	○	○
Orange (Orange)	○	○	○
Yellow (Yellow)	○	○	○
Green (Green)	○	○	●
Blue (Blue)	○	●	○
Violet (Violet)	●	○	○

1.3. <u>Calculate the difference between $^3T_{1g}$ (F) $\leftarrow$ $^3A_{2g}$ transition energies of $[Ni(H_2O)_6]^{2+}$ (substance A) and $[Ni(NH_3)_6]^{2+}$ (substance B), providing an answer in electronvolts (eV).</u>

$\lambda_{max}(A)$ = 550 nm
$\lambda_{max}(B)$ = 580 nm
$$E_A = \frac{h\,c}{\lambda} = \frac{6.6261 \times 10^{-34}\,J\ s \times 2.9979 \times 10^8\,m\ s^{-1}}{5{,}50 \times 10^{-7}\,m} = 3.612 \times 10^{-19}J$$
$$E_B = \frac{h\,c}{\lambda} = \frac{6.6261 \times 10^{-34}\,J\ s \times 2.9979 \times 10^8\,m\ s^{-1}}{5{,}80 \times 10^{-7}\,m} = 3.425 \times 10^{-19}J$$
$$\Delta E = E_A - E_B = 3.612 \times 10^{-19}J - 3.425 \times 10^{-19}J = 1.868 \times 10^{-20}J$$
$$\Delta E = 1.868 \times 10^{-20}J \div 1.6 \times 10^{-19} eV \times J^{-1} = \boxed{0.117\ eV}\ (answer)$$

1.4. Which of the following statements best describe the colour change of $((CH_3)_2\text{-}NH_2)_2[NiCl_4]$ upon heating?

e) With an increasing temperature, enough energy is passed to material to surpass the activation energy of reforming crystal lattice and formation of more thermodynamically stable $((CH_3)_2\text{-}NH_2)_2[NiCl_4]$ stereoisomer.

f) A decomposition reaction of organic ligands is taking place followed by the change of chemical composition of coordination compound.

g) Because of the increased temperature, hydrogen bonds are weakened and infinite two-dimensional structure is destroyed, accompanied by the shift from octahedral to tetrahedric coordination geometry.

h) The temperature excites the electrons in Ni^{2+} *d* orbitals, enabling the electronic transitions within the semiconductor bandgap.

1.5. Draw all possible coordination stereoisomers of $((CH_3)_2\text{-}NH_2)_2[NiCl_4]$. If there are any optically active stereoisomers (enantiomers) – mark them.

