

Student code:

XIX Baltic Chemistry Olympiad



Theoretical Problems

Answer sheets

Code:

1.	2.	3.	4.	5.	6.	Σ

**15-17 April 2011
Vilnius, Lithuania**

Student code:

Problem 1. Aluminium

a)

Calculations:

$$n = 9.48 \text{ g} / 474 \text{ g/mol} = 0.0200 \text{ mol}$$

$$m(\text{H}_2\text{O}) = 100 + 0.02 \cdot 12 \cdot 18 = 104.32 \text{ g}$$

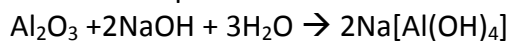
$$c_m = 0.0200 \text{ mol} / 0.10432 \text{ kg} = 0.1917 \text{ mol/kg}$$

$$\Delta T = -4 \cdot 1.86 \text{ }^\circ\text{C kg/mol} \cdot 0.1917 \text{ mol/kg} = -1.43 \text{ }^\circ\text{C}$$

Freezing point is: -1.43 °C

b)

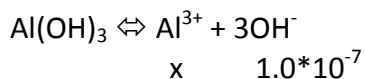
Molecular equation:



c)

Calculations:

K_{sp} is so small that main source of OH^- is water, not $\text{Al}(\text{OH})_3$. So we can assume that $[\text{OH}^-] = 1.0 \cdot 10^{-7}$.



$$1.3 \cdot 10^{-33} = x \cdot (1.0 \cdot 10^{-7})^3 \qquad x = 1.3 \cdot 10^{-12}$$

Will dissolve $1.3 \cdot 10^{-12} \cdot 10 = 1.3 \cdot 10^{-11} \text{ mol} \rightarrow m = 1.0 \cdot 10^{-9} \text{ g of Al}(\text{OH})_3$

Mass = $1.0 \cdot 10^{-9} \text{ g}$

Student code:

d)

Calculations:

$$n(\text{EDTA}) = 0.0500 \text{ M} \cdot 50.00 \text{ mL} = 2.5 \text{ mmol}$$

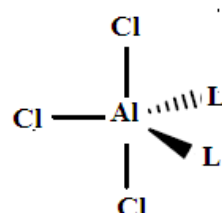
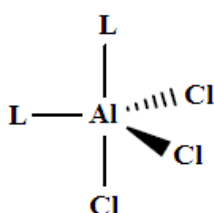
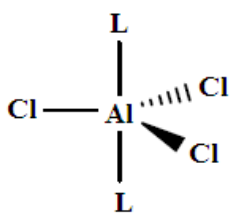
$$n(\text{Zn}^{2+}) = 0.0500 \text{ M} \cdot 23.25 \text{ mL} = 1.1625 \text{ mmol}$$

$$n(\text{Al}^{3+}) = 2.5 - 1.1625 = 1.13375 \text{ mmol}$$

$$c = 1.13375 \text{ mmol} / 20.00 \text{ mL} = 0.0669 \text{ mol/L}$$

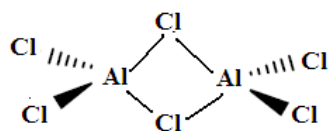
e)

Isomers:



f)

Al_2Cl_6 molecule



Student code:

Problem 2

Beware of light!

1. Formulas for compounds:

A	KI	E	I ₃ ⁻
B	KOH	F	Cl ₂
C	I ₂	G	KIO ₃
D	KI ₃		

Reaction 1: $5KI + 2H_2O + O_2 \rightarrow 4KOH + I_2 + KI_3$

Reaction 2: $KI + I_2 \rightarrow KI_3$

Reaction 3: $6KOH + KI + 3Cl_2 \rightarrow KIO_3 + 6KCl + 3H_2O$

Reaction 4: $KIO_3 + 5KI + 6H^+ \rightarrow 3I_2 + 6K^+ + 3H_2O$

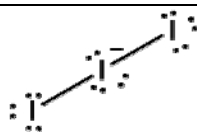
Reaction 5: $2KIO_3 + 12HCl \rightarrow I_2 + 5Cl_2 + 2KCl + 6H_2O$

2. Mark correct answer(-s):

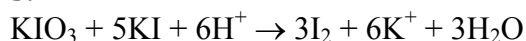
A	B	C	D	E
X		X		

3. Solubility is higher due to ... Solubility increases due to formation of complex anion I₃⁻.

4. Lewis formula for E



5.



