



UNIVERSITY OF TARTU
Youth Academy



J. MOLNER



Uniting Elements, Strengthening Bonds, Shaping Tomorrow!



30th Baltic Chemistry Olympiad

Tartu, Estonia, May 4th–6th, 2024

Theoretical exam solutions

Student's code:

--	--	--	--	--	--

Problem	1	2	3	4	5	6
Points						

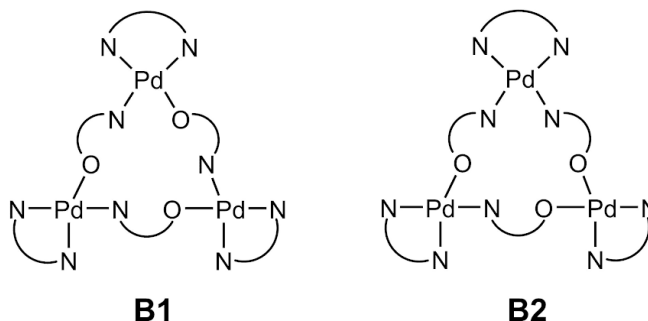
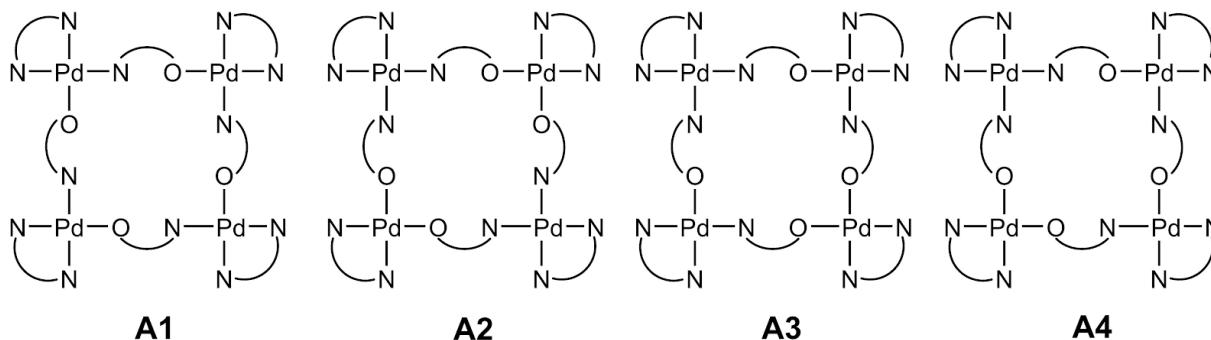
May 5th, 2024
Tartu, Estonia

Problem 1. Polygonal chemistry. Author: Siim Kaukvera) Dinitro(*N,N,N',N'*-tetramethylethylenediamine)palladium(II)

(2 pts)

b) Structures of **A1–A4** and **B1–B2**: *Each correct structure gives 3 points.*

(18 pts)

c) $a = 3, b = 4$

(2 pts)

d) First, ΔH has to be found using the Van't Hoff equation:

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

Substituting $T_1 = 313$ K, $T_2 = 333$ K, $K_1 = 21.5$ and $K_2 = 32.1$ and calculating, we get $\Delta H = 17.38$ kJ·mol⁻¹.

(3 pts)

A new equation can now be written to calculate K_3 . It can be assumed ΔH is constant in the given temperature range. Whether K_3 is found via K_1 or K_2 makes no difference – both approaches are equally valid.

$$\ln\left(\frac{K_3}{K_1}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right)$$

By substituting known parameters and calculating, we get $K_3 = 26.4$.

(3 pts)

e) Equilibrium constant K for the reaction $3\mathbf{A} \rightleftharpoons 4\mathbf{B}$ can be written as $K = \frac{[\mathbf{B}]^4}{[\mathbf{A}]^3}$.

(1 pt)

Let the ratio $\frac{[\mathbf{B}]}{[\mathbf{A}]}$ be equal to x . Hence, $K = [\mathbf{B}] \cdot x^3$.

(2 pts)

Mass balance for Pd: $c_0 = 4 \cdot [\mathbf{A}] + 3 \cdot [\mathbf{B}]$.

(2 pts)

By dividing the mass balance equation by $[\mathbf{B}]$, the following equation is obtained:

$$\frac{c_0}{[\mathbf{B}]} = \frac{4}{x} + 3, \text{ from which } [\mathbf{B}] = \frac{c_0 x}{3x + 4}.$$

(2 pts)

Now, K can be expressed as: $K = [\mathbf{B}] \cdot x^3 = \frac{c_0 x^4}{3x + 4}$.