Only one possible stereoisomer
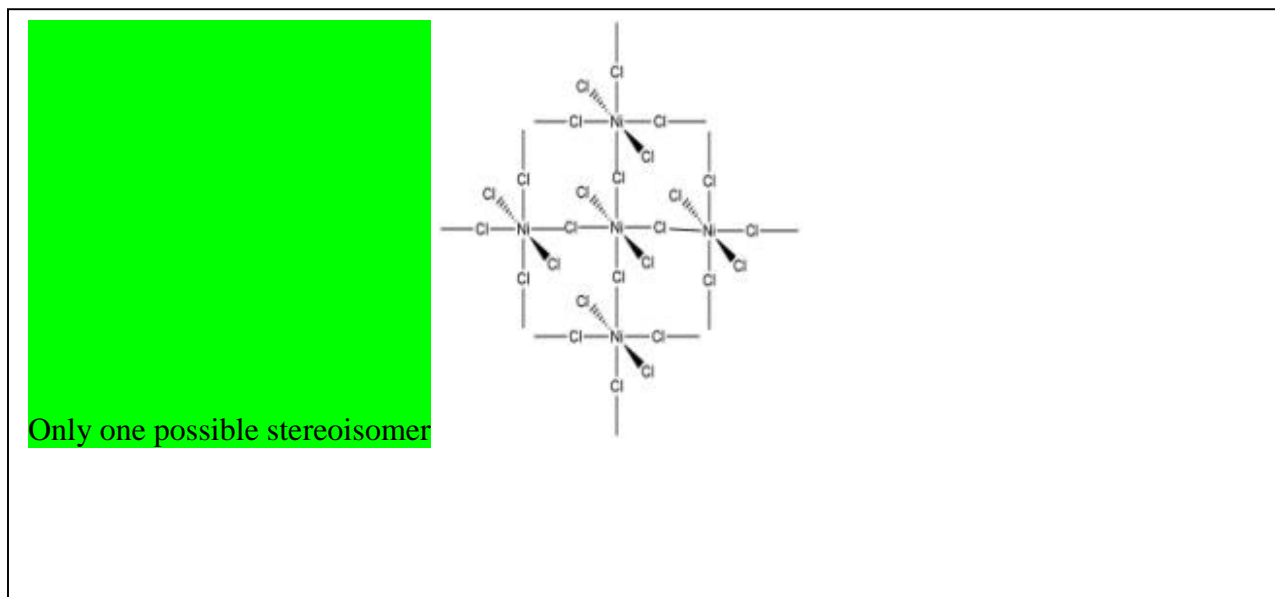
1.6. Schematically depict the absorbance spectra of thermochromic nickel coordination compound before heating (substance D), at thermochromic shift temperature (substance E) and after cooling back to room temperature (substance F). Only one absorption band per material is required to draw.
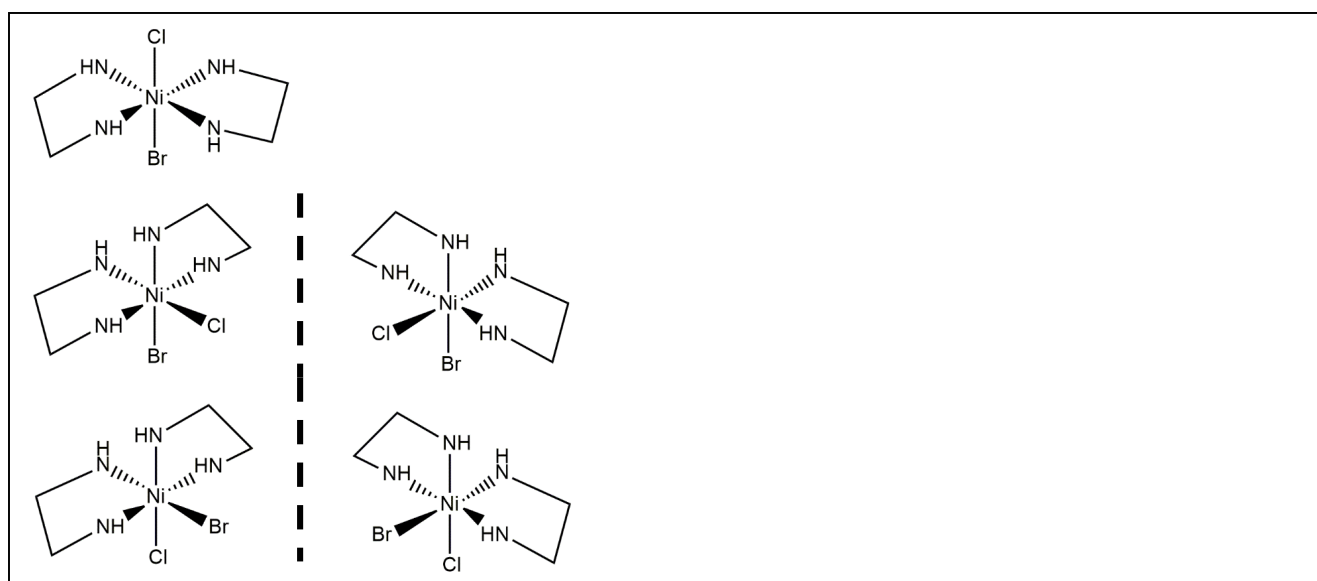
Code
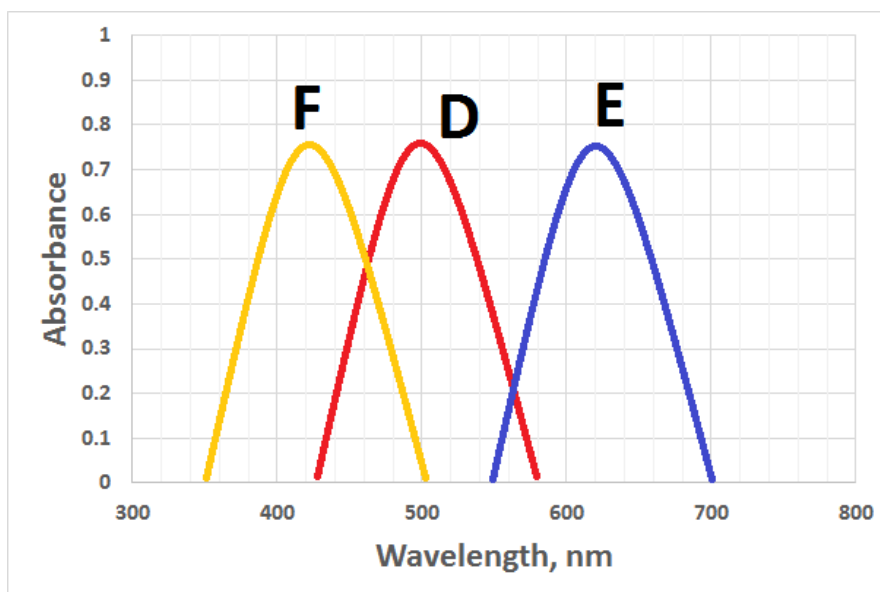
1.7. Which conclusion can we draw from the absorbance spectra above?