Nernst equation for reduction halfreaction:

$$E = E^\circ - \frac{RT}{zF} \ln \frac{c_{red}}{c_{oks}}$$

E for halfreaction (2):

$$E_2 = E^\circ_2 - \frac{RT}{zF} \ln \frac{[I^-]}{1} = 0,536 - \frac{8,314 \cdot 298}{1 \cdot 96485} \ln(0,10) = 0,595V$$

E for halfreaction (2), as a function of pH:

$$E_1 = E^\circ_1 - \frac{RT}{zF} \ln \frac{1}{[IO_3^-] \cdot [H^+]^6} = E^\circ_1 - \frac{RT}{zF} \ln \frac{1}{[IO_3^-]} - \frac{RT}{zF} \ln \frac{1}{[H^+]^6} =$$

$$E^\circ_1 - \frac{RT}{zF} \ln \frac{1}{[IO_3^-]} - 2,303 \cdot 6 \cdot \frac{RT}{zF} pH = 1,195 - \frac{8,314 \cdot 298}{5 \cdot 96485} \ln \frac{1}{0,25} - 2,303 \cdot 6 \cdot \frac{8,314 \cdot 298}{5 \cdot 96485} pH =$$

$$= 1,188 - 0,0710 pH$$

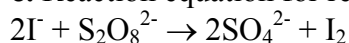
pH, when $E_1 = E_2$:

$$0,595 = 1,188 - 0,0710 pH$$

$$pH = \frac{1,188 - 0,595}{0,071} = 8,35$$

Student code:

6. Reaction equation for reaction of A with persulphate:



7. Partial rate orders: 1 with respect to A and 1 with respect to $\text{S}_2\text{O}_8^{2-}$.

Kinetic equation: $\text{rate} = k \cdot [\text{I}^-][\text{S}_2\text{O}_8^{2-}]$

Reaction rate constant calculations:

$$\text{Rate constant: } k = \frac{v}{[\text{I}^-][\text{S}_2\text{O}_8^{2-}]} = \frac{1.1 \cdot 10^{-8}}{0.1 \cdot 10 \cdot 10^{-6}} = 0.011 \text{ L}/(\text{mol} \cdot \text{s})$$

8. Temperature calculations:

Reaction rate increases due to change of rate constant. Using Arrhenius equation:

$$\ln \frac{k_{25}}{k_T} = \frac{E_A}{R} \left(\frac{1}{T_T} - \frac{1}{T_{25}} \right)$$

$$\ln \frac{k_{25}}{10 \cdot k_{25}} = \frac{42000}{8.314} \left(\frac{1}{T_T} - \frac{1}{298} \right) = \ln 0.1$$

$$\frac{1}{T_T} - \frac{1}{298} = \frac{8.314 \cdot \ln 0.1}{42000} = -4.558 \cdot 10^{-4}$$

$$\frac{1}{T_T} = -4.558 \cdot 10^{-4} + \frac{1}{298} = 2.9 \cdot 10^{-3}$$

$$T = 344.8 \text{ K} \approx 345 \text{ K} = 72 \text{ }^\circ\text{C}$$

9. Reaction time calculations:

For calculations use second order rate equation (as concentrations for all reactants are equal):

$$\frac{1}{C} - \frac{1}{C_0} = k \cdot t$$

$$\frac{1}{0.1 \cdot 10^{-3}} - \frac{1}{1 \cdot 10^{-3}} = 0.011 \cdot t$$

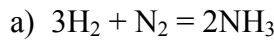
$$t = 818181 \text{ s} = 227 \text{ h} \approx 230 \text{ h}$$

Reaction time is 230 hours.

Student code:

Problem 3

Reacting gas



b)

	3H_2	N_2	2NH_3	Σ
$t = 0$	n_0	n_0	0	
$t = \infty$	$n_0 - 3yn_0$	$n_0 - 3yn_0$	$2yn_0$	$2n_0 - 2yn_0$
x_∞	$\frac{n_0 - 3yn_0}{2n_0 - 2yn_0} = \frac{1-3y}{2-2y}$	$\frac{n_0 - yn_0}{2n_0 - 2yn_0} = \frac{1-y}{2-2y}$	$\frac{2yn_0}{2n_0 - 2yn_0} = \frac{2y}{2-2y}$	1

$$x_{\text{NH}_3} = \frac{2y}{2-2y}$$

$$K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{H}_2}^3 p_{\text{N}_2}} = \frac{x_{\text{NH}_3}^2 p^2}{x_{\text{H}_2}^3 p^3 x_{\text{N}_2} p} = \frac{(2-2y)^2 \cdot 4y^2}{(1-3y)^3 \cdot (1-y)} \cdot \frac{1}{p^2} = \frac{16 \cdot (1-y) \cdot y^2}{(1-3y)^3 p^2}$$

c)

