Baltic 22 Chemistry Olympiad

Theoretical Exam

Vilnius 2014

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**1** 1.00794 **H** 0.28																	**2** 4.00260 **He** 1.40
2	**3** 6.941 **Li**	**4** 9.01218 **Be**											**5** 10.811 **B** 0.89	**6** 12.011 **C** 0.77	**7** 14.0067 **N** 0.70	**8** 15.9994 **O** 0.66	**9** 18.9984 **F** 0.64	**10** 20.1797 **Ne** 1.50
3	**11** 22.9898 **Na**	**12** 24.3050 **Mg**											**13** 26.9815 **Al**	**14** 28.0855 **Si** 1.17	**15** 30.9738 **P** 1.10	**16** 32.066 **S** 1.04	**17** 35.4527 **Cl** 0.99	**18** 39.948 **Ar** 1.80
4	**19** 39.0983 **K**	**20** 40.078 **Ca**	**21** 44.9559 **Sc**	**22** 47.867 **Ti** 1.46	**23** 50.9415 **V** 1.33	**24** 51.9961 **Cr** 1.25	**25** 54.9381 **Mn** 1.37	**26** 55.845 **Fe** 1.24	**27** 58.9332 **Co** 1.25	**28** 58.6934 **Ni** 1.24	**29** 63.546 **Cu** 1.28	**30** 65.39 **Zn** 1.33	**31** 69.723 **Ga** 1.35	**32** 72.61 **Ge** 1.22	**33** 74.9216 **As** 1.20	**34** 78.96 **Se** 1.18	**35** 79.904 **Br** 1.14	**36** 83.80 **Kr** 1.90
5	**37** 85.4678 **Rb**	**38** 87.62 **Sr**	**39** 88.9059 **Y**	**40** 91.224 **Zr** 1.60	**41** 92.9064 **Nb** 1.43	**42** 95.94 **Mo** 1.37	**43** (97.905) **Tc** 1.36	**44** 101.07 **Ru** 1.34	**45** 102.906 **Rh** 1.34	**46** 106.42 **Pd** 1.37	**47** 107.868 **Ag** 1.44	**48** 112.41 **Cd** 1.49	**49** 114.818 **In** 1.67	**50** 118.710 **Sn** 1.40	**51** 121.760 **Sb** 1.45	**52** 127.60 **Te** 1.37	**53** 126.904 **I** 1.33	**54** 131.29 **Xe** 2.10
6	**55** 132.905 **Cs**	**56** 137.327 **Ba**	**57-71** **La-Lu**	**72** 178.49 **Hf** 1.59	**73** 180.948 **Ta** 1.43	**74** 183.84 **W** 1.37	**75** 186.207 **Re** 1.37	**76** 190.23 **Os** 1.35	**77** 192.217 **Ir** 1.36	**78** 195.08 **Pt** 1.38	**79** 196.967 **Au** 1.44	**80** 200.59 **Hg** 1.50	**81** 204.383 **Tl** 1.70	**82** 207.2 **Pb** 1.76	**83** 208.980 **Bi** 1.55	**84** (208.98) **Po** 1.67	**85** (210) **At**	**86** (222.02) **Rn** 2.20
7	**87** (223) **Fr**	**88** (226.03) **Ra** 2.25	**89-103** **Ac-Lr**	**104** (261.11) **Rf**	**105** (262.11) **Db**	**106** (263.12) **Sg**	**107** (262.12) **Bh**	**108** (265) **Hs**	**109** (266) **Mt**	**110** (271) **Ds**	**111** (272) **Rg**	**112** (285) **Cn**	**113** (284) **Uut**	**114** (289) **Fl**	**115** (288) **Uup**	**116** (292) **Lv**	**117** (294) **Uus**	**118** (294) **UUo**

Atomic number → **1** ← Atomic weight
Atomic symbol ← **H** ← Covalent radius, Å

57 138.906 **La** 1.87	**58** 140.115 **Ce** 1.83	**59** 140.908 **Pr** 1.82	**60** 144.24 **Nd** 1.81	**61** (144.91) **Pm** 1.83	**62** 150.36 **Sm** 1.80	**63** 151.965 **Eu** 2.04	**64** 157.25 **Gd** 1.79	**65** 158.925 **Tb** 1.76	**66** 162.50 **Dy** 1.75	**67** 164.930 **Ho** 1.74	**68** 167.26 **Er** 1.73	**69** 168.934 **Tm** 1.72	**70** 173.04 **Yb** 1.94	**71** 174.04 **Lu** 1.72
89 (227.03) **Ac** 1.88	**90** 232.038 **Th** 1.80	**91** 231.036 **Pa** 1.56	**92** 238.029 **U** 1.38	**93** (237.05) **Np** 1.55	**94** (244) **Pu** 1.59	**95** (243.06) **Am** 1.73	**96** (247.07) **Cm** 1.74	**97** (247.07) **Bk** 1.72	**98** (251.08) **Cf** 1.99	**99** (252.08) **Es** 2.03	**100** (257.10) **Fm**	**101** (258.10) **Md**	**102** (259.1) **No**	**103** (260.1) **Lr**

Problem 1. Silver compounds **9 points**

Silver forms with chloride, bromide, iodine and cyanide low solubility salts (K_L values $1.77 \cdot 10^{-10}$, $5.2 \cdot 10^{-13}$, $8.3 \cdot 10^{-17}$, $5.97 \cdot 10^{-17}$ respectively)

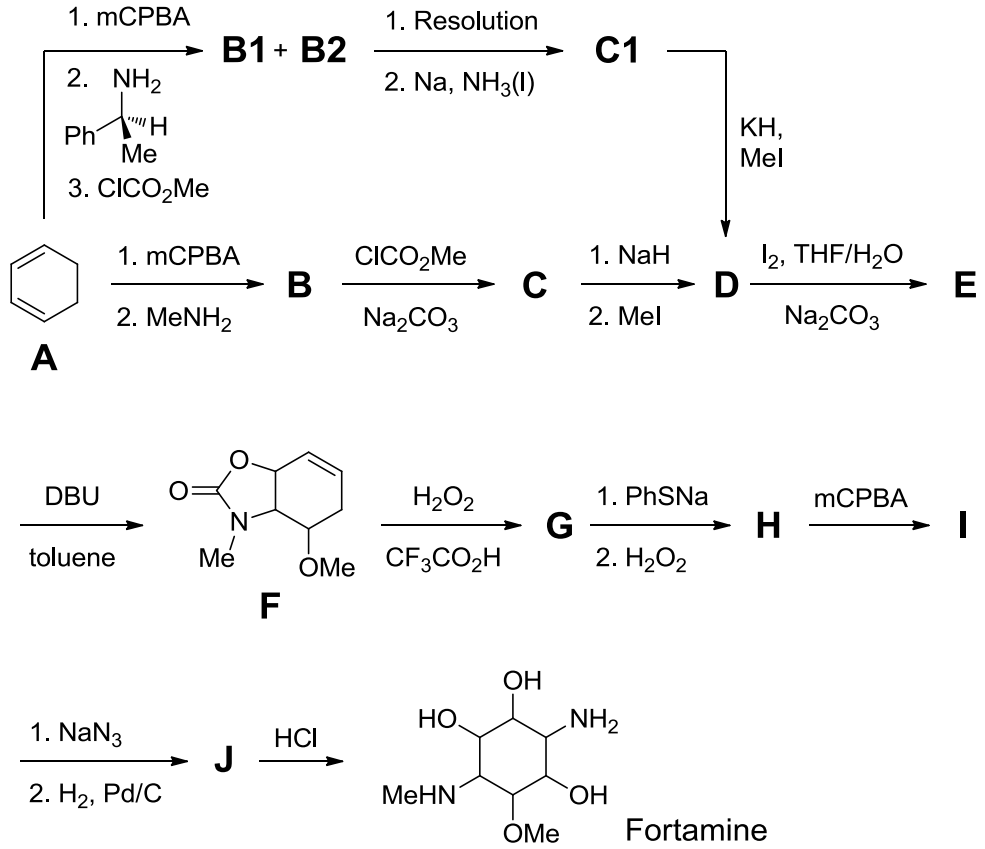
1. Determine the order of precipitation of the anions in equimolar solution. Assume that precipitation is the only reaction and that cyanide ions do not hydrolyze.
2. How much (in per cent) bromide ion have precipitated at the moment when chloride ions start precipitation?
3. Actually cyanide ions correspond to a week acid hydrogen cyanide (pKa=9.21) and is therefore hydrolysed in a different extent depending on the pH of the solution. If the pH of the solution is 7.0, what extent of the cyanide ions has been hydrolysed?
4. Determine the order of precipitation of the chloride, bromide, iodine and cyanide anions in the equimolar solution (pH=7.0) while taking into account the hydrolyses of the cyanide ions.
5. Is it possible to selectively (left into the solution less the 0.1% of the starting concentration) precipitate iodine so that other ions do not coprecipitate? The pH of the solution is 7.0.
6. In the solutions with high halogen content often ammonia (pKb=4.75) is added to avoid the precipitation. In the solution two possible complexes are formed:

   $Ag^+ + NH_3 <-> Ag(NH_3)^+$ $\quad K_f(AgNH_3^+)=2.1 \cdot 10^3$
   $Ag(NH_3)^+ + NH_3 <-> Ag(NH_3)_2^+$ $\quad K_f(Ag(NH_3)_2^+)=1.7 \cdot 10^7$

   Determine how large fraction of silver is not bound to the complexes if the solution contains 0.1 mol/l Ag^+, 0.5 mol/l ammonia and the pH of the solution is 7.0?
7. How much silver is it possible to dissolve in 0.1 mol/l chloride solution, that also contains 0.5 mol/l ammonia and the pH is 7.0?