Compared with the $((CH_3)_2-NH_2)_2[NiCl_4]$ at thermochromic shift temperature, after cooling to room temperature, the required energy for *d-d* electronic transitions is:

d) Lower than at thermochromic shift temperature
e) Higher than at thermochromic shift temperature (yellow colour, therefore absorbs shorter wavelengths)
f) Same as at thermochromic shift temperature

Finally Cheminykas decided to treat the thermochromic nickel complex with some bromine and ethylenediamine (H2N-CH2-CH2-NH2, en) which is common bidentate ligand in coordination chemistry. He obtained a compound $[NiBrCl(en)_2]$, coordination number of which is 6.

1.8. Draw all possible coordination stereoisomers of $[NiBrCl(en)_2]$. If there are any optically active stereoisomers (enantiomers) – mark their pairs.

Problem 5. Cleaning oil pipes (solutions)

This task is based on scientific publication:
Ngugen D.A., Iwaniw M.A., Fogler H.S. Kinetics and mechanism of reaction between ammonium and nitrite ions: experimental and theoretical studies, *Chemical Engineering Science*, 58, 2003, 4351-4362
http://www.sciencedirect.com/science/article/pii/S0009250903003178

1. Complete and balance reaction equation (reaction 1):
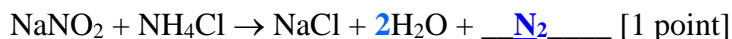
   $NaNO_2 + NH_4Cl \rightarrow NaCl + \mathbf{2}H_2O + \underline{\quad \mathbf{N_2} \quad}$ [1 point]
   and calculate standard enthalpy change for reaction, enthalpies of formation are: -359.4 kJ · mol^{-1} for sodium nitrite, -314.43 kJ · mol^{-1} for ammonium chloride, -411.12 kJ · mol^{-1} for sodium chloride and -285.8 kJ · mol^{-1} for water.
   $\Delta H_{rx} = \Delta H_f(NaCl) + 2*\Delta H_f(H_2O) + \Delta H_f(N_2) - \Delta H_f(NaNO_3) - \Delta H_f(NH_4Cl) =$
   $= 2*(-285.8) -411.12 + 0 + 359.4 + 314.43 = \mathbf{-309\ kJ}$
   Other comments: kJ/mol as units also accepted; if coefficients are ignored, then -23.09 kJ, 0.25 point (except ECF (error carried forward) from 1st part of question), if wrong answer but correct expression, then 0.5 points

2. It is known that reaction 1 equilibrium constant is approximately $K = 10^{60}$. Based on this information and calculations before what can be stated about reaction 1, choose one most correct answer:
   a. reaction is endothermic and reversible;
   b. **reaction is exothermic and irreversible**; (correct answer), 1 point.
   c. reaction is endothermic and irreversible; (correct answer if answer in question 1 is positive, no double punishment), 1 point.
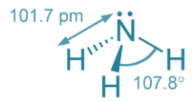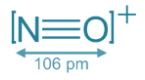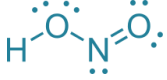   d. reaction is exothermic and reversible.