(1 pt)

Finding the exact solution is impossible under exam conditions, but a simplification can be made.

As $3x \gg 4$, it can be assumed that $3x + 4 \approx 3x$. Therefore, $K = \frac{c_0 x^4}{3x + 4} \approx \frac{c_0 x^3}{3}$. (3 pts)

Finally, $x = \sqrt[3]{\frac{3K}{c_0}} = \sqrt[3]{\frac{3 \cdot 26.4}{1.154 \cdot 10^{-3}}} \approx 41$. (1 pt)

Note: the exact solution is $x = 41.38$, hence the simplification is justified.

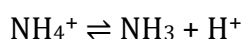
Problem 2. Unknown amino acid. Author: Andreas Päck

a) $n(\text{N}) = n(\text{NH}_3) = n(\text{HCl}) - n(\text{NaOH})$ (1 pt)

$$n(\text{N}) = 0.1350 \text{ mol} \cdot \text{dm}^{-3} \cdot 0.04000 \text{ dm}^3 - 0.1500 \text{ mol} \cdot \text{dm}^{-3} \cdot 0.01683 \text{ dm}^3 = 0.002875 \text{ mol}$$

$$w(\text{N}) = \frac{0.002875 \text{ mol} \cdot 14.01 \text{ g} \cdot \text{mol}^{-1}}{0.3425 \text{ g}} \cdot 100\% \approx 11.76\% \quad (1 \text{ pt})$$

b) Ammonium ions, which remain in the titrated solution, act as a weak acid:



As the equilibrium is considerably shifted to the left, $[\text{H}^+]_{\text{eq}} = [\text{NH}_3]_{\text{eq}}$, therefore:

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = \frac{[\text{H}^+]^2}{[\text{NH}_4^+]} \Rightarrow [\text{H}^+] = \sqrt{K_a \cdot c(\text{NH}_4^+)} = \sqrt{K_a \cdot \frac{n(\text{HCl}) - n(\text{NaOH})}{V(\text{HCl}) + V(\text{NaOH})}} \quad (2 \text{ pts})$$

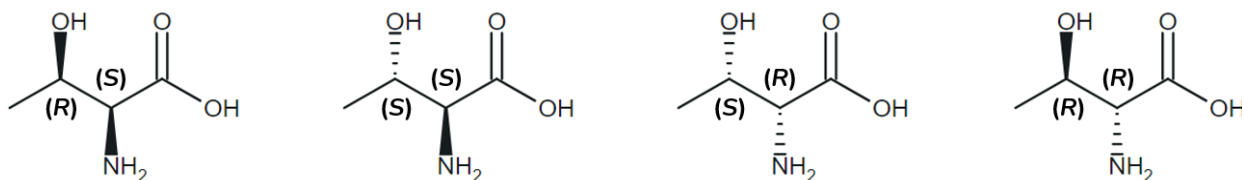
$$\text{pH} = -\log[\text{H}^+] = -\log\left(\sqrt{5.6 \cdot 10^{-10} \cdot \frac{0.002875 \text{ mol}}{0.05683 \text{ dm}^3}}\right) \approx 5.27 \quad (1 \text{ pt})$$

c) Since **X** has two given dissociation constants, it can be assumed that there is only one ionizable amino group in its structure. The general formula of amino acids is $\text{R}-\text{CH}(\text{NH}_2)\text{COOH}$ or $\text{R}-\text{CH}(\text{NH}_3^+)\text{COO}^-$ (zwitterionic form), where the R group represents a specific side chain.

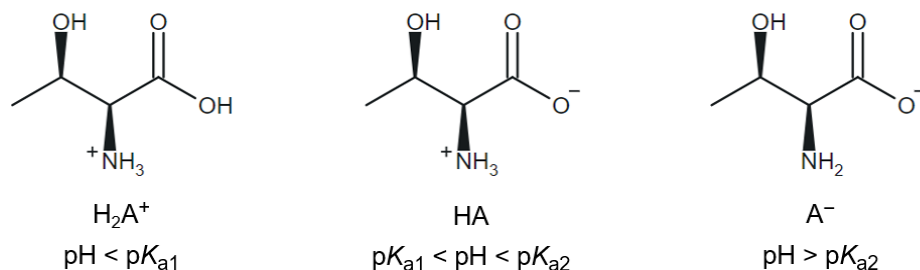
$$M(\text{R}) = \frac{1 \cdot 14.01 \text{ g} \cdot \text{mol}^{-1} \cdot 100\%}{11.76\%} - M(\text{C}_2\text{H}_4\text{NO}_2) = 45.07 \text{ g} \cdot \text{mol}^{-1} \quad (1 \text{ pt})$$