Problem 2 Fortamine 10 points

Antibiotic Fortamine has an interesting structure – all of its cyclohexane carbon atoms are chiral. You will need to deduce the absolute configuration for all of them (besides the other questions). The stereochemical information must be shown unambiguously for all the compounds.



The starting material **A** was treated with *m*-chloroperoxybenzoic acid followed by methylamine to produce compound **B**. The reaction of **B** with methylchloroformate and then NaH/MeI yields racemic product **D**. Since Fortamine must be enantiomerically pure, an alternative method to access single enantiomer of **D** was proposed via intermediates **B1** and **B2** (which are diastereomers to each other). During the resolution of **B1** and **B2** the (*S*,*S*,*S*)-compound was isolated and treated with sodium in liquid ammonia to produce enantiomerically pure **C1**.

1. Draw the structures of compounds **B**, **B1**, **B2**, **C** and **C1**.

The conversion of **D** to **E** is a modification of a classical reaction, where a carboxyacid is used instead of an ester. However, both ester and acid would yield the same product **E**. The latter was treated with a non-nucleophilic base DBU to give an elimination product **F**.

2. Draw the structures of compounds **D** and **E**.
3. Show the mechanism for reaction **D** → **E**.

Unlike mCPBA and other peroxyacids, CF_3CO_3H is able to coordinate not only to hydrogen-bond donors (alcohols, etc) but also to protected alcohols. In this case it leads to a stereoselective reaction. Treatment of **G** with PhSNa followed by elimination gives compound **H**, which, after a few subsequent reactions is transformed into enantiomerically pure Fortamine.

4. Show the structure of the intermediate molecular complex of reaction **F** → **G**.
5. Draw the structural formulas for compounds **G** – **J**.
6. Indicate the configuration of all the chiral carbons of Fortamine using R/S nomenclature.

Problem 3. 10 points

Redox flow battery

A redox flow battery consists of two electrolyte tanks and two (usually carbon) electrodes, which are separated by a proton exchange membrane. One of the tanks contains oxidizer aqueous solution, another reducing agent aqueous solution. If the oxidation-reduction reactions are reversible, the system can be used as a rechargeable battery. Some high energy density flow battery systems are promising candidates as an energy source for an electric car.

In the case of vanadium redox battery (VRB), both electrolytes contain vanadium redox species, which exist in oxidation states of V, IV, III, and II. The cathode electrolyte (negative electrode side) with 1 M vanadium cation concentration was prepared by dissolving vanadium(V) oxide in 4 M sulphuric acid, yielding an hydrated cation with molecular mass of 155 g mol^{-1}. The anode electrolyte was prepared by electrochemical reduction of the cathode electrolyte.

During VRB discharging, the cathode electrolyte changes from yellow to green and finally blue; anode electrolyte turns from violet to green.

If ammonium vanadate(V) is reduced with zinc in sulphuric acid solution, the following color changes can be seen: yellow -> green -> blue -> green -> purple.

a) Deduce the reactions taking place during ammonium vanadate(V) reduction with zinc.

b) Identify redox compounds and write i) anode, ii) cathode, and iii) summary reaction during discharging of VRB.

c) i) Give formula for calculating electromotive force *E* of the VRB cell as a function of vanadium redox potentials and concentration of cations. ii) How much does the voltage of VRB change when pH is one unit lower?

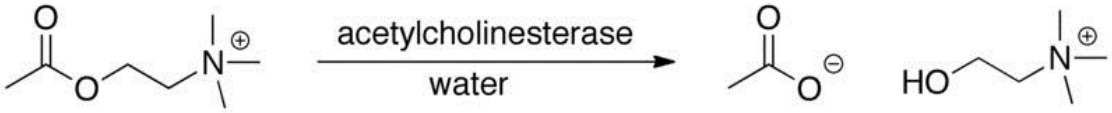
d) Experimental voltage of VRB is 1.4 V. Calculate i) Gibbs energy and ii) equilibrium constant *K*.

e) i) Calculate and compare the energy density of VRB with lead-acid battery (40 Wh kg^{-1}). For simplification, the volume of the VRB can be taken equal to the electrolyte solutions with density of 1.3 g cm^{-3}. ii) How to increase the energy density of the VRB described?

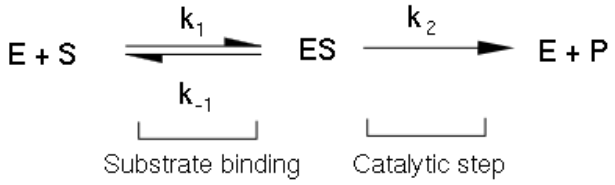
Problem 4 10 points

Kinetics of neuromuscular enzyme

Acetylcholinesterase is the enzyme in neuromuscular junction which catalyses degradation of acetylcholine – neurotransmitter released by parasympathetic nervous system. Inhibitors of this enzyme are used in medicine to treat glaucoma and postural tachycardia syndrome. In this problem, kinetics of this enzyme is analysed.



It is known, that the first step of this enzymatic reaction is reversible binding of the acetylcholine (substrate, S) to the acetylcholinesterase (enzyme, E) producing enzyme-substrate complex (ES). Second step is reaction itself and release of the products (P) and free enzyme (E), and it is known that this is rate determining step.

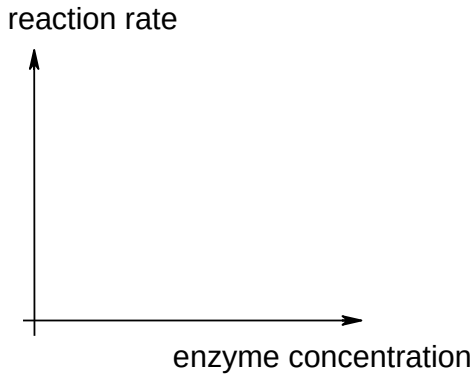


It is also known, that this reaction obeys the Michaelis – Menten kinetics,

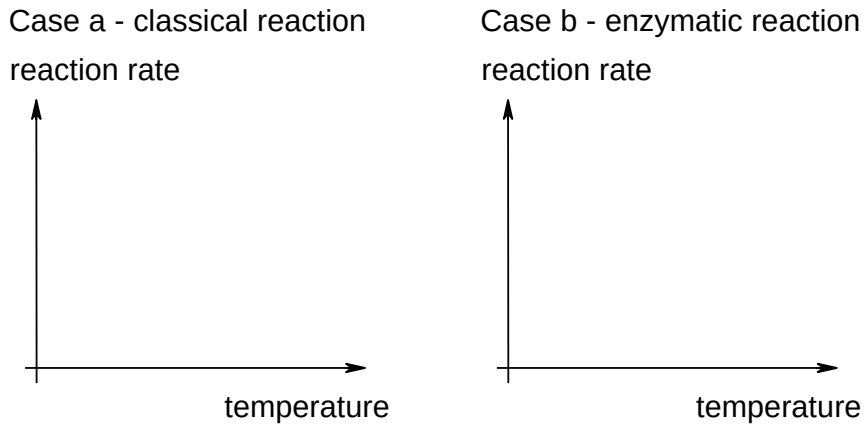
$$v = \frac{v_{\max}[S]}{K_M + [S]}$$ Michaelis – Menten equation

where V_{max} is the maximum rate of the reaction and K_M is Michaelis constant.