If reaction 1 is planned to use in oil industry, then reaction rate and reaction mechanism should be known. Scientists proposed different mechanisms for this reaction, for example, scientist group I proposed that reaction is second order and rate determining step is the reaction of nitrosyl ion (NO^+) with molecular ammonia (NH_3) while other scientist group II proposed that reaction is a third order with rate determining step attack of N_2O_3, derived from HNO_2, on NH_3.

3. Draw Lewis structures for all compounds or particles mentioned, if there are resonance structures, then draw them: (0.5 points for each structure, 0.25 if there is only one resonance structure)

NH_3	NO^+	HNO_2	N_2O_3
	 particle :N$^{(+)}$=Ö: is not accepted as it does not correspond to octet rule	 no resonance structures, H-O-N=O and O=N-O-H are not resonance structures as "atoms move" but in resonance structures atoms do not change their positions (no penalty for this)	

One more scientist group (abbreviated as scientist group III) repeated and modified experiments done by scientist groups I and II. They took 150 mL of sodium nitrite solution and 150 mL of ammonium chloride solution and mixed both solutions at various temperatures and pH levels (adjusted by adding HCl solution or NaOH solution to reaction mixture). Before reaction apparatus was swept with nitrogen gas to minimize side reactions. Experimental setup for investigation reaction 1 kinetics is shown in figure 1.

4. Which reactions can be as side reactions in experiment if pH values were in interval from 3 to 7. Choose one or more answers.
   a. $NO + ½ O_2 \rightarrow NO_2$ (correct answer)
   b. $2HNO_2 \Leftrightarrow NO_2 + NO + H_2O$ (correct answer)
   c. $NH_4Cl + NaOH \rightarrow NH_3 + H_2O + NaCl$ ($pK_a(NH_4^+) = 9,25$)
   d. $NaNO_2 + ½O_2 \rightarrow NaNO_3$

   Each correct answer will give 1 point, each incorrect answer stated as correct gives minus 0.5 points, but not less than 0 for this question.

If side reactions are eliminated then reaction 1 rate can be determined from gas formed this reaction volume.

5. Obtain or give rate expression for reaction 1 as function of gas volume, use standard abbreviations for variables.

$$\frac{dC}{dt} = \text{reaction rate} = \ldots$$

Answer: reaction rate $= \dfrac{1}{V_{solution}} \dfrac{d\,n(N_2)}{dt} = \dfrac{p(N_2)}{R \cdot T(N_2) \cdot V_{solution}} \dfrac{d\,V(N_2)}{dt}$

2 points

Calculated reaction rates at various concentrations of nitrite and ammonium ions were plotted, graph obtained is shown in figure 2 (at 25ºC temperature, pH = 5). Use graph provided and determine reaction orders with respect to both reactants.

6. Reaction order with respect to ammonium ions (ammonium chloride) __1__ 1 point
7. Reaction order with respect to nitrite ions (nitrous acid..)__2__ 1 point

8. Determine value and units for reaction rate constant (at 25°C temperature, pH = 5).

Numerical value of reaction rate constant is equal to reaction rate when concentrations of reactants are 1 mol dm^{-3}, it is **1…3 * 10^{-5}**. (1 point)
Units: **L^2 / (mol$^2 \times$ s)** (1 point for units)
Comment: Calculated rate constant and units must correspond to reaction order determined in questions 6 and 7. If question 6 or 7 is wrong, then no penalty for ECF.

A temperature range of 4–50°C was used to study the reaction of ammonium chloride with sodium nitrite at an initial concentration of each reactant of 0.5 mol dm^{-3} and pH 4, 5, and 6 as a function of temperature. As expected, the reaction rate follows the Arrhenius equation, corresponding data are provided in figure 3.