R corresponds to the hydroxylated carbon chain $\text{CH}_3\text{CH}(\text{OH})-$, thus the condensed structural formula of **X** is $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}$ or $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{NH}_3^+)\text{COO}^-$ (Thr). (1 pt)

d) Each correctly drawn stereochemical structure gives 1 point – in total 4 points. Each pair of correct configuration indications (S/R) gives 0,5 points – in total 2 points.

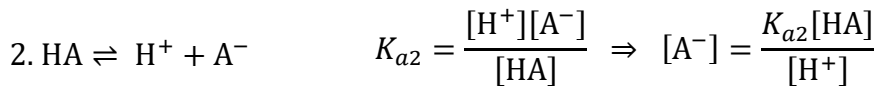
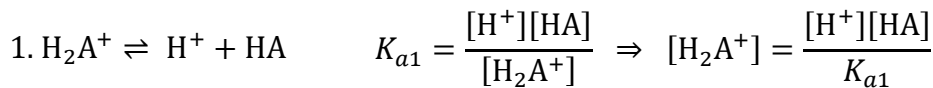


e) Each correctly drawn stereochemical ionic form gives 1 point – in total 3 points.



f) Two-step dissociation of X:

(2 pts)

At the isoelectric point $[\text{H}_2\text{A}^+] = [\text{A}^-]$, therefore:

(4 pts)

$$\frac{[\text{H}^+][\text{HA}]}{K_{a1}} = \frac{K_{a2}[\text{HA}]}{[\text{H}^+]} \Rightarrow \frac{[\text{H}^+]}{K_{a1}} = \frac{K_{a2}}{[\text{H}^+]} \Rightarrow [\text{H}^+] = \sqrt{K_{a1}K_{a2}} = \frac{K_{a1}K_{a2}}{2}$$

$$\text{pH} = -\log[\text{H}^+] = \frac{-\log K_{a1} - \log K_{a2}}{2} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2} = \frac{2.09 + 9.10}{2} \approx 5.60$$

Problem 3. Reverse engineering. Author: Ritums Cepītis

a) $\ln[A] = \ln[A]_0 - kt$, where $k = \frac{\ln(0.05) - \ln(1)}{30 \text{ s}} = 0.1 \text{ s}^{-1}$

(2 pts)

b) $k_{300} = 0.1 \text{ s}^{-1}$; $k_{2024} = 1.0 \text{ s}^{-1}$

$$\ln\left(\frac{k_{300}}{k_{2024}}\right) = \frac{E_a}{8.314} \left(\frac{1}{2024} - \frac{1}{300}\right), \text{ where } E_a = 6.7 \text{ kJ} \cdot \text{mol}^{-1}$$

(3 pts)

c) T_1 and t_2 .

(2 pts)

d) If T_1 is chosen, the answer is $T_1 = 1230 \text{ K}$.

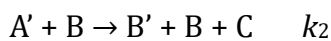
(2 pts)

If t_2 is chosen, the answer is $t_2 = 3.79 \cdot 10^{-8} \text{ s}$.

(2 pts)

e) The equations for the missing elementary steps:

(4 pts)



Mechanism correspondence to the given reaction law:

$$\frac{d(\text{B}')}{dt} = 0 = k_2[\text{A}'][\text{B}] - k_3[\text{A}'][\text{B}'] \Rightarrow [\text{B}'] = \frac{k_2[\text{A}'][\text{B}]}{k_3[\text{A}']} = \frac{k_2[\text{B}]}{k_3}$$

$$\frac{d(\text{A}')}{dt} = 0 = k_1[\text{A}] - k_{-1}[\text{A}'][\text{B}] - k_2[\text{A}'][\text{B}] - k_3[\text{A}'][\text{B}'] =$$

$$= k_1[\text{A}] - k_{-1}[\text{A}'][\text{B}] - k_2[\text{A}'][\text{B}] - k_2[\text{A}'][\text{B}'] =$$

$$= k_1[\text{A}] - [\text{A}'](k_{-1}[\text{B}] + 2 \cdot k_2[\text{B}])$$

$$\Rightarrow [\text{A}'] = k_1[\text{A}]$$

$$-\frac{d(\text{A})}{dt} = k_1[\text{A}] - k_{-1}[\text{A}'][\text{B}] = k_1[\text{A}] - \frac{k_{-1}k_1[\text{A}]}{(k_{-1} + 2 \cdot k_2)} = \left(\frac{2 \cdot k_{-1}k_1}{k_{-1} + 2 \cdot k_2}\right)[\text{A}]$$