1. *By assuming that enzyme substrate complex is in steady state, derive the Michaelis – Menten equation!*
2. *Using Michaelis-Menten equation determine reaction rate order with respect to the substrate in two cases: a) substrate concentration in solution is huge; b) substrate concentration is very small.*
3. *Using differential equations from question 1 or your knowledge sketch the graph showing reaction rate dependence on the enzyme concentration.*



4. *Reaction rate is temperature dependent. Sketch two graphs showing reaction rate as function of temperature in classical reaction (case a) and in enzymatic reaction (case b).*



In the experiment, the rate of this enzymatic reaction was measured at various acetylcholine concentrations. The results were plotted in Figure 1.

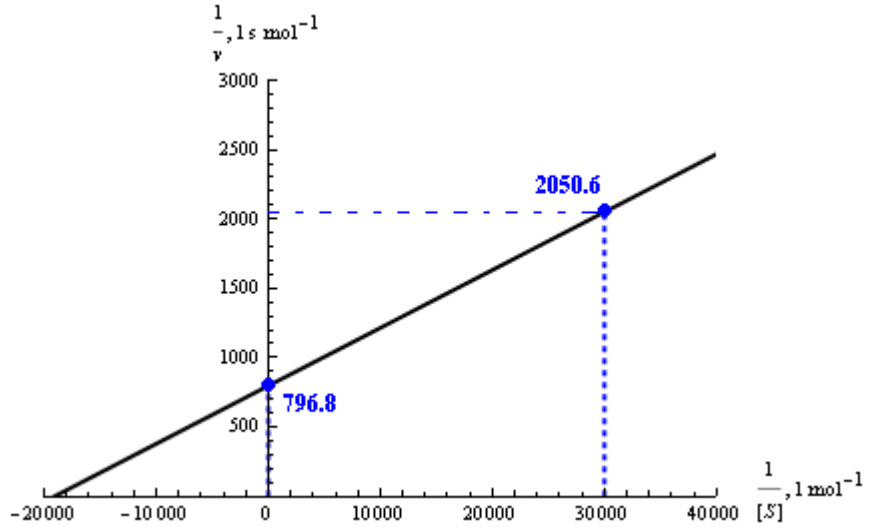


Figure 1. Plot of inverse of rate against the inverse of substrate (acetylcholine) concentration. Note: two data points are marked in the graph.

5. *Mark with "X" one of following methods, which is more suitable for investigation of acetylcholine hydrolysis reaction:*

☐	gasometry
☐	gravimetry
☐	conductometry
☐	titrimetry

6. *Linearize the Michaelis - Menten equation to obtain an equation consistent with the data presented in the Figure 1!*

7. *Calculate V_{max} and concentration of the substrate at which the reaction rate is half the maximum!*

In the experiment mentioned above total concentration of the acetylcholinesterase was $2.00 \cdot 10^{-5}$ mol·l^{-1}

8. *Calculate the rate constant k_2!*

Activity of acetylcholinesterase was tested in the presence of 3 different inhibitors:

- Physostigmine – competitive inhibitor, used in treatment of glaucoma
- Caffeine – non-competitive inhibitor, effects of coffee partly originate from this inhibition. Caffeine can bind with both free enzyme and enzyme-substrate complex, rate of both reactions is the same.
- A2435 – new uncompetitive inhibitor which binds only to the enzyme-substrate complex.

Effects of these three inhibitors are shown in Figure 2.

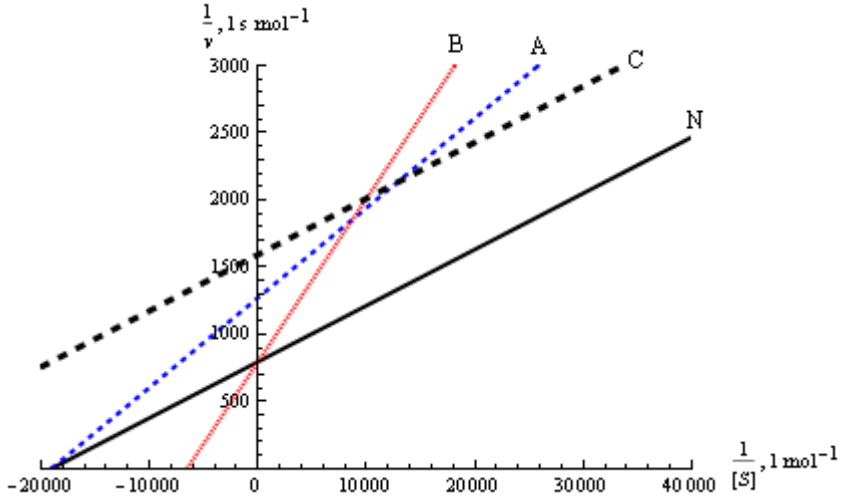


Figure 2. Plot of inverse of rate against the inverse of substrate concentration (in presence of inhibitors – cases A, B, C and without inhibitor – case N).

9. *State which of the lines A, B or C in Figure 2 correspond to each of the inhibitors mentioned above! (Wrong answer deletes half of the points received for the correct answer, but no less than 0 points are given for this task)*

A2435	Caffeine	Physostigmine

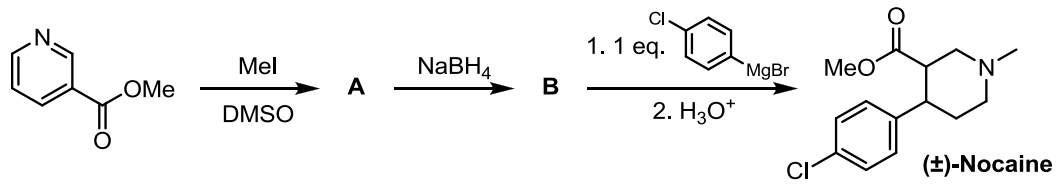
There is another way of linearizing the Michaelis – Menten equation to a different form. In this form plotting $\frac{[S]}{v}$ against _?_(x value) gives a straight line.

10. *Linearize the Michaelis Menten equation to get $\frac{[S]}{v}$ as a linear function of _____(x value) ! You may start from given Michaelis-Menten equation or may use equation obtained in question 6. What is abbreviated as argument x?*

Problem 5 **10 points**

Nocaine

Nocaine effects on CNS are similar to those of cocaine, but due to its less pronounced addictive effect it has been used in cocaine addiction treatment. Some of its derivatives show enhanced activity, while others have an entirely different mode of action.



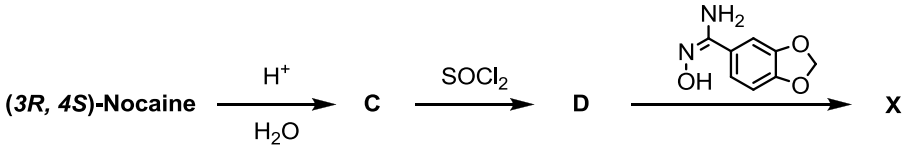
NMR spectra of compound **B**:

^{1}H NMR (500 MHz) δ: 2.37 (2H, dt, *J* = 6.0, 3.0 Hz), 2.41 (3H, s), 2.50 (2H, t, *J* = 6.0 Hz), 3.15 (2H, s), 3.74 (3H, s), 7.00 (1H, t, *J* = 4.0 Hz).

^{13}C NMR (125 MHz) δ: 26.5, 45.6, 50.7, 51.4, 53.2, 128.9, 137.5, 166.9.

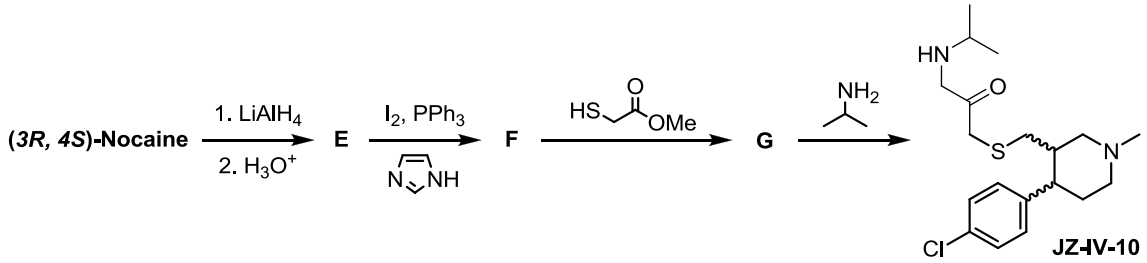
1. Draw structures for compounds **A** and **B**.
2. Assign NMR signals to their respective atoms. It will be taken into account that some of the ^{13}C signals cannot be assigned unambiguously.