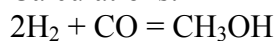
$$x_{\text{NH}_3} = \frac{2y}{2-2y} = 0.1111 \Rightarrow y = \frac{2 \cdot 0.1111}{2 + 2 \cdot 0.1111} = 0.1000$$

$$K_p = \frac{16 \cdot (1-y) \cdot y^2}{(1-3y)^3 p^2} \Rightarrow p = \sqrt{\frac{16 \cdot (1-y) \cdot y^2}{(1-3y)^3 K_p}} = \sqrt{\frac{16 \cdot 0.9 \cdot 0.1^2}{0.7^3 \cdot 1.60 \cdot 10^{-4} \text{ bar}^{-1}}} = 51.2 \text{ bar}$$

d)

A No **B Yes**

Calculations:



$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{p_{\text{CH}_3\text{OH}}}{99 p_{\text{CH}_3\text{OH}} \cdot (10 p_{\text{CH}_3\text{OH}})^2}$$

$$= 21.21 \text{ kJ/mol} + 4.157 \text{ kJ/mol} \cdot \ln \frac{1}{9900 \cdot (0.1)^2} = 2.11 \text{ kJ/mol}$$

Methanol would not form, equilibrium is shifter towards the production of reagent.

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

e)

$$Q = \exp\left(-\frac{\Delta_r G}{RT}\right) = Q_{\text{max}} = 0.00608$$

Q is maximal value, below this value methanol production is favorable.

Student code:

Problem 4

Smart robot

a)

A P	B PCl ₅	C H ₃ PO ₄	D HCl
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b)

b) Equations

1	$2P + 5Cl_2 = 2PCl_5$
2	$PCl_5 + 4H_2O = H_3PO_4 + 5HCl$
3	$HCl + NaOH = NaOH + HCl$
4	$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O$

c)

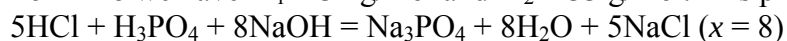
If **A** and NaOH relate through a set of equations as 1:x, then

$$M(A) = \frac{m}{n} = \frac{mx}{Vc} = \frac{10.0 \text{ mg} \cdot x}{0.1234 \text{ M} \cdot 19.95 \text{ cm}^3} = 4.062x \frac{\text{g}}{\text{mol}}$$

According to gas diffusion results sample contains two isotopes in equimolar quantities. Let their masses be M_1 and M_2 , then

$$\frac{4.92 \text{ mg}}{M_1} = \frac{5.08 \text{ mg}}{M_2} \text{ and } \frac{M_1 + M_2}{2} = 4.062x \frac{\text{g}}{\text{mol}}$$

For $x = 8$ we have $M_1 = 32 \text{ g/mol}$ and $M_2 = 33 \text{ g/mol}$. **A** is phosphorus.



d)

$$k_1 = \frac{a_1 M_1}{m_1 N_A} = \frac{5.19 \cdot 10^{13} \text{ s}^{-1} \cdot 32 \text{ g/mol}}{0.00492 \text{ g} \cdot 6.02 \cdot 10^{23} \text{ mol}^{-1}} = 5.61 \cdot 10^{-7} \text{ s}^{-1}$$

$$k_2 = \frac{a_2 M_2}{m_2 N_A} = \frac{2.94 \cdot 10^{13} \text{ s}^{-1} \cdot 33 \text{ g/mol}}{0.00508 \text{ g} \cdot 6.02 \cdot 10^{23} \text{ mol}^{-1}} = 3.17 \cdot 10^{-7} \text{ s}^{-1}$$

Initial $a_0 = a_1 + a_2$. final activity is $a_f = 0.001a_0$ and almost entirely due to decay of ^{33}P as this isotope has a smaller constant of decay. Therefore,

$$a_f = 0.001a_0 = k_2 N_2 \exp(-k_2 t)$$

$$t = -\frac{1}{k_2} \ln\left(\frac{0.001a_0}{k_2 N_2}\right) = 215$$

$$t = -\frac{1}{3.17 \cdot 10^{-7} \text{ s}^{-1}} \ln\left(\frac{0.001 \cdot (5.19 \cdot 10^{13} + 2.94 \cdot 10^{13}) \text{ s}^{-1} \cdot 33 \text{ g/mol}}{3.17 \cdot 10^{-7} \text{ s}^{-1} \cdot 0.00508 \text{ g} \cdot 6.02 \cdot 10^{23} \text{ mol}^{-1}}\right) = 1.86 \cdot 10^7 \text{ s} = 215 \text{ d}$$

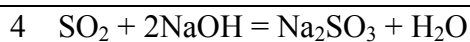
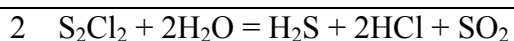
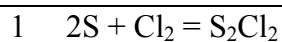
Time = 215 d

e)