9. Determine activation energy form data provided.

As all three experiments give Arrhenius plot with similar slope we can choose one:
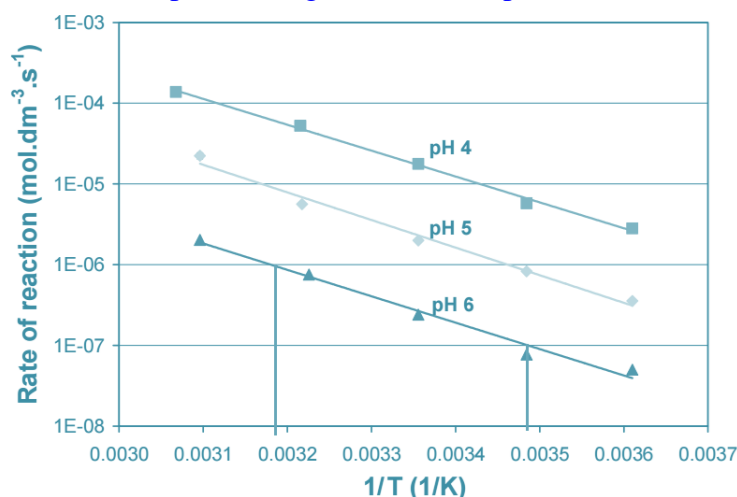
$| \text{tg } \alpha | = (\ln (1*10^{-6}) - \ln(1*10^{-7})) / (0,00348 - 0,00318) = \sim 7600$
$E = | \text{tg } \alpha | \times R = $ **64 kJ/mol**
Comments: Any number in range 64 ± 4 kJ/mol gives 2 points, in range 64 ± 10 kJ/mol gives 1 point; additional 0.5 points are given for units.

Scientist group III continued their studies with aim to determine reaction mechanism. They firstly postulated that an intermediate that can form the two final products N_2 and H_2O in the fast step, then propose different reaction pathways to form the intermediate from the two true reactants, NH_3 and HNO_2 or its derivatives. It is believed that nitrosamine $H_2N-N=O$ is the most plausible intermediate which proceeds to the final two products.

10. Propose mechanism for decomposition of nitrosamine.
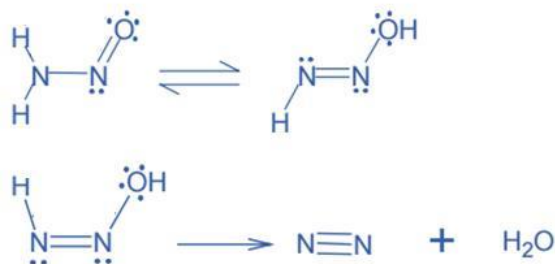
Comment: any mechanism with <u>more than one step</u> without electron transitions or with quite realistic electron transitions was accepted. Mechanism were awarded with 3 points.

38

There are several ways for formation of nitrosamine from initial reactants. One way to investigate the feasibility of a possible formation pathway is to compare its intrinsic Arrhenius (E^*) activation energy with the experimental Arrhenius activation energy (E) obtained from kinetics study. Assume activation energy of reaction as 60 kJ/mol if you were not able to calculate it in question 9.

The intrinsic Arrhenius activation energy can be obtained from molecular modelling

$$E^* = \Delta H^* + RT$$

where ΔH^*- enthalpy of formation for transition state.

11. There has been proved that $HNO_{2(aq)}$ are in equilibrium with N_2O_3, NO and NO_2. Write reaction equations shoving equilibrium existing.

$$2HNO_2 \Leftrightarrow N_2O_3 + H_2O$$
$$N_2O_3 \Leftrightarrow NO + NO_2$$

Comment: there should be equilibrium between acid and nitrogen(III) oxide and second equilibrium between three oxides. 1 point for each equation.

Scientists proposed multiple mechanisms for production of nitrosamine. Three of them are shown below in table:
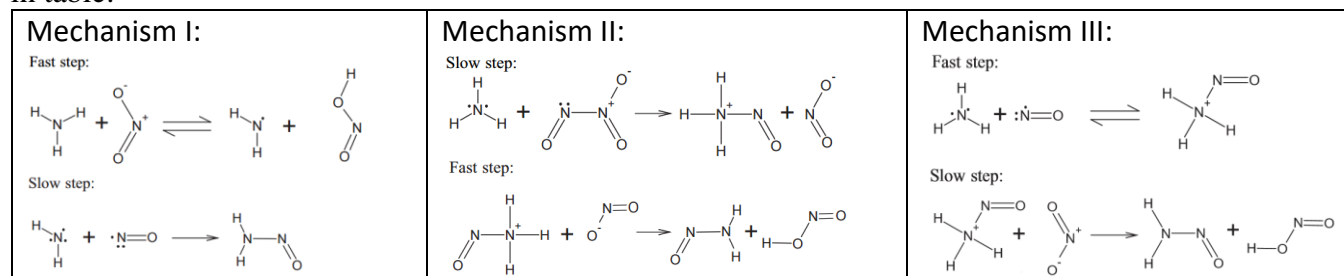
12. Write rate expression for each mechanism in terms of concentrations of HNO_2 and NH_3. Show your calculations. Comment on mechanism – does it correspond to reaction.