1, 2, 4-oxadiazoline derivative **X** is both more potent and more resistant to metabolism than nocaine, which means it can be used in lower doses.



3. Draw structures for compounds **C**, **D** and **X**.
4. Provide the mechanism for the formation of 1, 2, 4-oxadiazoline ring (**D** → **X**).

Another nocaine derivative *JZ-IV-10* does not display cocaine-like euphoric and stimulant effects however it does increase wakefulness and reduces the need for sleep. It can be used as a treatment for narcolepsy.



5. Draw structures for compounds **E** – **G**.
6. 3R, 4S stereoisomer of the nocaine derivatives is usually the most active. Draw *JZ-IV-10* structure indicating the correct absolute configuration.
7. Provide the mechanism for **E** → **F** transformation. Reaction also produces triphenylphosphine oxide and imidazolium iodide.
8. Which method could theoretically be used to separate (3R, 4S)-nocaine from (3S, 4R)-nocaine?

Problem 6 11 points

Chemistry of superacids (34.5 trial points)

a.k.a. "I have a good peeling about this"

According to the classical definition a superacid is an acid with an acidity greater than that of 100% sulfuric acid. According to the modern definition, superacid is a medium in which the chemical potential of the proton is higher than in pure sulphuric acid.

The simplest class of superacids is the Brønsted superacids. The first acid named accordingly was chlorine containing **A** because of its ability to protonate aldehydes and ketones. Due to its explosive hazard, its use is partially limited. By adding anhydrous **A** to concentrated nitric acid, salt **B** can be obtained.

1. Provide the chemical formula for **A** and **B** and Lewis structure formulas for both ions in **B**! What geometrical shape do these ions owe? Write down all resonance structures of the cation in **B**!

A superacid **C** is considered to be the strongest between superacids known so far, and is prepared in a simple reaction between a Lewis acid **D** and Brønsted acid **E,** both being binary compounds containing a common chemical element. The ratio of the weight fraction of this element in **D** and **E** is 2.1668. It is known that **C** is ionic and consists of two ions $\mathbf{C}_{+}$ and $\mathbf{C}_{-}$.

2. Give the chemical formulas and Lewis structures of **D** and **E**. What is the geometrical shape of **D**? Write down the equation of the chemical reaction described!
3. Give the chemical formula of **C**. Give the Lewis structures of $\mathbf{C}_{+}$ and $\mathbf{C}_{-}$. What is the geometrical shape of these ions?

This extraordinarily strong acid is able to protonate nearly all organic compounds. It has been shown it removes H_2 from isobutane (2-methylpropane) and methane from 2,2-dimethylpropane. *Note that in this way cation* $\boldsymbol{K}_{+}$ *is obtained!*

4. Write down the equations of these chemical reactions by showing the carbon atom which will be protonated. What considerations will determine which carbon atom gets protonated?

Recently a group of scientists from Freiburg, Germany had reported the superacidity of **F**, which is prepared in a simple reaction between a Brønsted acid **G** and a Lewis acid **H,** both containing a common chemical element. It is known that the weight fraction of element **X** (not present in **G**) in **H** is 0.10117, and also that **F** is ionic and its anion can exist in two chemically distinct forms for which molecular weight ratio $\mathbf{F}_{-B}$: $\mathbf{F}_{-A}$ is 1.7695.

5. Give the chemical formula of **F**, $\mathbf{F}_{-A}$, $\mathbf{F}_{-B}$, **G** and **H**. Give the Lewis structures and predict the geometry of $\mathbf{F}_{-A}$ and **H**. Illustrate the geometry of $\mathbf{F}_{-B}$.

F can protonate benzene by producing an ionic compound **J** containing anion $\mathbf{F}_{-B}$.

6. Write down the chemical structure of **J**! How many signals there will be in the ^{1}H, ^{13}C and **X** NMR spectra of **J**?

Interestingly, the reaction between the Lewis acid **H** and 2-bromo-2-methylpropane produced an ionic compound **K** with the same anion $\mathbf{F}_{-B}$ and a cation $\mathbf{K}_{+}$.

7. Write down the chemical structure of **K**! How many signals there will be in the ^{1}H, ^{13}C and **X** NMR spectra of **K**?

It has been shown that for ionic compounds similar to **K** thermodynamic characteristics can be calculated by the use of empiric equations. As an input data experimentally determined compound properties or those obtained from quantum chemical calculations can be used. Equations for calculation of vaporization, solvation (enthalpy for transition from ions in gas phase to ions in the liquid state) and lattice enthalpies are given below:

$$\Delta_{vap}H = aV_m^{\frac{2}{3}} + bH_g^* + c$$
$$\Delta_{solv}H = -(\Delta_{vap}H + \Delta_{diss}H)$$
$$\Delta_{latt}H = \mathrm{d}\Delta_{solv}H + e\ ,$$

where a = -224 kJ·mol^{-1}·nm^{-2}, b = 0.0929, c = 194 kJ·mol^{-1}, d = –0.685, and e = 172 kJ·mol^{-1}.

8. Use the provided equations (consistent with Born–Haber cycle) to calculate the lattice enthalpy of **K**, if V_m of **K** is 0.4175 nm^3 (determined by single-crystal X-Ray diffraction), H_g^* = 394.9 kJ·mol^{-1}, and $\Delta_{diss}H$ = 395.9 kJ·mol^{-1} (both found by quantum chemical calculations).

The reaction between 0.100 mol of **H** and 0.100 mol of 2-bromo-2-methylpropane were performed in calorimeter filled with $2.00 \cdot 10^2$ g of ethanol (specific heat capacity = 2.44 $J \cdot g^{-1} \cdot K^{-1}$). By performing the reaction at 0 °C it was found that the temperature of ethanol increased by 5.94 °C, while by performing the same reaction at 20 °C, temperature of ethanol increased by 2.46 °C (assume the calorimeter constant to be 0 and enthalpy being temperature independent). It was determined that the melting point of **K** is 2 °C.

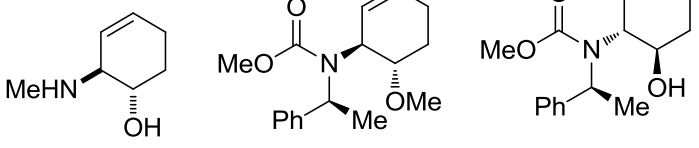
9. Calculate the reaction enthalpy at 0 °C and at 20 °C. Calculate the enthalpy of fusion of **K**.
10. Use the Born–Haber cycle to calculate the enthalpy of fusion of **K** from the results in point 8! Identify the main cause of errors for each of the approaches used to determine the enthalpy of fusion!

Experimental enthalpy of vaporization of 2-bromo-2-methylpropane (+32 $kJ \cdot mol^{-1}$) and the sublimation enthalpy of **H** (+85 $kJ \cdot mol^{-1}$) are tabulated in handbooks of physical chemistry.

11. Use the Born–Haber cycle to calculate the reaction enthalpy for reaction between **H** and 2-bromo-2-methylpropane in gas phase (where separated ions $\mathbf{F_{-B}}$ and $\mathbf{K_{+}}$ in gaseous state are obtained).

Solutions
Problem 2. Fortamine

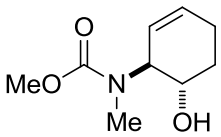
1. Draw the structures of compounds **B**, **B1**, **B2**, **C** and **C1**.



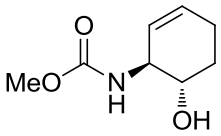
B

B1

B2



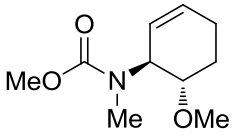
C



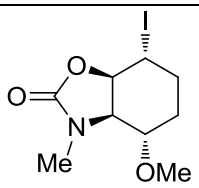
C1

For each compound: correct structure – 0.8 pt, correct stereochemistry – 0.2 pt. Total 5 pts.