Problem 4. Have you heard about cerium? Author: Deimantas Šmigelskas**Part I. Minerals**

a) There are 4 tetrahedral PO_4^{3-} ions and 4 Ce atoms in a unit cell which consists of **24** atoms in total. (1 pt)

b) **Th** isotopes are radioactive while La and Nd have stable isotopes. (1 pt)

c) $\Delta m = n(\text{U}) \cdot M(\text{U}) - n(\text{Ce}) \cdot M(\text{Ce}) = 4.53 \text{ g}$

$$97.91n = 4.53 \Rightarrow n = 0.0463 \quad (1 \text{ pt})$$

$$\frac{n}{n_0} = \frac{0.0463}{\frac{m(\text{CePO}_4)}{M(\text{CePO}_4)}} = \mathbf{0.71} \quad (1 \text{ pt})$$

d) $N_n(^{238}\text{U}) = N_0 e^{-\lambda_U t}$

Since there was no pre-existing lead in the mineral: $N_0 = N_n(^{238}\text{U}) + N_n(^{206}\text{Pb})$ (1 pt)

$$\frac{N_n(^{238}\text{U})}{N_n(^{238}\text{U}) + N_n(^{206}\text{Pb})} = e^{-\lambda_U t} \Rightarrow \ln\left(\frac{N_n(^{238}\text{U})}{N_n(^{238}\text{U}) + N_n(^{206}\text{Pb})}\right) = -\lambda_U t \Rightarrow$$

$$t = \frac{\ln\left(\frac{N_n(^{238}\text{U})}{N_n(^{238}\text{U}) + N_n(^{206}\text{Pb})}\right)}{-\lambda_U} = \frac{\ln\left(\frac{N_n(^{238}\text{U}) + N_n(^{206}\text{Pb})}{N_n(^{238}\text{U})}\right)}{\lambda_U} = \frac{\ln\left(1 + \frac{N_n(^{206}\text{Pb})}{N_n(^{238}\text{U})}\right)}{\lambda_U} \quad (2 \text{ pts})$$

$$\lambda = \frac{\ln(2)}{t_{0.5}}$$

Moles of atoms can be used instead of the number of atoms and Pb mass is 206 because of $^{238}\text{U} \rightarrow ^{206}\text{Pb}$ decay.

$$t = \frac{\ln\left(1 + \frac{n_n(^{206}\text{Pb})}{n_n(^{238}\text{U})}\right)}{\frac{\ln(2)}{t_{0.5}}} = \frac{\ln\left(1 + \frac{\frac{6.05 \text{ g} \cdot 0.0001}{222 \text{ g} \cdot \text{mol}^{-1}}}{2 \cdot \frac{6.05 \text{ g} \cdot 0.0037}{524 \text{ g} \cdot \text{mol}^{-1}}}\right)}{\ln(2)} \cdot t_{0.5} = 0.0453 \cdot t_{0.5} = \mathbf{2.02 \cdot 10^8 \text{ years}} \quad (1 \text{ pt})$$

e) 1 mol of CO_3^{2-} produces 1 mol of CO_2 , which gives:

$$n(\text{CO}_2) = \frac{m(\text{CO}_2)}{M(\text{CO}_2)} = 0.014224 \text{ mol} \quad (0.5 \text{ pts})$$

$$M(\text{Ce}_{0.48}\text{La}_{0.37}\text{Nd}_{0.1}\text{Pr}_{0.04}\text{Sm}_{0.01}\text{CO}_3\text{F}) = \frac{m}{n(\text{CO}_3^{2-})} = 219.235 \text{ g} \cdot \text{mol}^{-1} \quad (0.5 \text{ pts})$$