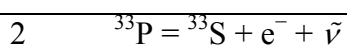
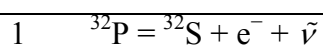
E:	F:	G:	H:
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Student code:

f) Chemical equations:



Radioactive decay equations:



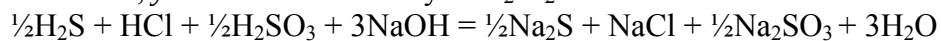
g)

Calculations:

If **E** and NaOH relate through a set of equations as 1:y, then

$$M(\text{E}) = \frac{m}{n} = \frac{mx}{Vc} = \frac{10.0 \text{ mg} \cdot y}{0.4321 \text{ M} \cdot 2.136 \text{ cm}^3} = 10.83y \frac{\text{g}}{\text{mol}}$$

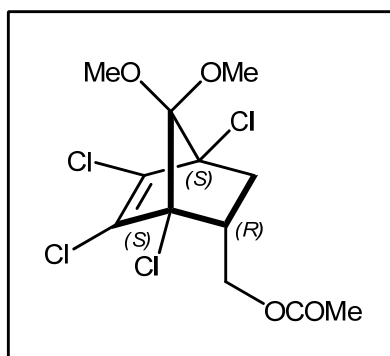
Therefore, $y = 3$. Thus F can only be S_2Cl_2 .



Student code:

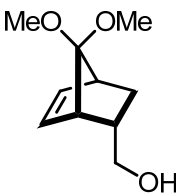
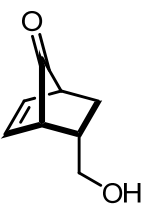
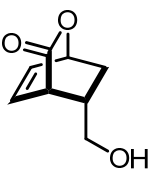
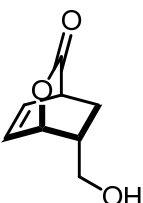
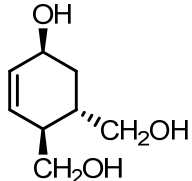
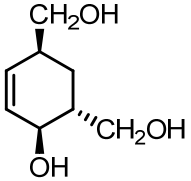
Problem 5. Chiral polyhydroxylated cyclohexanoids.

1. Which class of enzymes will catalyze this reaction? (select the appropriate class of enzymes)
 - a) oxidoreductase
 - b) isomerase
 - c) lipase**
 - d) ligase
2. What is the maximum yield of compound **B**?
 - a) 100 %
 - b) 90 %
 - c) 75 %
 - d) 50 %**
3. Find chiral centers of compound **B** and indicate their configurations.



Student code:

4. Draw the entire structures of compounds **D-G**.

D: 	E: 
F1: 	F2: 
G1: 	G2: 

5. In respect to each other compounds **G1** and **G2** are:

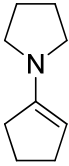
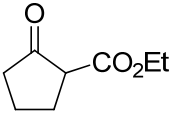
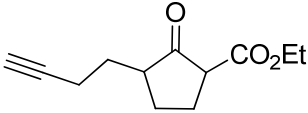
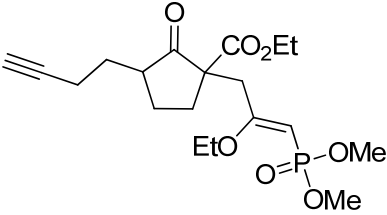
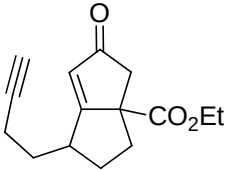
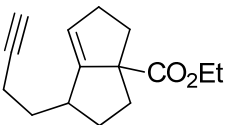
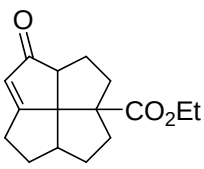
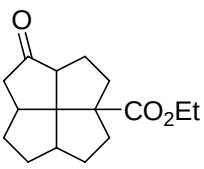
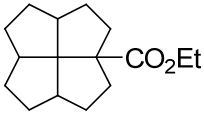
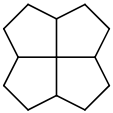
- a) enantiomers
- b) structural isomers**
- c) diastereomers
- d) conformers.

Student code:

Problem 6.

Flat carbon

21 active points. Total points are calculated dividing active points with 21 and multiplying with 13.

A 1 pt  or iminium	B 2 pts 
C 3 pts, 1 for wrong regioisomer 	D 3 pts, 1 for wrong regioisomer 
E 4 pts, -1 for each little mistakes like misplaced double bond 	F 1 pt, only for correct structure 
G 0.5 pt 	H 0.5 pt 
I 1 pt 	J 1pt 

Student code:

2. Mechanism. 2 points for aldol reaction leading to Horner-Emmons intermediate, 2 points for Horner-Emmons reaction. 1pt for anything that looks like aldol.