2. Draw the structures of compounds **D** and **E**.



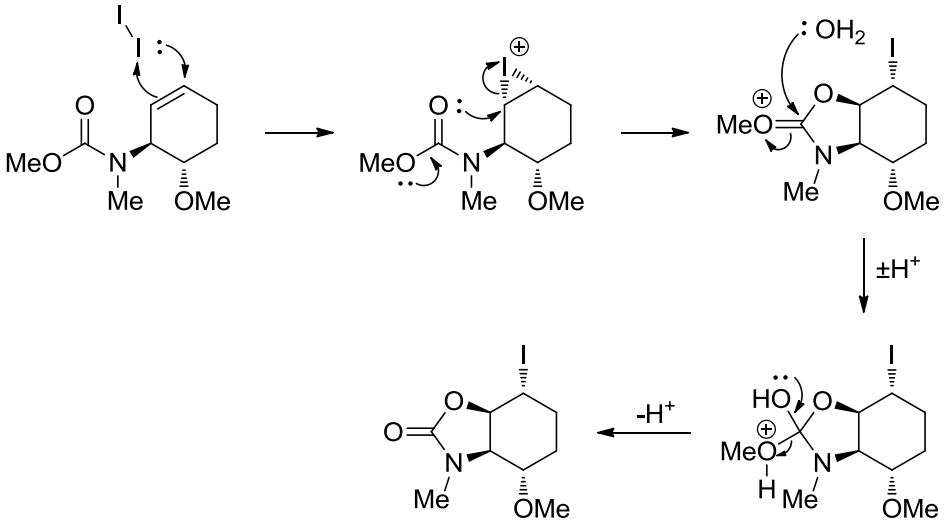
D



E

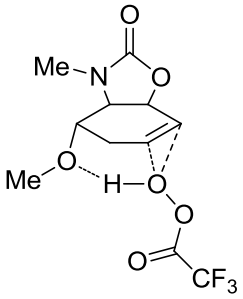
For each compound: correct structure – 0.8 pt, correct stereochemistry – 0.2 pt. Total 2 pts.

3. Show the mechanism for reaction **D** → **E**.



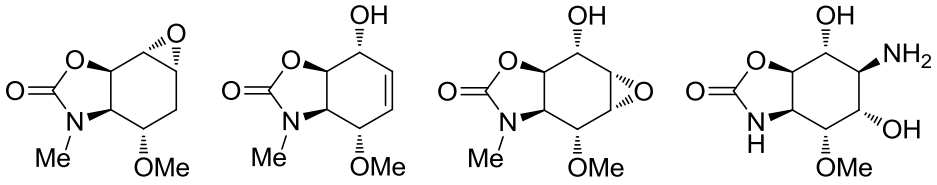
Correct flow – 1.5 pts. Correct stereochemistry – 0.5 pts. Total 2 pts.

4. Show the structure of the intermediate molecular complex of reaction **F** → **G**.



1 pt.

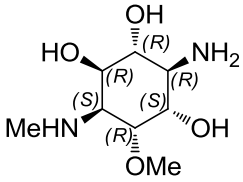
5. Draw the structural formulas for compounds **G** – **J**.



G **H** **I** **J**

For each compound: correct structure – 0.8 pt, correct stereochemistry – 0.2 pt. Total 4 pts.

6. Indicate the configuration of all the chiral carbons of Fortamine using R/S nomenclature.



Correct configuration for each chiral center – 1/3 pt. Total – 2 pts.

Total for this problem – 16 pts.

Problem 3. 10 points

Redox flow battery

a) i) $2VO_3^-$ (aq) + Zn (s) + 8H+(aq) ---> $2VO^{2+}$(aq) + Zn^{2+}(aq) +$4H_2O$
yellow blue

Green colour appears when the VO_3^-/ VO^{2+} ratio is close to 1.

ii) $2VO^{2+}$(aq) + Zn + $4H^+$(aq) ---> $2V^{3+}$(aq) + Zn^{2+}(aq)+ $2H_2O$
blue green

iii) $2V^{3+}$(aq) + Zn ----> $2V^{2+}$ (aq) + Zn^{2+} (aq)
green purple

b) M(vanadium cation) = 155 g mol^{-1}

The formula is $[VO_2(H_2O)_4]^+$

i) Anode: V^{2+} --(discharge)--> V^{3+} + e^-

ii) Cathode: $VO_2^+ + 2H^+ + e^-$ --(discharge)--> $VO^{2+} + H_2O$

iii) Summary: : $V^{2+} + VO_2^+ + 2H^+$ --(discharge)--> $V^{3+} + VO^{2+} + H_2O$

c) i) $E = E^0(VO^{2+}/VO_2^+) - E^0(V^{2+}/V^{3+}) - 0.059*\log([V^{3+}][VO^{2+}]/[V^{2+}]/[VO_2^+]/[H^+]^2)$

ii) $\Delta E = 0.059*\log(1/[0.1]^2) = 0.118$ V

d) i) $\Delta G^0 = -nFE^0 = -1*96485*1.4 = -135$ kJ mol^{-1}

ii) $\Delta G^0 = -RT\ln K \rightarrow K = e(-\Delta G^0/RT) = 2 * 10^{-24}$

e) i) The mass of 1 mol battery is 2 L * 1.3 kg L^{-1} = 2.6 kg, and energy density is 135/2.6 = 51.9 kJ kg^{-1} / 3.6 kJ Wh^{-1} = 14.4 Wh kg^{-1}. Thus the energy density of the described VRB is lower than in lead-acid battery.

ii) Increase vanadium salt and sulphuric acid concentration. Newer VRB designs with more concentrated solutions (yet there is a limited solubility) or with a different chemistry are more promising.

1. Stationary state equation:

$$\frac{d[ES]}{dt} = k_1 \cdot [E][S] - k_{-1}[ES] - k_2[ES] = 0$$ 5 points

(if stationary state equation is wrong max 2 points (if one reaction is missing) but no points for further calculations with wrong equation)

Reaction rate equation as 2nd step is rate limiting:

$$v = k_2[ES]$$

(2 points, also if it is not given as statement but student has used this idea)

Enzyme concentration in solution can be expressed $C(E,tot) = [E] + [ES]$

$$[E] = C(E) - [ES]$$

$$k_1 \cdot [E][S] - k_{-1}[ES] - k_2[ES] = 0$$

$$k_1 \cdot [E][S] - [ES](k_{-1} + k_2) = 0$$

$$k_1 \cdot [S] \cdot C(E) - [ES](k_{-1} + k_2 + k_1[S]) = 0$$

$$[ES] = \frac{k_1 \cdot [S] \cdot C(E)}{k_{-1} + k_2 + k_1[S]}$$

$$v = \frac{k_2 \cdot k_1 \cdot [S] \cdot C(E)}{k_{-1} + k_2 + k_1[S]}$$

abreviate $k_2 \cdot C(E) = v_{max}$

$$\frac{1}{v} = \frac{k_{-1} + k_2 + k_1[S]}{v_{max} \cdot k_1 \cdot [S]} = \frac{k_{-1} + k_2}{v_{max} \cdot k_1 \cdot [S]} + \frac{k_1[S]}{v_{max} \cdot k_1 \cdot [S]}$$

abreviate $\frac{k_{-1} + k_2}{k_1} = K_M$

$$\frac{1}{v} = \frac{K_M}{v_{max}} \cdot \frac{1}{[S]} + \frac{1}{v_{max}} = \frac{K_M + [S]}{v_{max} \cdot [S]}$$

$$v = \frac{v_{max} \cdot [S]}{K_M + [S]}$$

(5 points – any mathematical operations leading to final equation)

Q1 = 12 points

2. Case a) huge substrate concentration

$$[S] >> K_M$$

$$K_M + [S] \approx [S]$$

$$v = \frac{v_{max} \cdot [S]}{[S]} = v_{max}$$

zero order reaction

(2 points for reaction order, 2 points for explanation)

Case b) small substate concentration

$$[S] << K_M$$

$$K_M + [S] \approx K_M$$

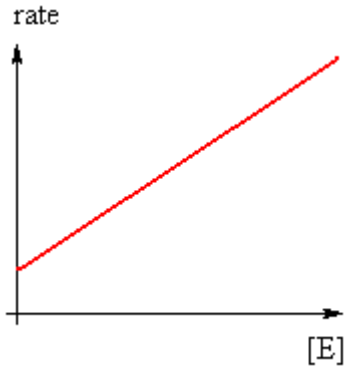
$$v = \frac{v_{max} \cdot [S]}{K_M}$$

1st order raction

(2 points for reaction order, 2 points for explanation)

Q2 = 8 points

3. Graph

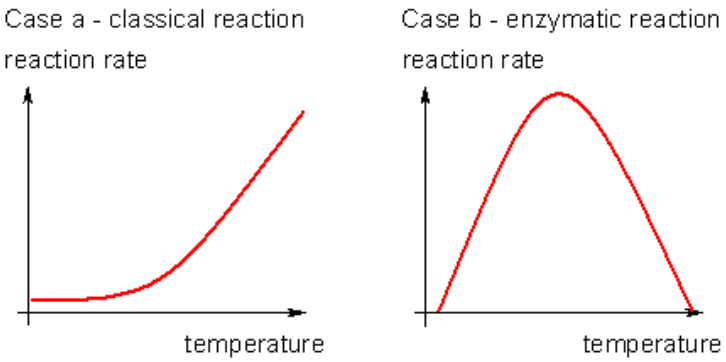


3 points – straight line with positive slope, exponential line or curved line – no points

2 points – line not starting from (0;0) point as reactions proceed also without catalyst

Q3 = 5 points

4. Graphs



Classical reaction: 4 points – exponential line, straight line with positive slope 1 point, other cases – no points. Enzymatic reaction: 4 points – line with maximum, other cases no points.