Mass balance: (1.5 pts)

$$x \cdot M(\text{La}) + y \cdot M(\text{Nd}) = 219.235 - n(\text{Ce}) \cdot M(\text{Ce}) - n(\text{Pr}) \cdot M(\text{Pr}) - n(\text{Sm}) \cdot M(\text{Sm}) - n(\text{C}) \cdot M(\text{C}) - n(\text{O}) \cdot M(\text{O}) - n(\text{F}) \cdot M(\text{F}) \quad (0.5 \text{ pts})$$

$$x \cdot M(\text{La}) + y \cdot M(\text{Nd}) = 65.827 \quad (1 \text{ pt})$$

Charge balance: (0.5 pts)

$$3 \cdot [n(\text{Ce}^{3+}) + n(\text{La}^{3+}) + n(\text{Nd}^{3+}) + n(\text{Pr}^{3+}) + n(\text{Sm}^{3+})] = 2 \cdot n(\text{CO}_3^{2-}) + n(\text{F}^-)$$

$$n(\text{La}^{3+}) + n(\text{Nd}^{3+}) = 0.47 \quad (1 \text{ pt})$$

The system of equations yields:

$$\begin{cases} x \cdot M(\text{La}) + y \cdot M(\text{Nd}) = 65.827 \\ x + y = 0.47 \end{cases} \Rightarrow (x; y) = (0.37; 0.1)$$



f) There are 6 atoms closely located to cerium in the same plane plus 3 above and 3 below the plane – in total 12 atoms, which means the coordination number of Ce is **12**. (1 pt)

g) $2\text{CeO}_2 + 8\text{HCl} \rightarrow 2\text{CeCl}_3 + 4\text{H}_2\text{O} + \text{Cl}_2$ (1 pt)

$$n(\text{HCl}) = 4 \cdot n(\text{CeO}_2) = 4 \cdot \frac{5.0 \cdot 10^3 \text{ kg} \cdot w(\text{Ce})}{M(\text{CeO}_2) \cdot 100\%} = 45675.14 \text{ mol}$$

$$V(\text{HCl}) = \frac{n}{c} = 91350.27 \text{ dm}^3 \approx \mathbf{91 \text{ m}^3} \quad (1 \text{ pt})$$

h) β -cerium ($a = 0.3681 \text{ nm}$, $c = 1.1857 \text{ nm}$). DHCP structure can be subdivided into 6 rhombic prism unit cells each of which has 2 atoms inside it: (3 pts)

$$\rho = \frac{m(\text{atoms})}{V(\text{unit cell})} = \frac{2 \cdot \frac{M(\text{Ce})}{N_A}}{\frac{\sqrt{3}}{2} a^2 \frac{c}{2}} = \mathbf{6.69 \text{ g} \cdot \text{cm}^{-3}}$$

γ -cerium ($a = 0.5161 \text{ nm}$). FCC unit cell contains 4 atoms of Ce: (2 pts)

$$\rho = \frac{m(\text{atoms})}{V(\text{unit cell})} = \frac{4 \cdot \frac{M(\text{Ce})}{N_A}}{a^3} = \mathbf{6.77 \text{ g} \cdot \text{cm}^{-3}}$$

Thus, γ -cerium is more dense than β -cerium. (0.5 pts)

Part II. Cerium loves redox

i) $\text{H}^+ + [\text{Ce}(\text{NO}_3)_6]^{2-} + \text{Fe}(\text{OH})_2 + \text{Cu}_2\text{O} \rightarrow \text{Ce}^{3+} + \text{Fe}^{3+} + \text{Cu}^{2+} + \text{H}_2\text{O} + \text{NO}_3^-$

Oxidation half-equations:



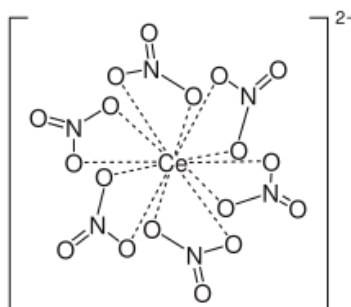
Reduction half-equation:



The sum of oxidation and reduction half-equations:



j) The structure of the anion of CAN: (1 pt)



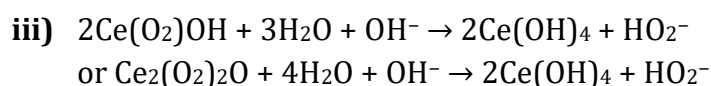
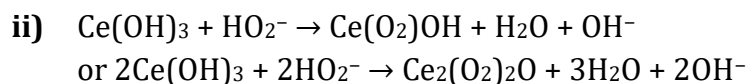
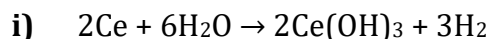
k) *Each identified compound A–C gives 1 point.* (3 pts)