Mechanism I:
rate = k * $[NH_2]$ * [NO] (slow step)
equilibrium constant for fast step K_{fast} = $[NH_2][HNO_2]$ / $[NH_3][NO_2]$
form reactions in question 11:
K_1 = $[N_2O_3]$ / $[HNO_2]^2$
K_2 = $[NO][NO_2]$ / $[N_2O_3]$
[NO] = K_2 * $[N_2O_3]$ / $[NO_2]$
$[NH_2]$ = K_{fast} * $[NH_3][NO_2]$ / $[HNO_2]$
$[N_2O_3]$ = K_1 * $[HNO_2]^2$
Substitution leads to:
[NO] = K_2 * $[N_2O_3]$ / $[NO_2]$ = K_2 * K_1 * $[HNO_2]^2$ / $[NO_2]$
rate = k* (K_{fast} * $[NH_3]\cancel{[NO_2]}$ / $[HNO_2]$) * (K_2 * K_1 * $[HNO_2]^2$ / $\cancel{[NO_2]}$)
rate = k' * $[HNO_2]$ * $[NH_3]$ .. does not correspond to observations

Mechanism II:
rate = k * $[NH_3]$ * $[N_2O_3]$
Substitution: rate = k' * $[NH_3]$ * $[HNO_2]^2$ which corresponds to observations

Mechanism III:
rate = k * $[NO_2]$ * $[NH_3NO]$
equilibrium constant for fast step K_{fast} = $[NH_3NO]$ / $[NH_3][NO]$
$[NH_3NO]$ = K_{fast} * $[NH_3][NO]$
form reactions in question 11: $[NO_2]$ = K_2 * K_1 * $[HNO_2]^2$ / [NO]
Substitution: rate = k * (K_2 * K_1 * $[HNO_2]^2$ / [NO]) * K_{fast} * $[NH_3][NO]$

rate = k' * [HNO$_2$]^2 * [NH$_3$] .. which corresponds to observations

Calculations give 3 points for mechanism I, 2 points for mechanism II and 3 points for mechanism III.

    13. Which of these mechanisms could be the correct one comparing intrinsic Arrhenius activation energies at standard conditions (25°C)?
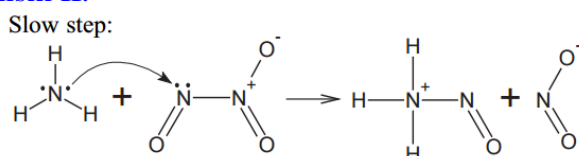

E* = ΔH* + RT (formula is correct, there is no need for Δn * R * T as Δn = 0)

ΔH = Sum of enthalpies for bonds broken minus sum of enthalpies for bonds formed

In complex reaction activation energy of slowest step is activation energy of reaction.

If calculations in question II were correct, then it is not necessary to test reaction mechanism III in this question.

Mechanism II:

Calculation of standard enthalpies of formation from bond enthalpies:

    E* ≈ ... unrealistic number (very small), it is not realistic

Mechanism III:
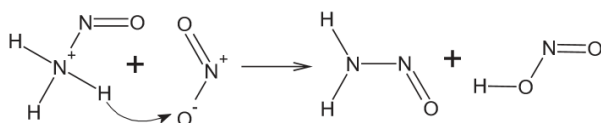
    ΔH$_f$(H$_2$NN=O) = 68,5 kJ/mol;

    ΔH$_f$(HONO) = -93,5 kJ/mol.

    ΔH = 68,5 - 93,5 + 24 - 106,5 = 57 kJ

    E* = -57 * 10^3 + 8,314 * 298 ≈ 59,5 kJ, which is close to calculated value of 64 kJ/mol for activation energy

Possible mechanism is mechanism III.