Q4 = 8 points

5. Conductometry. 2 points, Other answers or more than one answer – no points.

Q5 = 2 points

6. Inverse ofMichaelis-Menten equation:

$$\frac{1}{v} = \frac{K_M}{v_{max}} \cdot \frac{1}{[S]} + \frac{1}{v_{max}}$$

$$y = ax + b$$

$$y = \frac{1}{v}$$

$$x = \frac{1}{[S]}$$

$$a = \frac{K_M}{v_{max}}$$

$$b = \frac{1}{v_{max}}$$

(only first row is required, 5 points, other answers 0 points)

Q6 = 5 points

7. As b = $1/v_{max}$:

$$v_{max} = \frac{1}{b} = \frac{1}{796.8} = 1.26 \cdot 10^{-3} \frac{mol}{l \cdot s}$$

Accept values from $1.2*10^{-3}$ to $1.3*10^{-3}$. 3 points, $1*10^{-3}$ = 1 point
Correct units added +2 points (also in case of incorrect numeric value).
Total for calculation of v(max) = 5 points.

Concentration value at which rate is half of maximum is Michaelis constant.
2 points for this (statement is not required, student may calculate K_M without explanation, then he/she also receive 2 points)

As a = K_M/v(max), we need to calculate slope.

slope = a = $tg\frac{2050.6 - 796.8}{30\,000} = 0.04179\ s$

2 points for correct slope calculation (accept values between 0.04 and 0.045, no units are required)

$$K_M = a \cdot v(max) = 0.04179 \cdot 1.26 \cdot 10^{-3} = 5.25 \cdot 10^{-5}\ M$$

Accept values from $5*10^{-5}$ to $5.5*10^{-5}$. 3 points
Correct units added +2 points (also in case of incorrect numeric value).
Total for calculation of K_M = 9 points
If v(max) value is wrong student may receive points for slope, for K_M idea, for units but not for K_M value if it is not in interval required.

Q7 = 14 points

8. $$v_{max} = k_2 \cdot C(E)$$

$$k_2 = \frac{v_{max}}{C(E)} = \frac{1.26 \cdot 10^{-3}}{2.00 \cdot 10^{-5}} = 63\,s^{-1}$$

Accept values from 60 to 65. This gives 3 points. Do not accept any other values (also if they are right from wrong v(max)).
Correct units added +2 points (also in case of incorrect numeric value).

Q8 = 5 points

9. Correct answers in table:

A2435	Caffeine	Physostigmine
C	***A***	***B***

Each correct answer 6 points. Each incorrect answer -3 points. Total not less than zero, it it is less than zero points, award 0 points for task.

Q9 = 18 points

10. Let's use equation from question 6:

$$\frac{1}{v} = \frac{K_M}{v_{max}} \cdot \frac{1}{[S]} + \frac{1}{v_{max}}$$

$$\frac{[S]}{v} = \frac{K_M}{v_{max}} \cdot \frac{1}{[S]} \times [S] + \frac{1}{v_{max}} \times [S]$$

$$\frac{[S]}{v} = \frac{1}{v_{max}} \cdot [S] + \frac{K_M}{v_{max}}$$

$\frac{[S]}{v}$ is linear function of $[S]$

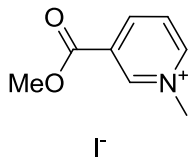
6 points for transformation of equation, 2 points for identification of x, if x is stated as 1/(v(max), then 1 point, other cases – no points

Q9 = 8 points

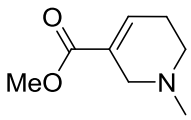
TOTAL 85 trial points

Problem 5 Nocaine

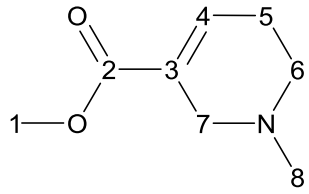
1. A



B



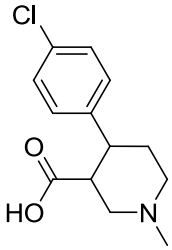
2.



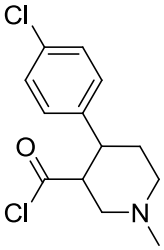
^{1}H:
1 – 3.74
4 – 7.00
5 – 2.37
6 – 2.50
7 – 3.15
8 – 2.41

^{13}C:
1 – 53.2
2 – 166.9
3 – 128.9
4 – 137.5
5 – 26.5
6 – 50.7
7 – 51.4
8 – 45.6

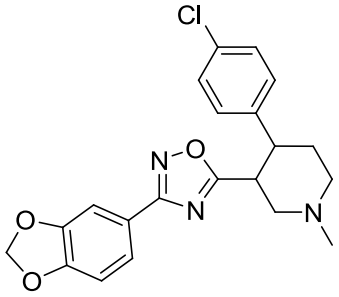
3. C



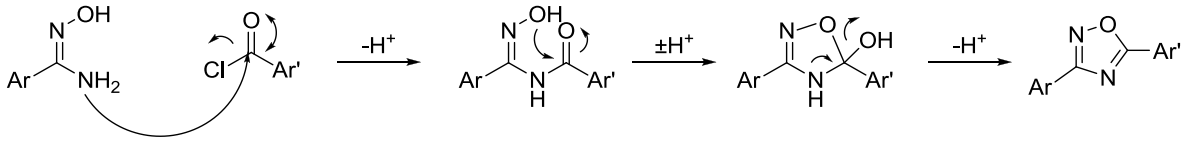
D



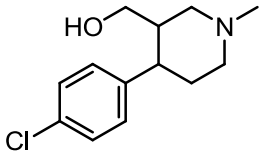
X



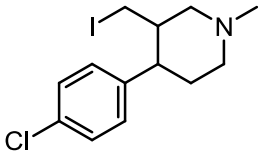
4. D → X



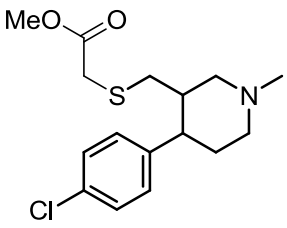
5. E



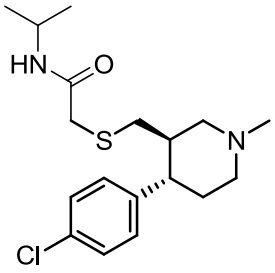
F



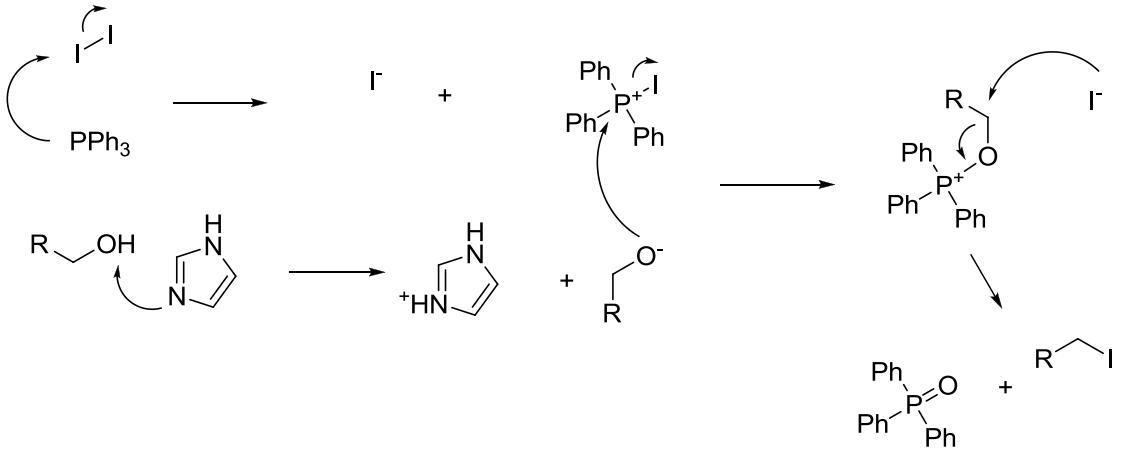
G



6.