A must contain Ce and O. Hydrogen in water is a weak oxidizing agent, so Ce will be in +3 form, and out of Ce_2O_3 , $\text{CeO}(\text{OH})$, $\text{Ce}(\text{OH})_3$, or other non-polymeric formulas, $\text{Ce}(\text{OH})_3$ gives the right answer. In the second reaction peroxide ion is consumed and water is produced, meaning that the HO_2^- ion has lost its hydrogen and replaced two OH^- ions in hydroxide resulting in **B**

$\text{Ce}(\text{O}_2)\text{OH}$ (Ce cannot be +4 here because no oxidation occurs for cerium). However, anhydride $\text{Ce}_2(\text{O}_2)_2\text{O}$ formed after dimerization of $\text{Ce}(\text{O}_2)\text{OH}$ followed by H_2O abstraction is also a possible choice. Ce must be +4 in **C** due to oxidation and since all oxygens have the same oxidation number CeO_2 or $\text{Ce}(\text{OH})_4$ are possible. The absence of stronger base to deprotonate OH^- leaves us with the choice of $\text{Ce}(\text{OH})_4$.

Balanced reaction equations:

(3 pts)

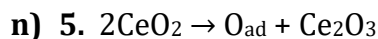


l) Ceria (CeO_2) plays a special role in heterogeneous catalysis. In the ideal cell of CeO_2 , the structure consists of a **face-centered** cubic unit cell of cations with anions occupying the **tetrahedral** holes. In the structure, each cerium cation is coordinated by **8** nearest-neighbor oxygen anions, while each oxygen anion is coordinated by **4** nearest-neighbor cerium cations. Ceria can also be doped with other metal cations to alter electric conductivity. When cerium cations are replaced with lower oxidation state elements ($\text{M}^{2+}/\text{M}^{3+}$), the lattice oxygen atoms in CeO_2 are **removed**. The ceria crystal usually exhibits a few defects due to the co-existence of Ce^{4+} and Ce^{3+} ions. /.../ Because the metal surfaces are essentially saturated in CO when excess CO is present, the rate-limiting step for the reaction is **2**. /.../

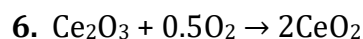
(3 pts)

m) **I** – NO_x (NO , NO_2); **J** – O_2 ; **K** – O ; **I** – Ce_2O_3 ; **M** – H_2 .

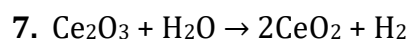
(3 pts)



(1 pt)



(1 pt)



(1 pt)

o) $\text{Ce}(5,5'-(\text{Cl})_2\text{-salen})_2$ is a stronger oxidizing agent, because methoxy-substituted aromatic rings are more electron-rich, therefore, stabilizing central $\text{Ce}(\text{IV})$.

(1 pt)

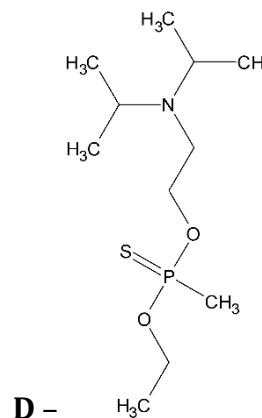
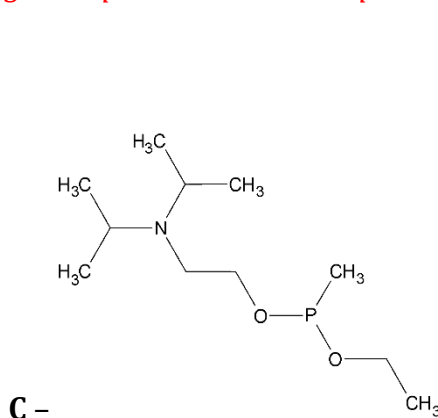
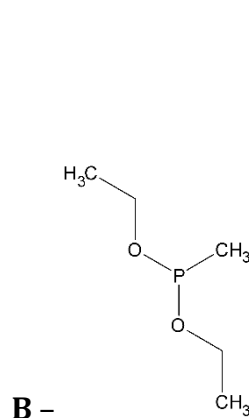
Problem 5. Poisonous chemicals. Author: Denis Sokol