In this question 3 points are for calculations leading to realistic and unrealistic E* values and 1 point is awarded for correct choose of mechanism.

Additional comments:

- *mechanism III is not stated as most favourable in research paper cited on first page, but it is same as mechanism for diazotisation of amines;*
- *in question 13, there is assumption that energy of intermediate is close (almost same) to energy of transition state.*
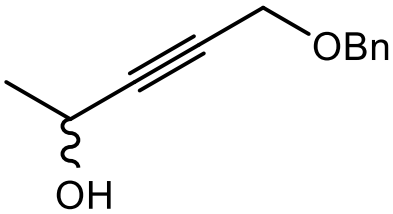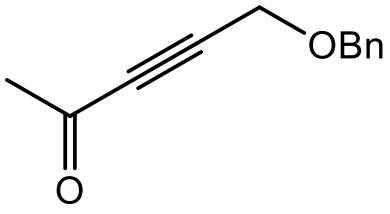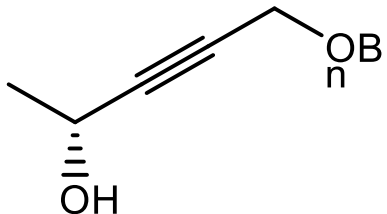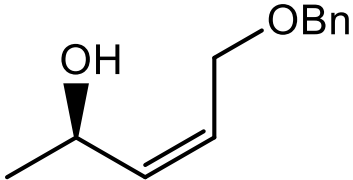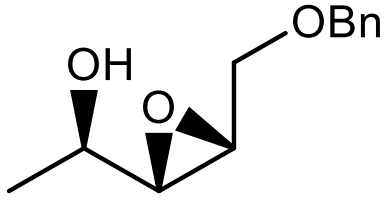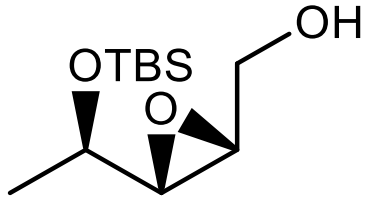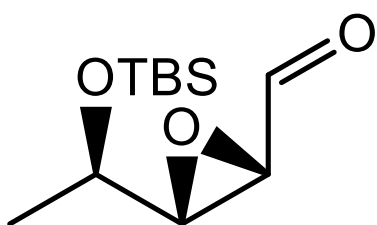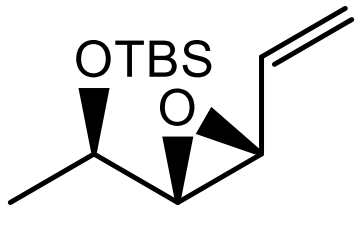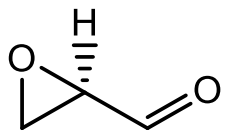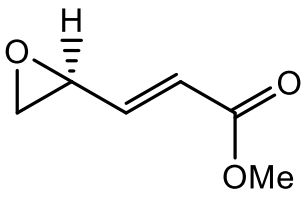
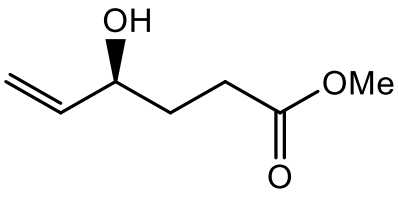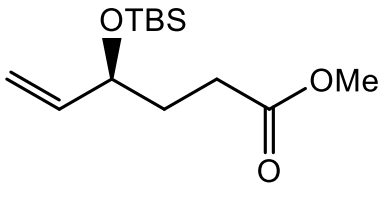## Problem 6. The synthesis of Stagonolide D (solutions)

1. *Deduce the structures **A – N**. Show the appropriate stereochemistry, where necessary.*

A	B	C – 3pt
2 pt	2 pt	

D – 2pt	E – 2pt	F – 1pt

G- 2 pt	H – 1pt	I – 2 pt

J – 2pt	K – 2pt	L – 1 pt

M – 3 pt

N – 2 pt

2. *Provide a mechanism for the transformation leading to* **K**.

5 pt Total

3. *Provide a mechanism for the transformation* **F -> G**.

6 pt total