7. E → F



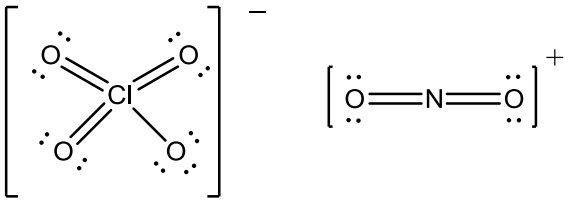
8.

A Kolonėlinė chromatografija
B Nokaino L-laktato perkristalinimas
C Nokaino acetato perkristalinimas
D Distiliacija

Problem 6 **11 points** Superacids

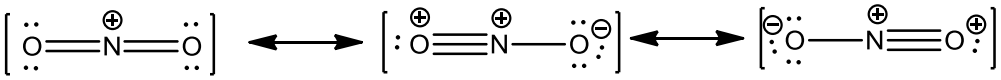
1. Provide the chemical formula for **A** and **B** and Lewis structure formulas for both ions in **B**! What geometrical shape do these ions owe? Write down all resonance structures of the cation in **B**!

A = $HClO_4$ 0.5 pt.
B = $NO_2^+ClO_4^-$ 1 pt



1 pt.

NO_2^+ = linear; ClO_4^- = tetrahedral 0.5 pt



1 pt.

A binary superacid **C** is considered to be the strongest between superacids known so far, and is prepared in a simple reaction between a Lewis superacid **D** and Brønsted superacid **E,** both being binary compounds containing a common chemical element. The ratio of the weight fraction of this element in **D** and **E** is 2.1667. It is known that **C** is ionic and consists of two ions $\mathbf{C_+}$ and $\mathbf{C_-}$.

2. Give the chemical formulas and Lewis structures of **D** and **E**. What is the geometrical shape of **D**? Write down the equation of the chemical reaction described!

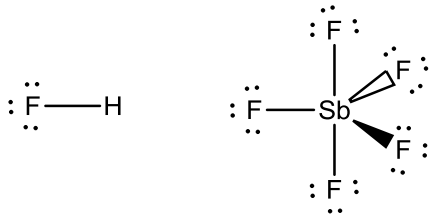
D = SbF_5, **E** = HF 1.5+0.5 pt.

Weight fraction of F in HF is 0.94962, therefore in **D** it is 0.94962/2.1667 = 0.43828. We have to find the element which forms binary fluoride YF_n (**D**), where weight percent of F is:

$$w_F = \frac{n \cdot A_F}{n \cdot A_F + A_Y} = 0.43828$$

$$A_Y = \frac{n \cdot A_F(1 - w_F)}{w_F} = \frac{10.6727n}{0.43828} = 24.351n$$

By varying n and calculating the atomic masses of the unknown element we find that the only suitable solution is n = 5 and A_Y = 121.76 → **Sb**.



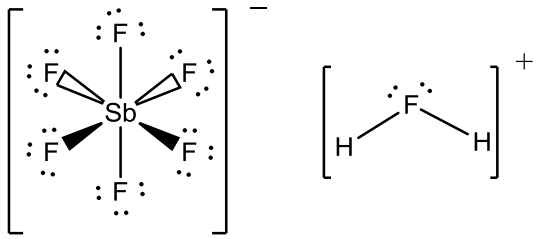
0.75 pt.

SbF_5 = trigonal bipyramidal. 0.25 pt.

$2HF + SbF_5 \rightarrow H_2F^+[SbF_6]^-$ 1 pt.
($HF + SbF_5 \rightarrow H^+[SbF_6]^-$ 0.5 pt.)

3. Give the chemical formula of **C**. Give the Lewis structures of $\mathbf{C_+}$ and $\mathbf{C_-}$. What is the geometrical shape of these ions?

C = $H_2F^+[SbF_6]^-$ ($H^+[SbF_6]^-$) *0.5 pt (only if no equation of the chemical reaction is given in point 2)*

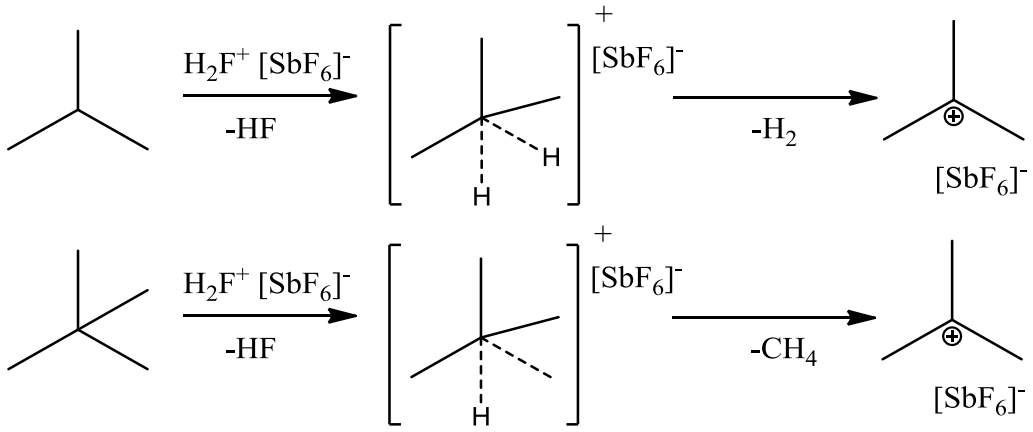


1 pt.

H_2F^+ = bent, $[SbF_6]^-$, = octahedral. 0.5 pt.

This extraordinarily strong acid is able to protonate nearly all organic compounds. It has been shown it removes H_2 from isobutane (2-methylpropane) and methane from 2,2-dimethylpropane. *Note that in this way cation* ***K*** *is obtained!*

4. Write down the equations of these chemical reactions by showing the carbon atom, which will be protonated. What considerations will determine which carbon atom gets protonated?



2 pt.

Considering all possible sites of protonation, the most stable intermediate and resulting carbocation is that being more substituted

0.5 pt.

Recently a group of scientists from Freiburg, Germany had reported the superacidity of **F**, which is prepared in a simple reaction between a Brønsted acid **G** and a Lewis acid **H,** both containing a common chemical element. It is known that the weight fraction of element **X** (not present in **G**) in **H** is 0.10112, and also that **F** is ionic and its anion can exist in two chemically distinct forms for which molecular weight ratio $\mathbf{F_{-B}}$: $\mathbf{F_{-A}}$ is 1.7695.

5. Give the chemical formula of **F**, $\mathbf{F_{-A}}$, $\mathbf{F_{-B}}$, **G** and **H**. Give the Lewis structures and predict the geometry of $\mathbf{F_{-A}}$ and **H**. Illustrate the geometry of $\mathbf{F_{-B}}$.

G = HBr, **H** = $AlBr_3$, **F** = $H[AlBr_4]$ 1+1+1 pt.

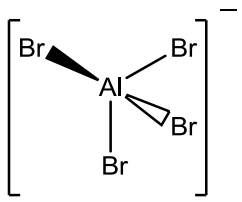
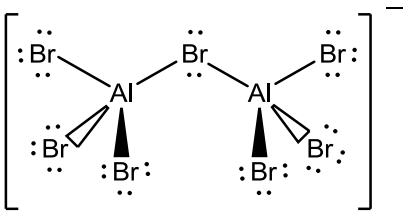
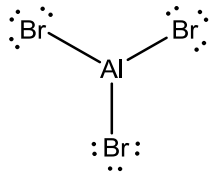
As possible Brønsted acids we will check HCl and HBr. Therefore the common element is either Cl or Br. Weight fraction of **X** in Lewis acid is therefore given as:

$$w_X = \frac{A_X}{n \cdot A_{Cl/Br} + A_X} = 0.10112$$

$$A_X = \frac{w_X \cdot n \cdot A_{Cl/Br}}{1 - w_X} = \frac{0.10112n \cdot A_{Cl/Br}}{0.89888} = 0.11250n \cdot A_{Cl/Br}$$

By varying n and halogen, and calculating the atomic masses of the unknown element we find that the only suitable solution is for Br with n = 3 and A_X = 26.97 → **Al**.

$\mathbf{F_{A-}}$ = $[AlBr_4]^-$ and $\mathbf{F_{B-}}$ = $[Al_2Br_7]^-$ 1 pt for $[Al_2Br_7]^-$ (*and 0.5 pt. for* $[AlBr_4]^-$ *but only if* ***F*** *is not given)*

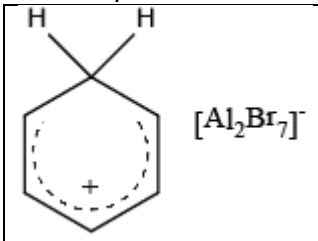




0.5 pt. + 1 pt. for $[Al_2Br_7]^-$

$[AlBr_4]^-$ = tetrahedral and $AlBr_3$ = trigonal planar. 0.5 pt.

F can protonate benzene by producing an ionic compound **J** containing anion **F_{-B}**.

6. Write down the chemical structure of **J**! How many signals there will be in the ^1H, ^{13}C and **X** NMR spectra of **J**?

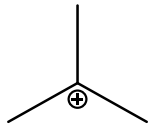


1.5 pt.

2 in ^1H, 2 in ^{13}C and 1 in ^{27}Al (as all the 5 hydrogens and 5 carbons in the disturbed benzene are identical). 1 pt. *(0.5 points for 4 in ^1H and 4 in ^{13}C)*

Interestingly, the reaction between the Lewis acid **H** and 2-bromo-2-methylpropane produced an ionic compound **K** with the same anion **F_{-B}** and a cation **K_+**.

7. Write down the chemical structure of **K**! How many signals there will be in the ^1H, ^{13}C and **X** NMR spectra of **K**?



1 pt.

1 in ^1H, 2 in ^{13}C and 1 in ^{27}Al. 1 pt.

It has been shown that for ionic compounds similar to **K** thermodynamic characteristics can be calculated by the use of empiric equations. As an input data experimentally determined compound properties or those obtained from quantum chemical calculations can be used. Equations for calculation of vaporization, solvation (enthalpy for transition from ions in gas phase to ions in the liquid state) and lattice enthalpies are given below:

$$\Delta_{vap}H = aV_m^{\frac{2}{3}} + bH_g^* + c$$

$$\Delta_{solv}H = -(\Delta_{vap}H + \Delta_{diss}H)$$

$$\Delta_{latt}H = \mathrm{d}\Delta_{solv}H + e\,,$$

where a = -224 kJ·mol^{-1}·nm^{-2}, b = 0.0929, c = 194 kJ·mol^{-1}, d = –0.685, and e = 172 kJ·mol^{-1}.

8. Use the provided equations (consistent with Born–Haber cycle) to calculate the lattice enthalpy of **K**, if V_m of **K** is 0.4175 nm^3 (determined by single-crystal X-Ray diffraction), H_g^* = 394.9 kJ·mol^{-1}, and $\Delta_{diss}H$ = 395.9 kJ·mol^{-1} (both found by quantum chemical calculations).

$$\Delta_{vap}H = aV_m^{\frac{2}{3}} + bH_g^* + c = -224 \cdot (0.4175)^{\frac{2}{3}} + 0.0929 \cdot 394.9 + 194 = 105.6\ \mathrm{kJ \cdot mol^{-1}}$$
$$\Delta_{solv}H = -\left(\Delta_{vap}H + \Delta_{diss}H\right) = -(105.6 + 395.9) = -501.5\ \mathrm{kJ \cdot mol^{-1}}$$
$$\Delta_{latt}H = \mathrm{d}\Delta_{solv}H + e = 515.5\ \mathrm{kJ \cdot mol^{-1}}$$

2 pt.

The reaction between 0.100 mol of **H** and 0.100 mol of 2-bromo-2-methylpropane were performed in calorimeter filled with $2.00 \cdot 10^2$ g of ethanol (specific heat capacity = 2.44 $J \cdot g^{-1} \cdot K^{-1}$). By performing the reaction at 0 °C it was found that the temperature of ethanol increased by 5.94 °C, while by performing the same reaction at 20 °C, temperature of ethanol increased by 2.46 °C (assume the calorimeter constant to be 0 and enthalpy being temperature independent). It was determined that the melting point of **K** is 2 °C.

9. Calculate the reaction enthalpy at 0 °C and at 20 °C. Calculate the enthalpy of fusion of **K**.

$$Q_{0^\circ} = m \cdot c_{spec} \cdot \Delta T = 200 \cdot 2.44 \cdot 5.94 = 2899\,J$$
$$Q_{20^\circ} = m \cdot c_{spec} \cdot \Delta T = 200 \cdot 2.44 \cdot 2.46 = 1200\,J$$
$$\Delta_{reac}H_{0^\circ} = \frac{-Q}{n} = \frac{-2899}{0.100} = -29.0\ \text{kJ} \cdot \text{mol}^{-1}$$
$$\Delta_{reac}H_{20^\circ} = \frac{-Q}{n} = \frac{-1200}{0.100} = -12.0\ \text{kJ} \cdot \text{mol}^{-1}$$

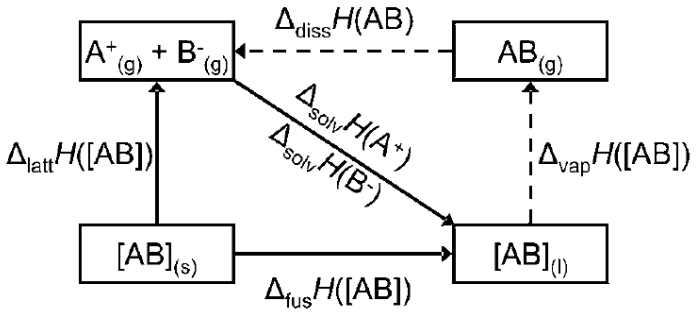
1.5 pt.

$$\Delta_{fus}H = \Delta_{reac}H_{20^\circ} - \Delta_{reac}H_{0^\circ} = -12.0 - (-29.0) = 17.0\ \text{kJ} \cdot \text{mol}^{-1}$$

1 pt.

10. Use the Born–Haber cycle to calculate the enthalpy of fusion of **K** from the results in point 8! Identify the main cause of errors for each of the approaches used to determine the enthalpy of fusion!

The Born–Haber cycle can be written as:



Therefore enthalpy of fusion can be calculated as:

$$\Delta_{fus}H = \Delta_{latt}H + \Delta_{solv}H = 515.5 + (-501.5) = 14.0\ \text{kJ} \cdot \text{mol}^{-1}$$

or

$$\Delta_{fus}H = \Delta_{latt}H - \Delta_{diss}H - \Delta_{vap}H = 515.5 - 395.9 - 105.6 = 14.0\ \text{kJ} \cdot \text{mol}^{-1}$$

2 pt (for cycle or correct equation with signs) + 1 pt. (for correct result)

The main causes of errors for calorimetric method are: reaction yield is not 100%, possible heat losses.

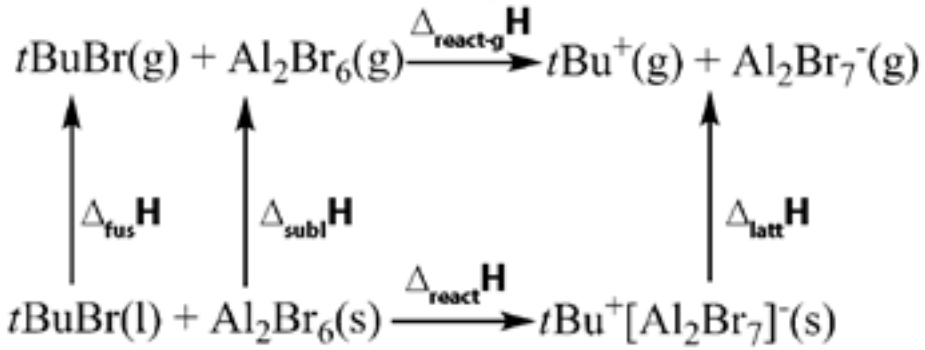
The main causes of errors for computational method are: calculations are not completely accurate, the constants in equations can be inappropriate for the compound studied.

1 pt.

Experimental enthalpy of vaporization of 2-bromo-2-methylpropane (+32 $kJ \cdot mol^{-1}$) and the sublimation enthalpy of **H** (+85 $kJ \cdot mol^{-1}$) are tabulated in handbooks of physical chemistry.

1. Use the Born–Haber cycle to calculate the reaction enthalpy for reaction between **H** and 2-bromo-2-methylpropane in gas phase (where separated ions $\mathbf{F_{-B}}$ and $\mathbf{K_{+}}$ in gaseous state are obtained).

The Born–Haber cycle can be written as:



Therefore reaction enthalpy in gas phase can be calculated as:

$$\Delta_{react-g}H = -\Delta_{latt}H - \Delta_{react}H + \Delta_{subl}H + \Delta_{fus}H$$
$$= -(515.5) - (-29.0) + 32 + 85 = 370\ \mathrm{kJ \cdot mol^{-1}}$$

2 pt (for cycle or correct equation with signs) + 1 pt. (for correct result)