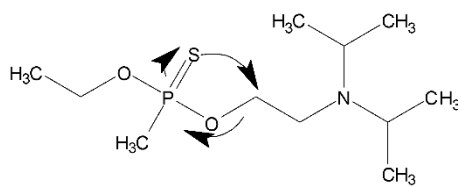
a) **A** – $[\text{PCl}_3\text{CH}_3]^+[\text{AlCl}_3\text{I}]^-$

(4 pts)

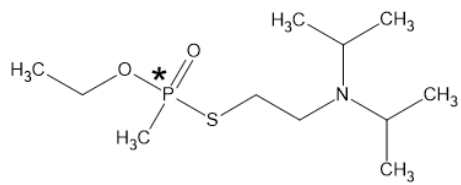
b) *Each correct structure gives 4 points – in total 12 points.*

(12 pts)

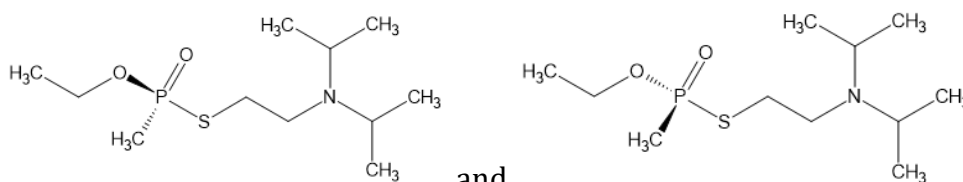




c) (4 pts)

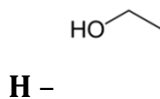
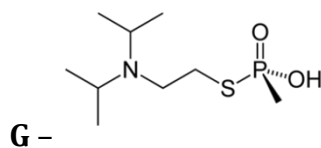
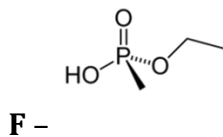
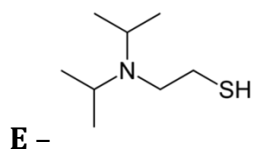


d) (2 pts)

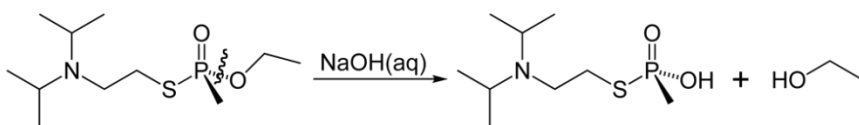
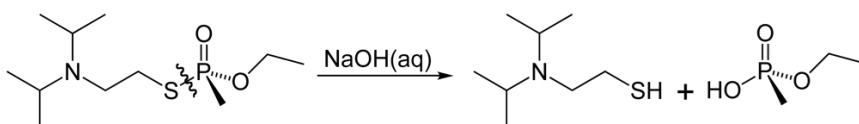


e) 2 isomers: (1 pt)

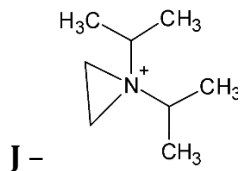
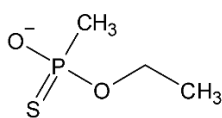
f) Each correct structure gives 2 points – in total 8 points. (8 pts)



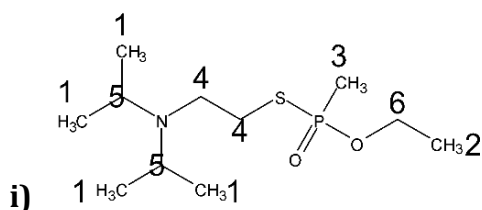
Hydrolysis reactions with aqueous sodium hydroxide:



g) G (2 pts)



(8 pts)


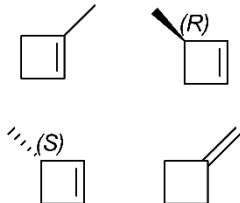
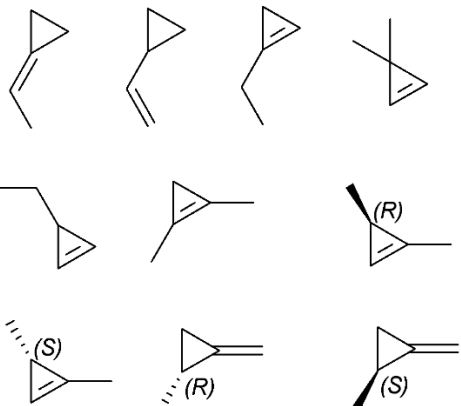



(4 pts)

- j) Phosphorus (4 pts)
- k) **qd, sept, s** (should be multiplet in a real spectrum), **d, t, d**. (2 pts)
- l) $LD = \frac{7 \text{ mg} \cdot 30 \text{ dm}^3}{1000 \text{ dm}^3} = 0.21 \text{ mg} = \mathbf{0.00021 \text{ g}}$ (1 pt)
- m) $LD = \frac{0.00021 \text{ g}}{80 \text{ kg}} = \mathbf{2.62 \cdot 10^{-6} \text{ g} \cdot \text{kg}^{-1}}$ (1 pt)
- n) **3816** lethal doses. (1 pt)

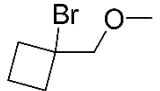
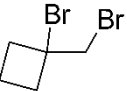
Problem 6. Simple organic chemistry. Author: Nauris Narvaišs

- a) *Structure drawing is not required, only a numerical answer.* (5 pts)


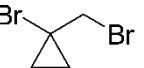
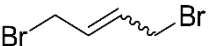
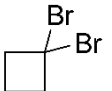
<p>i) 1 (1 pt)</p> 	<p>ii) 4 (2 pts)</p> 	<p>iii) 10 (2 pts)</p> 
---	---	---

- b) The structure of the symmetrical isomer:  (3 pts)

- c) The main product:  (3 pts)

Other products:  (1 pt) or  (0 pts)

- d) Structures of compounds **H1** and **B1–B3**: *Each correct structure gives 3 points.* (12 pts)

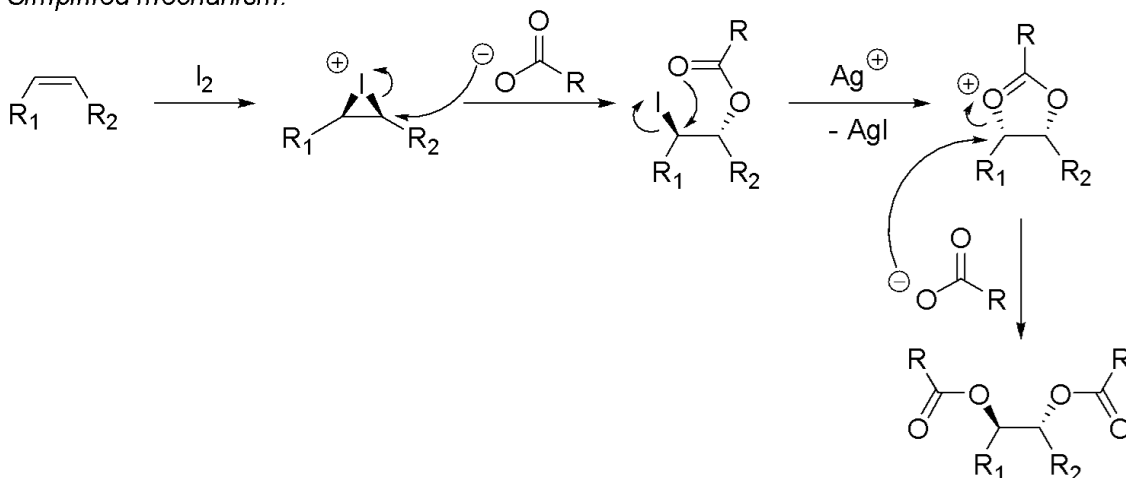
<p>H1</p> 	<p>B1</p> 	<p>B2</p>  <p>(either cis or trans)</p>	<p>B3</p> 
--	--	--	--

- e) Number of possible stereoisomers and products: *1 point for each correct answer.* (4 pts)

	i) (R1 = R2) ≠ H	ii) (R1 ≠ R2) ≠ H
Stereoisomers formed	2	2
Exist in total for product	3	4

- f) 1 pt for formation of iodonium, 1 pt for attack on iodonium, 1 pt for cyclization, 1 pt for attack of second carboxylate. If mechanism is just 2 S_N2 reactions, then 2 pts total. If relative stereochemistry is incorrect or missing, then 1 pt deduction.

Simplified mechanism:



- g) Compounds A1–A3:

(9 pts)

<p>A1</p>	<p>A2</p>	<p>A3</p>
<p>If stereochemistry is incorrect or not specified 2 pts in total.</p>	<p>3 pts</p>	<p>If stereochemistry is incorrect or not specified 2 pts in total.</p>

- h) 1 pt for bromonium formation, 2 pts for rearrangement, 1 point for elimination. 0.5 pts for E_2 instead of E_1CB .

Simplified mechanism:

