



# **28<sup>th</sup> International Chemistry Olympiad**

**14 - 23 July 1996, Moscow Russia**

## **Theoretical Examination**

### **Problems and Solutions**

## Problem 1.

The stereoregular polymerization of unsaturated hydrocarbons is usually considered as one of the most important for the industrial organic chemistry. The salts of big nonlinear cations carrying a sufficiently high charge to attack the electron density distributed along the  $\pi$ -bonds of the olefin molecules are usually used as the catalysts in these processes. Chloroaluminate anions (like  $\text{AlCl}_4^-$ ) possessing a highly delocalized negative charge are used usually as the anions. The necessity to develop new catalysts of this kind urged the chemists to study the interaction in the system A - B, where A=Te (cryst.) and B=( $\text{TeCl}_4+4\text{AlCl}_3$ ). The second component B was considered as an analog of Te(IV) chloroaluminate  $\text{Te}[\text{AlCl}_4]_4$  which however cannot be isolated as an individual compound. It was found out that the interaction of the components A and B can lead to the formation of three new compounds (I, II and III) in the systems containing initially 77.8, 87.5 and 91.7 mol.% of the component A respectively. It was also noticed that while in the case of compounds II and III no side products were formed, the formation of I was accompanied by the evolution of 1 mole of volatile  $\text{TeCl}_4$  per two moles of I.

The compounds I and II attracted a particular interest of investigators. They both have pinkish-purple color and both dissociate into three ions as the conductivity studies in melted  $\text{NaAlCl}_4$  showed. The cryoscopic measurements in  $\text{NaAlCl}_4$  melt enabled to determine the molecular weights of these compounds being equal to  $1126\pm 43$  g/mole and  $867\pm 48$  g/mole for I and II respectively. In the IR spectra of both compounds there is only one band observed which can be attributed to a vibration mode of a bond formed by Te atom. This band lies at  $133\text{ cm}^{-1}$  and is therefore so low in energy that this bond undoubtedly is a kind of Te—Te interaction. The  $^{27}\text{Al}$  NMR data for the complexes I and II show that in each compound there is only one type of tetrahedrally coordinated aluminum. However, the observed chemical shifts of aluminum for the compounds I and II are different, thus manifesting that Al atoms are different in them.

1. Determine Te:Al:Cl minimal atomic ratio for the complexes I, II and III.
2. Write the molecular-formulae of the compounds I and II.
3. Write the formulae of the anions and cations in compounds I and II
4. Draw stereochemical formulae of cations and anions in the structures of I and II assuming that the cations in I and II are examples of inorganic aromatic systems.
5. Which compound has a higher thermal stability, I or II, taking into account that  $\text{AlCl}_3$  is extremely volatile compound.
6. If one of the compounds I or II can be transformed into the other by heating, write the corresponding reaction equation.

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## The Solution Report Form

1. Te:Al:Cl minimum atomic ratios

	Te	Al	Cl
Compound I			
Compound II			
Compound III			

2. The molecular formulas of compounds I and II

Compound I	
Compound II	

3.

Chemical formulae of anion and cation of compounds I and II

	Cation	Anion
Compound I		
Compound II		

4.

	Cation	Anion
Compound I		
Compound II		

5.

Compare the thermal stability of compounds I and II. Draw > or < in the box.

Thermal stability of I  Thermal stability of II

6. The reaction equation

Answers and points (points are given in shaded square brackets)

### Grand total for the problem is [12]

1. Te:Al:Cl ratios. Each ratio brings [1] point only if all three numbers are given correctly.

Total - [3]

	Te	Al	Cl
Compound I [1]	2	2	7
Compound II [1]	2	1	4
Compound III [1]	3	1	4

solution:

The determination of the Te:Al:Cl ratios may be made using the data on the content of Te(cryst.) thus:

77.8% of Te(cryst.) corresponds to

$7\text{Te}(\text{cryst.}) + 2\text{TeCl}_4 + 8\text{AlCl}_3$  and the minimum atomic ratio for the composition from which the excess of  $\text{TeCl}_4$  is not subtracted is  $\text{Te} : \text{Al} : \text{Cl} = 9 : 8 : 32$ , where the contents of Al and Cl are even and can be divided by 4, while that of Te exceeding the analogous even number by 1. Subtracting one mole of  $\text{TeCl}_4$  from the obtained ratio and dividing by 2 we obtain  $4\text{Te} + 4\text{Al} + 14\text{Cl}$  and the ratio is  $\text{Te}:\text{Al}:\text{Cl}=2:2:7$ , which can be then verified by comparison with the molecular weight given

87.5% of Te(cryst.) corresponds to

$7\text{Te}(\text{cryst.}) + \text{TeCl}_4 + 4\text{AlCl}_3 = 8\text{Te} + 4\text{Al} + 16\text{Cl}$  and the ratio is  $\text{Te}:\text{Al}:\text{Cl} = 2:1:4$

91.7% of Te(cryst.) corresponds to

$11\text{Te}(\text{cryst.}) + \text{TeCl}_4 + 4\text{AlCl}_3 = 12\text{Te} + 4\text{Al} + 16\text{Cl}$  and the ratio is  $\text{Te}:\text{Al}:\text{Cl} = 3:1:4$

2. The molecular formulae of compounds I and II

Compound I [1]	$\text{Te}_4\text{Al}_4\text{Cl}_{14}$
Compound II [1]	$\text{Te}_4\text{Al}_2\text{Cl}_8$

Molecular formulae can be deduced from the data on molar weights. Both correspond to doubled simplest formula.

for I:  $2(\text{Te}_2\text{Al}_2\text{Cl}_7)$  gives calculated m.w. = 1114.7 against experimental value of  $1126 \pm 43$

for II:  $2(\text{Te}_2\text{AlCl}_4)$  gives calculated m.w. = 848 against experimental value of  $867 \pm 48$

3.

Chemical formulae of anions and cations of compounds I and II [0.5] points for each of cations and anions, total [2].

Compound I	$[\text{Te}_4]^{2+}$ [0.5]	$[\text{Al}_2\text{Cl}_7]^-$ [0.5]
Compound II	$[\text{Te}_4]^{2+}$ [0.5]	$[\text{AlCl}_4]^-$ [0.5]

The compositions of the ions included in the structures of I and II can be determined by taking into consideration that they both I and II are triionic electrolytes, and the fact that all the tellurium atoms should be equivalent according to IR and are bonded only to each other as well as that Al atoms are in both compounds tetrahedrally coordinated and equivalent. At least in one case this can be  $\text{AlCl}_4^-$  anions which seems probable for II, which therefore can

be formulated as  $[\text{Te}_4]^{2+}[\text{AlCl}_4]_2^-$ . As according to similar colouration the cations are likely to be the same in both cases, the structure of I should contain  $[\text{Te}_4]^{2+}$  cations and  $[\text{Al}_2\text{Cl}_7]^-$  anions, which seems also to be in a good agreement with NMR data, assigning to Al atoms in I a different tetrahedral geometry than that in II.

## 4. Total [3]

	Cation	Anion
Compound I		
Compound II		

The geometry of anions:

$\text{AlCl}_4^-$  is a single tetrahedron; [1]

$\text{Al}_2\text{Cl}_7^-$  is two tetrahedra sharing a common vertex (a chlorine atoms) - [1]

The geometry of the cation:

$[\text{Te}_4]^{2+}$  is a plane square due to proclaimed aromaticity [1].

The plane square configuration appears to be more favorable because the cation is mentioned to be aromatic, which means planar and possessing equal bond lengths for the sides of the corresponding aromatic ring.

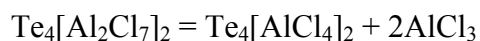
## 5.

Total [1]

Thermal stability of I  Thermal stability of II

The thermal stability of II should be higher than that of I - they both are ionic compounds with high melting points, but compound I can be transformed into II by the elimination of  $\text{AlCl}_3$ , which is a volatile solid and can be relatively easily removed on heating.

## 6. The reaction equation. Total [1]



## Problem 2.

The detection limit is one of the basic parameters in quantitative analysis of trace amounts of elements. The detection limit is expressed as the least mass of an element which can be determined by a given method with a given accuracy.

As an example we shall consider the method used for the determination of microscopic amounts of bismuth. In 1927 German chemist Berg suggested to precipitate bismuth as a practically insoluble salt: 8-hydroxyquinolinium tetraiodobismuthate  $[\text{C}_9\text{H}_6(\text{OH})\text{NH}][\text{BiI}_4]$  ( $M_r = 862.7$ ).

1. a) Draw the structural formulae of the cation and anion of this salt.

b) What is the oxidation state of Bi atom in this compound ?

2. Evaluate the smallest mass of bismuth (in *mg*), which can be determined reliably by Berg method, if the smallest mass of precipitate which can be reliably measured is *50.0 mg*.

For the determination of trace amounts of bismuth R. Belcher and coworkers from Birmingham developed a multiplicative method. According to this method a chain of reactions followed by a titration of the final product is carried out. A detailed description follows.

**Step 1.** To a given small amount ( $\approx 2 \text{ ml}$ ) of cold acidified solution containing trace amounts of  $\text{Bi}^{3+}$  *50 mg* of potassium hexathiocyanatochromate(III) ( $\text{K}_3[\text{Cr}(\text{SCN})_6]$ ) is added in the cold, that leads to practically quantitative precipitation of bismuth.

3. Write a balanced net ionic equation of this reaction.

**Step 2.** The precipitate is filtered off, washed by cold water, and treated with *5 ml* of 10% solution of sodium hydrogen carbonate. Upon this treatment the initial precipitate transforms into the precipitate of oxobismuth carbonate ( $(\text{BiO})_2\text{CO}_3$ ) with liberation of hexathiocyanatochromate(III) ions into solution.

4. Write a balanced net ionic equation of this reaction.

**Step 3.** To the slightly acidified filtrate transferred to a separatory funnel *0.5 ml* of saturated iodine solution in chloroform are added, and the mixture is vigorously shaken. Iodine oxidizes the ligand of the complex ion to ICN and sulfate ion.

5. Write a balanced net ionic equation of this reaction.

**Step 4.** Upon *5 minutes* *4 ml* of 2 M  $\text{H}_2\text{SO}_4$  solution are added to the mixture. The acidification leads to the reaction of coproportionation with the evolution of molecular iodine.

6. Write a balanced net ionic equation of the reaction occurred on acidification.

**Step 5.** Iodine is quantitatively extracted by 4 portions of chloroform. Aqueous layer is transferred to a flask, to which *1 ml* of bromine water is added, and the mixture is mixed for *5 minutes*.

7. Write the balanced net ionic equations of the reactions occurred upon the addition of bromine water. Note that an excess of bromine can react with hydrogen cyanide to give  $\text{BrCN}$ , and iodide is oxidized into  $\text{IO}_3^-$ .

**Step 6.** To eliminate an excess of molecular bromine *3 ml* of 90% methanoic (formic) acid is added to the mixture.

8. Write a balanced net ionic equation of this reaction.

**Step 7.** To the slightly acidic solution an excess (*1.5 g*) of potassium iodide is added.

9. Write the balanced net ionic equations of the reactions occurred upon the addition of KI, taking into consideration that iodide reacts with  $\text{BrCN}$  in a similar manner as with ICN to form molecular iodine.

**Step 8.** The resulting solution is titrated by a standard 0.00200 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The results thus obtained are used to calculate the content of bismuth in the sample taken for analysis.

10. a) How many moles of thiosulfate are equivalent to *1 mol* of bismuth in the initial sample ?

- b) What is the least mass of bismuth which can be determined by this method (assume that reliable determination requires no less than 1 *ml* of standard 0.00200 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution) ?
11. By how many times the multiplicative method just described is more sensitive than Berg's gravimetric method ?



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## The Solution Report Form

1.a)

The cation	The anion

1.b)

<i>The oxidation state of bismuth in 8-hydroxyquinolinium tetraiodobismuthate:</i>	
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2.

The smallest mass of bismuth determined reliable by Berg method, <i>mg</i>	
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3. Reaction equation

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4. Reaction equation

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5. Reaction equation

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6. Reaction equation

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7. Reaction equations

a)
b)

8. Reaction equation

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9. Reaction equations

a)
b)

10.

Place for calculations:

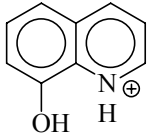
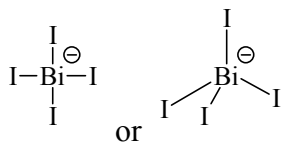
Place for calculations:		
a)	The number of moles of thiosulfate to 1 mole of bismuth	
b)	The least mass of bismuth, <i>mg</i>	

11.

	$\frac{\text{Detection limit of gravimetric method}}{\text{Detection limit of multiplicative method}} =$	
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## Answers and points (points are given in shaded square brackets)

1. a) total [1.0]

	
The cation [0.5]	The anion [0.5]

1.b)

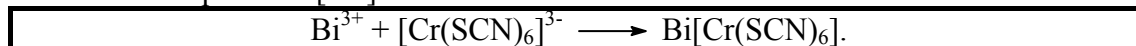
The oxidation state of bismuth in 8-hydroxyquinolinium tetraiodobismuthate:	+3 [0.5]
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2. [1]

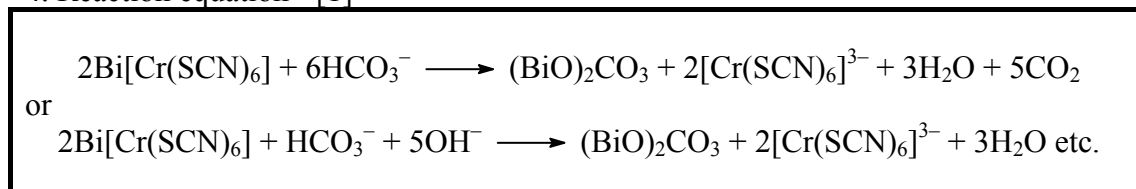
The smallest mass of bismuth determined reliably by Berg method, <i>mg</i>	12.1
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Molar mass of precipitate is 862.7 g, which contain 209.0 g of bismuth. Thus, 0.0500 g of precipitate correspond to  $1.21 \cdot 10^{-2} \text{ g} = 12.1 \text{ mg}$  of bismuth.

3. Reaction equation - [0.5]

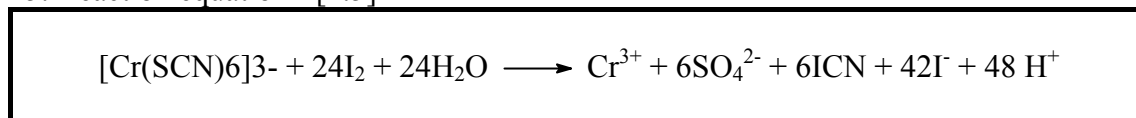


4. Reaction equation - [1]

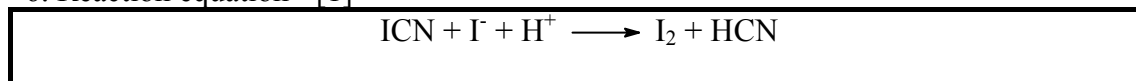


(variations are possible)

5. Reaction equation - [1.5]



6. Reaction equation - [1]



7. Reaction equations

a)	$3\text{Br}_2 + \text{I}^- + 3\text{H}_2\text{O} \longrightarrow \text{IO}_3^- + 6\text{Br}^- + 6\text{H}^+$	[0.5]
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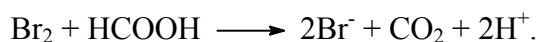
b)



[0.5]

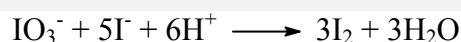
*comment:* from reaction 5 it is evident that considerably more of ions  $\text{I}^-$  are formed than of ICN molecules. Therefore, after the completion of reaction 6 an excess of  $\text{I}^-$  ions will be left.

8. Reaction equation - [1]



9. Reaction equations - total [1]

a)



[0.5]

b)



[0.5]

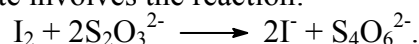
10. total [9]

a)	The number of moles of thiosulfate corresponding to 1 mol of bismuth	228	[8]
b)	The least mass of bismuth, mg	$1.83 \cdot 10^{-3}$	[1]

*Note: the arithmetic mistake leads to 2 points in 10a.*

*Solution:*

titration of iodine by thiosulfate involves the reaction:



Assume that the initial solution contained 1 mole of Bi. In the reaction 5 each mole of Bi leads to the formation of 42 moles of iodide (for convenience divide all coefficients of reaction 4 by 2), of which 6 moles of iodide-ion was consumed in reaction 6. Thus, 36 moles of iodide was consumed in reaction 7a to give 36 moles of  $\text{IO}_3^-$ , which in reaction 9a gave  $36 \cdot 3 = 108$  moles of  $\text{I}_2$ , which take  $108 \cdot 2 = 216$  moles of thiosulfate for titration. However, that is not all. Indeed, 6 moles of HCN are generated per mole of  $\text{Bi}^{3+}$  according to reactions 5 and 6. The oxidation of HCN by bromine in reaction 7b gives 6 moles of BrCN, which in its turn in reaction 9b gives 6 moles of iodine taking 12 more moles of thiosulfate. Thus, total amount of thiosulfate is  $216 + 12 = 228$ .

b) 1.00 ml of 0.00200 M thiosulfate solution contains  $2.00 \cdot 10^{-6}$  mole of  $\text{Na}_2\text{S}_2\text{O}_3$ , which corresponds to  $209.0 \cdot 2.00 \cdot 10^{-6} / 228 = 1.83 \cdot 10^{-6} \text{ g} = 1.83 \cdot 10^{-3} \text{ mg} = 1.83 \mu\text{g}$ .

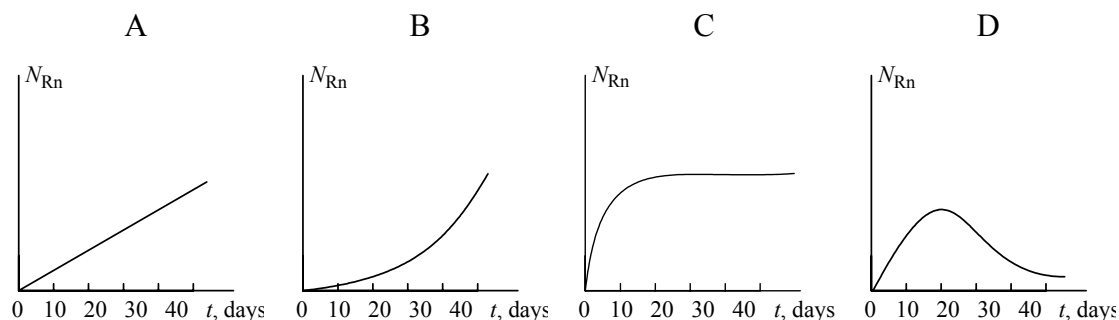
11.

$\frac{\text{Detection limit of gravimetric method}}{\text{Detection limit of multiplicative method}} =$	6600
	[0.5]

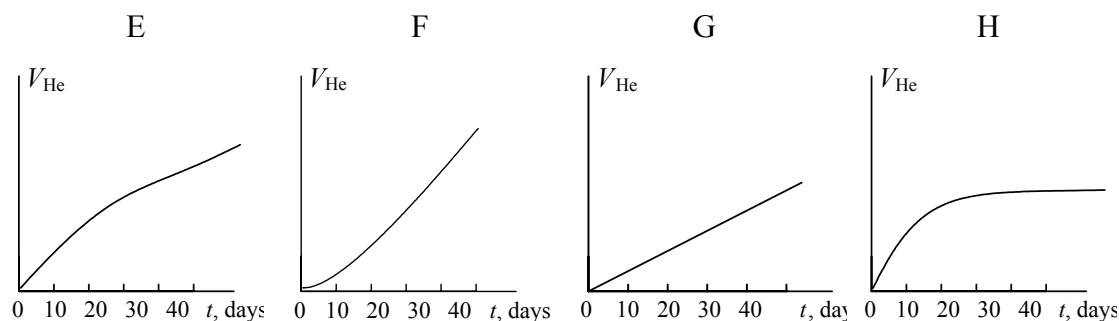
The multiplicative method is more sensitive than the gravimetric method by  $12.1 \text{ mg} / 1.83 \cdot 10^{-3} \text{ mg} = 6600$  times.



4. Choose which of the plots given below displays the time dependence of the number  $N_{\text{Rn}}$  of radon atoms in the course of the experiment.

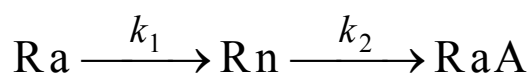


5. Choose which of the plots given below shows the time dependence of the volume of helium in the course of the experiment.



6. Choose the relation between the decay rate  $k$  of any given nuclide and its half-life  $T_{1/2}$ .

7. a) Using a short kinetic scheme



(where  $k_1$  and  $k_2$  are the rate constants of the corresponding reactions) and the plot which you have selected in question 4, write a relation between the number of radon atoms at the end of experiment  $N'_{\text{Rn}}$  and the number of radium atoms  $N_{\text{Ra}}$ .

- b) Evaluate  $N'_{\text{Rn}}$  using the rate of radium decay given above ( $x = 3.42 \cdot 10^{10}$   $\alpha$ -particles per gram of radium per second).

8. How many helium atoms could be formed from radon atoms remaining at the end of experiment  $N'_{\text{Rn}}$ , if all these atoms had decayed to RaD?

9. Using the solutions of the above questions calculate a better approximation to a) the number of helium atoms formed; b) the Avogadro's number.

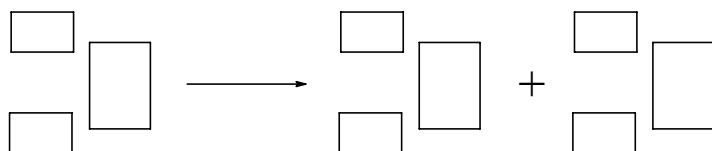
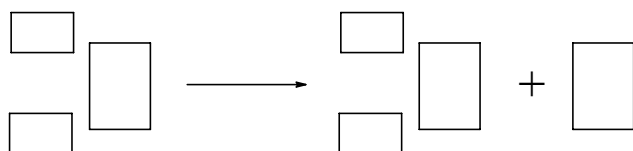
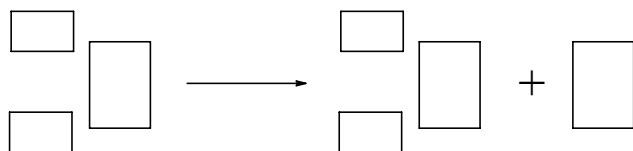
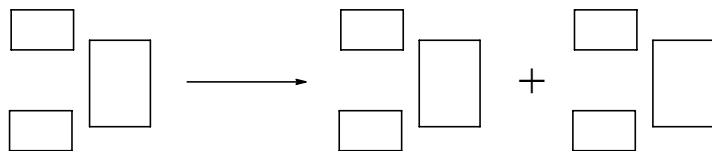
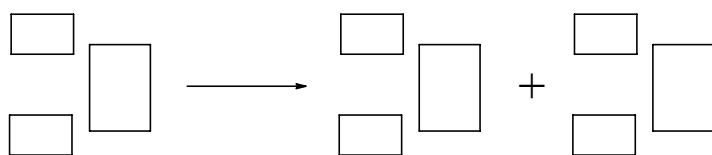
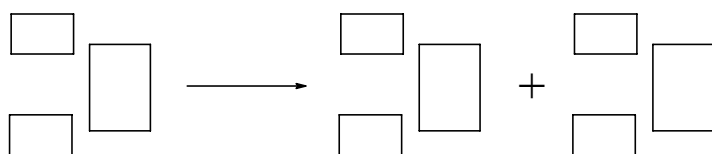
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**The Solution Report Form**

1. Fill in the templates for nuclear reactions (*hint*: the symbol of element is written in the large box, with mass number in the upper left box, and atomic number in the lower left box:





2. a) circle the correct answer

1	2	3	4	5
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b)

Number of helium atoms (rough estimate)	
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3.

Avogadro's number (rough estimate)	
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4. Write a check mark in the box below the right answer. Note that only one box must be marked. Otherwise the answer is considered wrong.

A	B	C	D
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

5. Write a check mark in the box below the right answer. Note that only one box must be marked. Otherwise the answer is considered wrong.

E	F	G	H
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

6. Underline the correct answer

$k = 1/T_{1/2}$	$k = \ln 2/T_{1/2}$	$k = \ln 2 \cdot T_{1/2}$	$k = \pi/T_{1/2}$
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7.

a) Underline the correct answer

$N'_{Rn} = k_1 \cdot N_{Ra} / k_2$	$N'_{Rn} = k_2 \cdot N_{Ra} / k_1$	$N'_{Rn} = k_1 \cdot N_{Ra} / 2k_2$	$N'_{Rn} = k_1 \cdot N_{Ra} / 3k_2$
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b) Insert the calculated value

$N'_{\text{Rn}}$	
------------------	--

8.

Underline the correct answer

$4N'_{\text{Rn}}$	$2N'_{\text{Rn}}$	$5N'_{\text{Rn}}$	$N'_{\text{Rn}}$	$3N'_{\text{Rn}}$
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9. a)

A more accurate estimate of the number of helium atoms	
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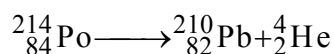
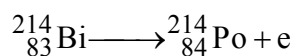
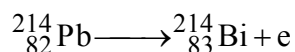
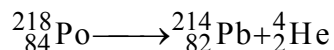
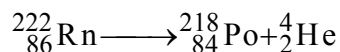
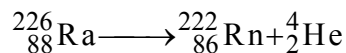
b)

A more accurate estimate of Avogadro's number ( $\text{mol}^{-1}$ )	
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**Answers and points (points are given in shaded square brackets)**

1.

[0.2] points for each reaction, total [1.2].



2. Total [1.5]

a) circle the correct answer

1	2	3	④	5
[0.5]				

b)

Number of helium atoms (rough estimate)	$1.9 \cdot 10^{17}$
$N_{\text{He}} = 4xmt = 1.9 \cdot 10^{17}$	[1]

3.

The first estimate of Avogadro's number	$6.4 \cdot 10^{23} \text{ mol}^{-1}$
	[1]

Solution. The Avogadro's number  $N_A$  is the number of particles in one mole.

$N_A = N_{\text{He}}/v_{\text{He}}$ , where  $N_{\text{He}}$  is number of helium atoms, and  $v_{\text{He}}$  is the number of moles of helium formed within time  $t$ . If we assume that all radon atoms formed from radium atoms decayed during the time of experiment (this assumption follows from the assumption that radon half-life can be neglected in comparison with 83 days, that introduces an error of about 5%), then we obtain that during time  $t$  the number of helium atom emitted is  $N_{\text{He}} = 4xmt$ , and

$$N_A = 4xmt/v_{\text{He}} = 4 \cdot 3.42 \cdot 10^{10} \cdot 0.192 \cdot (83 \cdot 24 \cdot 3600) / (6.58 \cdot 10^{-6} / 22.4) = 6.4 \cdot 10^{23} \text{ mol}^{-1}$$

4. Answer - C.

[2].

The number of radon atoms reaches a quasi-stationary state, which is sometimes otherwise called *the radioactive equilibrium*.

5. Answer - F.

[2]

In the beginning helium is formed only from  $\alpha$ -particles emitted by radium, but to the end of the experiment  $\alpha$ -particles are emitted both by radium and by decay products, the amount of which is four times that of radium.

6. Underline the correct answer - [0.5]

$k = 1/T_{1/2}$	<u><math>k = \ln 2/T_{1/2}</math></u>	$k = \ln 2 \cdot T_{1/2}$	$k = \pi/T_{1/2}$
-----------------	---------------------------------------	---------------------------	-------------------

7. Total [5]

a) Underline the correct answer [2]

<u><math>N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / k_2</math></u>	$N'_{\text{Rn}} = k_2 \cdot N_{\text{Ra}} / k_1$	$N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / 2k_2$	$N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / 3k_2$
--	--	---	---

The number of radon atoms reaches a quasi-stationary state, at which the rate of formation is equal to the rate of decay  $k_2 N'_{\text{Rn}} = k_1 N_{\text{Ra}}$ , whence  $N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / k_2$

b) [3]

$N'_{\text{Rn}}$	$3.14 \cdot 10^{15}$
------------------	----------------------

The rate of radium decay is  $k_1 N_{\text{Ra}} = xm$ , whence

$$N'_{\text{Rn}} = xm / (\ln 2 / T_{1/2(\text{Rn})}) = 3.42 \cdot 10^{10} \cdot 0.192 / (0.693 / 3.83 \cdot 24 \cdot 3600) = 3.14 \cdot 10^{15}$$

8.

[0.5]

$4N'_{Rn}$	$2N'_{Rn}$	$5N'_{Rn}$	$N'_{Rn}$	$\underline{3N'_{Rn}}$
------------	------------	------------	-----------	------------------------

9. Total [2.5]

a)

A more accurate estimate of the number of helium atoms	$1.79 \cdot 10^{17}$ [1.5]
--	-------------------------------

$$N_{\text{He}} = 4xmt - 3N'_{Rn} = 1.9 \cdot 10^{17} - 3 \cdot 3.14 \cdot 10^{15} = 1.79 \cdot 10^{17}$$

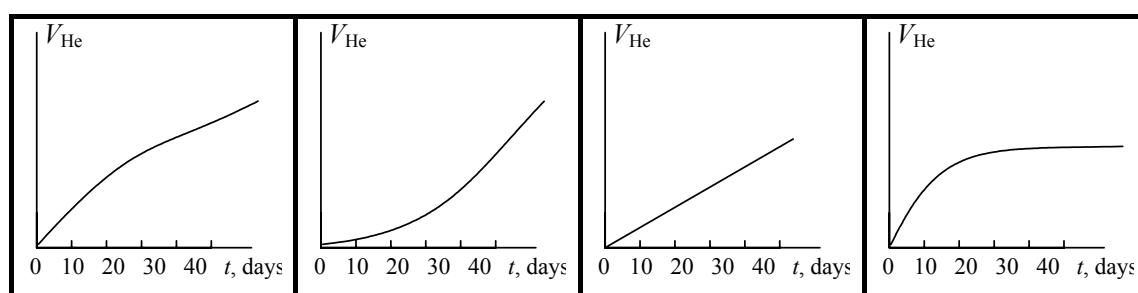
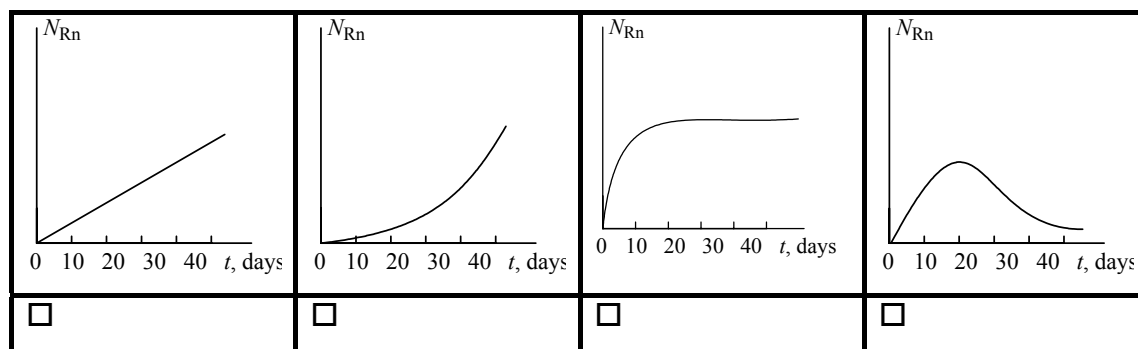
b)

A more accurate estimate of Avogadro's number ( $\text{mol}^{-1}$ )	$6.09 \cdot 10^{23}$ [1]
---	-----------------------------

$$N_A = N_{\text{He}}/v(\text{He}) = 1.79 \cdot 10^{17} / (6.58 \cdot 10^{-6} / 22.4) = 6.09 \cdot 10^{23}$$

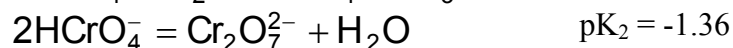
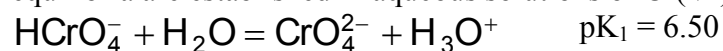
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**Total: 16.20**



## Problem 4.

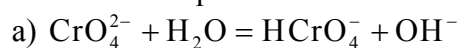
Potassium dichromate is one of the most widely used precipitating reagents. The following equilibria are established in aqueous solutions of Cr(VI).



All other equilibria with involving of chromium should be ignored. All the activity coefficients are assumed to be 1.

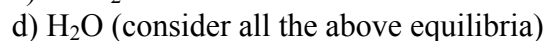
1. The ionic product of water  $K_w = 1.0 \cdot 10^{-14}$ .

Evaluate the equilibrium constants

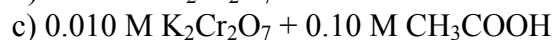
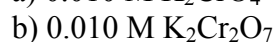


2. The solubility product of  $\text{BaCrO}_4$   $K_s = 1.2 \cdot 10^{-10}$ .  $\text{BaCr}_2\text{O}_7$  is very soluble in water.

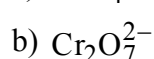
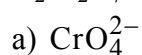
In what direction will the equilibrium 1b shift upon the addition of the following reagents to a moderately concentrated aqueous solution of potassium dichromate?



3. Dissociation constant of acetic acid  $K_a = 1.8 \cdot 10^{-5}$ . Calculate the pH value of the following solutions



4. Calculate the equilibrium concentrations of the following ions in a solution of 0.010 M  $\text{K}_2\text{Cr}_2\text{O}_7 + 0.10$  M  $\text{CH}_3\text{COOH}$



Surname \_\_\_\_\_

Personal code \_\_\_\_\_

Team \_\_\_\_\_

## The Solution Report Form

1.

a)

Equilibrium constant	
Place for calculations	

b)

Equilibrium constant	
Place for calculations	

2. Place a checkmark at the correct answer

The equilibrium will	shift to left	shift to right	not shift
a)			
b)			
c)			
d)			

3. pH values

a)



Place for calculations

b)

Place for calculations

c)

Place for calculations

## 4. Equilibrium concentrations

a)

Place for calculations

b)

Place for calculations

**Answers and points (points are given in shaded square brackets)**

Grand Total = [92] points

The points are given separately for the correct numerical solution, and to the description of the course of calculations (the derivation of formulas and correct manipulation with

numbers).

Comments to the subtask grading points are given as numbers in parentheses (common comments, given at the end of the answers section), and as asterisks in parentheses (some particular comments, given immediately below the commented subtask). In the comments we tried to describe the most common errors in solutions. In the case of non-standard solutions, the evaluation will be done in a similar unified manner as the described scheme. In some subtask solutions and points are given without any comments, the respective subtask is evaluated either with full points given for this subtask, or zero for erroneous result without any intermediate gradings.

a)

Equilibrium constant	$3.2 \cdot 10^{-8}$	[3] (1,3)
Place for calculations		
$\frac{[\text{HCrO}_4^-][\text{OH}^-]}{[\text{CrO}_4^{2-}]} = \frac{[\text{H}^+][\text{OH}^-]}{([\text{H}^+][\text{CrO}_4^{2-}]/[\text{HCrO}_4^-])} = K_w/K_1 =$ $1.0 \cdot 10^{-14}/3.16 \cdot 10^{-7} = 3.2 \cdot 10^{-8}$		
[4] (2)		

Comments: (\*) In agreement with the accuracy of the data used to solve the problems, the results (constants and concentration values) must be given with two significant digits, and logarithmic values (pH) must be given with 2 decimal digits after decimal point.

b)

Equilibrium constant	$4.4 \cdot 10^{13}$	[3] (1, 4)
Place for calculations		
$K = \frac{([\text{CrO}_4^{2-}][\text{H}^+]/[\text{HCrO}_4^-])^2/([\text{HCrO}_4^-]^2/[\text{Cr}_2\text{O}_7^{2-}])}{([\text{H}^+][\text{OH}^-])^2} =$ $K_1^2/(K_2K_w^2) = 10^{-2 \cdot 6.50}/(10^{1.36} \cdot 10^{-2 \cdot 14.00}) = 10^{13.64} = 4.4 \cdot 10^{13}$		
[5] (2)		

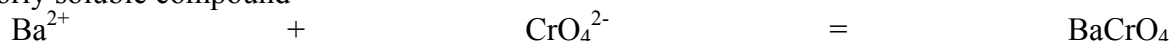
2. Place a checkmark at the correct answer

The equilibrium will	shift to left	shift to right	not shift
a) [1]		<input checked="" type="checkbox"/>	
b) [1]	<input checked="" type="checkbox"/>		
c) [1]		<input checked="" type="checkbox"/>	
d) [2]		<input checked="" type="checkbox"/>	

calculations:

a) and b) the answer is self-evident

c)  $\text{BaCl}_2$  shifts the equilibrium to the right due to the binding of chromate ion into a poorly soluble compound



d) this answer may appear as strange, as water is among the products specified in the right

part of the equilibrium equation. However, this is too formal. Actually in dilute aqueous solutions the concentration of water may be regarded as fairly constant and the addition of water would not affect it. Nevertheless, the addition of water to dichromate solution leads to the dilution, which in its turn shifts the dichromate ion dissociation equilibrium to the right. Second, in the aqueous solution of  $K_2Cr_2O_7$  the value of  $pH < 7$  due to the processes described in the problem statement (cf. also the solution to 3b). With the dilution of any aqueous solution pH is varying towards 7, that in this case means the increase of pH. This also shifts the equilibrium to the right.

### 3. pH values

a)	9.25	[3] (1,5)
b)	4.20	[3] (1,7)
c)	2.87	[3] (1,9)

calculations:

$$\begin{aligned}
 \text{a) } CrO_4^{2-} + H_2O &= HCrO_4^- + OH^- & K &= & 3.16 \cdot 10^{-8} & (*) \\
 c_{Cr} &= [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}] \approx [CrO_4^{2-}], & & & & (**) \\
 [HCrO_4^-] & & \approx & & [OH^-] & (**) \\
 [OH^-]^2/c_{Cr} &= K, [OH^-] = \sqrt{K c_{Cr}} = \sqrt{3.16 \cdot 10^{-8} \cdot 0.01} = 1.78 \cdot 10^{-5} \\
 [H^+] &= 5.65 \cdot 10^{-10}, pH = 9.25
 \end{aligned}$$

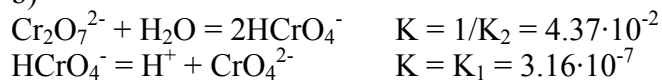
[7] (2,6)

comments:

(\*) the value of this constant was calculated earlier, cf. 1a

(\*\*) these approximations can be used just because  $K$  is sufficiently small (as chromate ion is a very weak base), while  $c_{Cr}$  is quite large. In this case for the calculation of pH a short square equation can be solved. See also the comments to 3b and 3c.

b)



$$[H^+] \approx [CrO_4^{2-}] \Rightarrow [H^+] = \sqrt{K_1 [HCrO_4^-]} (*)$$

$$[HCrO_4^-] = ?$$

$$c_{Cr} = 2.0 \cdot 10^{-2} \text{ M } (**) = [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}] \approx [HCrO_4^-] + 2[Cr_2O_7^{2-}] (***)$$

$$[HCrO_4^-] = x; K_2 = [Cr_2O_7^{2-}]/[HCrO_4^-]^2 = (c_{Cr} - x)/2x^2; 2K_2x^2 + x - c_{Cr} = 0$$

$$x = (-1 + \sqrt{1 + 8K_2 c_{Cr}}) / 4K_2 = (-1 + \sqrt{1 + 8 \cdot 22.9 \cdot 0.02}) / 4 \cdot 22.9 = 1.27 \cdot 10^{-2} \text{ M } (****)$$

$$\text{hence } [H^+] = (3.16 \cdot 10^{-7} \cdot 1.27 \cdot 10^{-2})^{1/2} = 6.33 \cdot 10^{-5}; pH = 4.20 (*****)$$

[20] (2,8)

comments:

(\*) again, a short square equation can be used

(\*\*) Do not forget that in 0.010 M  $K_2Cr_2O_7$  solution  $c_{Cr} = 2 \cdot 0.010 = 0.020 \text{ M } (!)$

(\*\*\*) As the dissociation constant of  $HCrO_4^-$  is very small, the assumption that  $[CrO_4^{2-}]$  can be neglected is fair.  $pH \ll pK$  and  $c_{Cr} \approx [HCrO_4^-] + 2[Cr_2O_7^{2-}]$

(\*\*\*\*) Here the full square equation must be solved, unlike as in earlier cases.

(\*\*\*\*\*) note that the resulting pH is indeed  $\ll pK_1 = 6.50$ . Therefore, the assumption (\*\*\*) is indeed fair.

c)

$$\text{In } 0.10 \text{ M } CH_3COOH [H^+] = (K_a c)^{1/2} (*) = (1.8 \cdot 10^{-5} \cdot 0.10)^{1/2} = 1.34 \cdot 10^{-3}$$

$$\text{pH} = 2.87 (**)$$

[10] (2,6,10)

comments:

(\*) as in 3a, a short square equation can be used

(\*\*) this value is indeed the value we need! The comparison of this value with pH for 0.10 M dichromate solution given above (cf. 3b, pH = 4.20) shows that the influence of  $\text{K}_2\text{Cr}_2\text{O}_7$  on pH can be safely neglected.

#### 4. Equilibrium concentrations

a)	$3.0 \cdot 10^{-6}$	[3] (1, 11)
b)	$3.7 \cdot 10^{-3}$	[3] (1, 11)

calculations:

Two different methods can be used.

##### Method 1.

a)

$$[\text{HCrO}_4^-] = 1.3 \cdot 10^{-2} (*)$$

$$[\text{CrO}_4^{2-}] = K_1[\text{HCrO}_4^-]/[\text{H}^+] = 3.16 \cdot 10^{-7} \cdot 1.3 \cdot 10^{-2} / 1.34 \cdot 10^{-3} = 3.0 \cdot 10^{-6} \text{ M}$$

[10] (2, 12)

b)

$$c_{\text{Cr}} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2[\text{Cr}_2\text{O}_7^{2-}]$$

$$[\text{Cr}_2\text{O}_7^{2-}] = \frac{1}{2}(c_{\text{Cr}} - [\text{CrO}_4^{2-}] - [\text{HCrO}_4^-]) = \frac{1}{2}(2.0 \cdot 10^{-2} - 3.0 \cdot 10^{-6} - 1.3 \cdot 10^{-2}) = 3.7 \cdot 10^{-3} \text{ M}$$

or otherwise

$$[\text{Cr}_2\text{O}_7^{2-}] = K_2[\text{HCrO}_4^-]^2 = 22.9 \cdot (1.3 \cdot 10^{-2})^2 = 3.9 \cdot 10^{-3} \text{ M}$$

[10] (2, 12)

comments:

(\*) from the calculation of  $[\text{HCrO}_4^-]$  (cf. 3b) it is evident that if  $\text{pH} \ll \text{pK}$ ,  $[\text{HCrO}_4^-]$  is independent on pH. In our case  $\text{pH} = 2.87$  is indeed  $\ll \text{pK} = 6.50$ , and therefore this value of  $[\text{HCrO}_4^-]$  is equal to that obtained in 3b.

##### Method 2

a)

$$[\text{CrO}_4^{2-}] = x; [\text{HCrO}_4^-] = x[\text{H}^+]/K_1$$

$$[\text{Cr}_2\text{O}_7^{2-}] = K_2[\text{HCrO}_4^-] = x^2 K_2 [\text{H}^+]^2 / K_1^2$$

$$c_{\text{Cr}} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2[\text{Cr}_2\text{O}_7^{2-}] = 2K_2 [\text{H}^+]^2 / K_1^2 x^2 + (1 + [\text{H}^+]/K_1)x$$

$$K_1 = 3.16 \cdot 10^{-7}; K_2 = 22.9; [\text{H}^+] = 1.34 \cdot 10^{-3}$$

$$8.24 \cdot 10^8 x^2 + 4.24 \cdot 10^3 x - 2.0 \cdot 10^{-2} = 0$$

$$x = 3.0 \cdot 10^{-6} \text{ M}$$

[10] (2, 12)

b)

$$[\text{Cr}_2\text{O}_7^{2-}] = K_2[\text{HCrO}_4^-] = K_2 [\text{H}^+]^2 / K_1^2 [\text{CrO}_4^{2-}]^2 = 4.12 \cdot 10^8 \cdot (3.0 \cdot 10^{-6})^2 = 3.7 \cdot 10^{-3} \text{ M}$$

[10] (2, 12)

#### General Comments

(1) All numerical values are evaluated by 3 points. 3 points are given if

- a) the value is given with with 2 significant digits (the value of pH is given with 2 decimal digits after decimal point) and  
 b) the value differs from that given in the answers by no more than 5 in the second significant digit (the pH values differ by no more than 0.2)

Less than 3 points are given if

- a) the value is given with 3 significant digits (pH values are given with 3 decimal digits after decimal point) - [2.5]  
 b) the value is given either with 1 or with more than 3 significant digits (pH values are given either with less than 2 or with more than 3 decimal digits) - [2]  
 c) if the value differs from that given in the answers by more than the acceptable allowance (see above) - [1.5] points.  
 d) if the value makes no sense no more than [1] points may be given. Several possible examples are given in the comments to particular tasks.

(2) In order to avoid penalizing twice for the same error, the correctness of the final formulae which are used to calculate the answers will be subject for penalty, even if the the numerical values substituted into the wrong formula are also in error.

If only the expression of equilibrium constant is correct (and other calculation formulae are wrong) [1]

(3) If  $K \leq 0$  [0]  
 If  $K > 1$  [0.5]

(4) If  $K \leq 0$  [0]  
 If  $0 < K < 1$  [0.5]

(5) If  $\text{pH} < 0$  or  $\text{pH} > 14$  [0]  
 If  $0 \leq \text{pH} < 7$  [0.5]

(6) The calculation of pH using the full form of square equation is not regarded as a fault

(7) If  $\text{pH} < 0$  or  $\text{pH} > 14$  [0]  
 If  $7 < \text{pH} \leq 14$  [0.5]

(8) Total of [20] separates into the following contributions

i) correct expression  $[\text{H}^+] = \sqrt{K_1 [\text{HCrO}_4^-]}$  [5]

ii) correct value  $c(\text{Cr}) = 2.0 \cdot 10^{-2} \text{ M}$  (and not  $1.0 \cdot 10^{-2} \text{ M}$ ) [5]

iii) correctly written full square equation for the calculation of  $[\text{HCrO}_4^-]$  [10]

iv) reduced square equation used [5]

v) chemically meaningless assumptions (as e.g.  $[\text{HCrO}_4^-] \approx c_{\text{Cr}}$  etc.) [0]

(9) If  $\text{pH} < 0$  or  $\text{pH} \geq 7$  [0]  
 If  $\text{pH} \leq 2$  [1]

(10) Attempts to treat the effect of  $\text{Cr}_2\text{O}_7^{2-}$  ion on pH values are not considered a fault, if these are based on correct assumptions and data  
 Chemically meaningless actions (e.g. summation of pH values computed separately for  $\text{CH}_3\text{COOH}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  solutions) [5]

Neglect of the contribution of  $\text{CH}_3\text{COOH}$  into pH value [0]

(11) If  $c \leq 0$  or  $c > 2.0 \cdot 10^{-2} \text{ M}$  [0]

(12) [10] points are given to the correct calculation performed by any method. If the calculation uses the material balance ( $c_{\text{Cr}} = 2[\text{Cr}_2\text{O}_7^{2-}] + [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-]$ ) which is written wrongly, e.g. as  $c_{\text{Cr}} = [\text{Cr}_2\text{O}_7^{2-}] + [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-]$  [5]

## Problem 5.

Potentiometric and spectrophotometric methods are widely used for the determination of equilibrium concentrations and equilibrium constants in solution. Both methods are frequently used in combination to achieve simultaneous determination of several species.

Acidified aqueous solution I contains a mixture of  $\text{FeSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$ , and aqueous solution II contains a mixture of  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{K}_3\text{Fe}(\text{CN})_6$ . The concentrations of iron-containing species satisfy the relations  $[\text{Fe}^{2+}]_{\text{I}} = [\text{Fe}(\text{CN})_6^{4-}]_{\text{II}}$  and  $[\text{Fe}^{3+}]_{\text{I}} = [\text{Fe}(\text{CN})_6^{3-}]_{\text{II}}$ .

The potential of platinum electrode immersed into the solution I is 0.652 V (relative to the standard hydrogen electrode), while the potential of platinum electrode immersed into solution II is 0.242 V (relative to the standard hydrogen electrode). The transmittance of the solution II measured relative to the solution I at 420 nm is 10.7% (optical pathlength  $l = 5.02$  mm). Assume that the complexes  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Fe}^{3+}\cdot\text{aq}$ ,  $\text{Fe}^{2+}\cdot\text{aq}$ , do not absorb light at 420 nm.

Molar absorptivity

$\epsilon(\text{Fe}(\text{CN})_6^{3-}) = 1100 \text{ L/mol}\cdot\text{cm}$  at this wavelength. Standard redox potential for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is 0.771 V. The factor before the decimal logarithm in the Nernst's equation is 0.0590 and before natural logarithm is 0.136. Assume that all the activity coefficients are equal to 1.

- Write Nernst's equations for redox systems of
  - the solution I
  - the solution II (in the solution the presence of any forms except cyano-complexes should be ignored)
- What is the units of pre-logarithm factor in the Nernst's equation?
- Calculate the ratio of the stability constants  $\beta\{\text{Fe}(\text{CN})_6^{3-}\}/\beta\{\text{Fe}(\text{CN})_6^{4-}\}$
- What is the absolute range of variation for the following physical magnitudes
  - transmittance  $T$ ; %
  - absorbance  $A$ .
- Draw a schematic view of plots of concentration dependencies satisfying Bouguer-Lambert-Beer law for
  - absorbance  $A$ ;
  - transmittance  $T$ ; %
  - molar absorptivity  $\epsilon$ .
- Calculate the concentrations of
  - $\text{Fe}^{3+}$  in solution I;
  - $\text{Fe}^{2+}$  in solution I.

Surname \_\_\_\_\_

Personal code \_\_\_\_\_

Team \_\_\_\_\_

## The Solution Report Form

### 1. Nernst's equations

a)	
b)	

### 2.

The units of pre-logarithm factor	
-----------------------------------	--



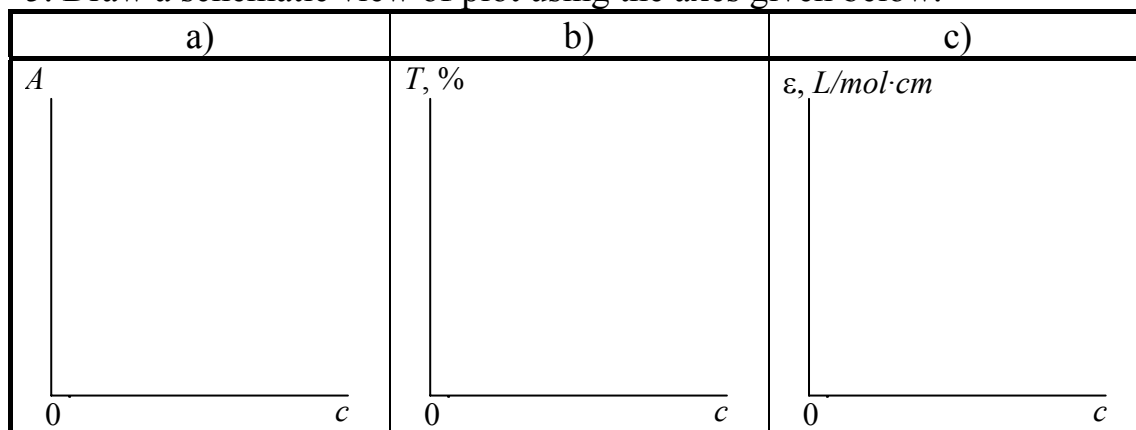
3.

The ratio of stability constants $\beta\{\text{Fe}(\text{CN})_6^{3-}\}/\beta\{\text{Fe}(\text{CN})_6^{4-}\}$ write only the final result of calculations in the blank cell →	
Calculations:	

4. The ranges of variation:

	from	to
a)		
b)		

5. Draw a schematic view of plot using the axes given below.



6. Fill in only the final results in the cells below.

a) Concentrations of $\text{Fe}^{3+}$	
Calculations:	
b) Concentrations of $\text{Fe}^{2+}$	
Calculations:	

## Answers and points (points are given in shaded square brackets).

### 1. Nernst's equations

a)	$E_1 = E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0590 \log [\text{Fe}^{3+}]/[\text{Fe}^{2+}]$	[1]
b)	$E_1 = E^\circ(\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}) + 0.0590 \log [\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]$	[1]

*Penalty points:*

Equation a)

- i) No penalty is imposed if Nernst's equation was written with  $E^\circ$  instead of  $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+})$  or  $RT/nF \ln \dots$  instead of  $0.0590 \log \dots$
- ii) Penalty of [-0.5] – for writing  $\log[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$  instead of  $\log[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$

Equation b)

- i) no penalty is imposed if Nernst equation was written with  $E^\circ$  instead of  $E^\circ(\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-})$  or  $RT/nF \cdot \ln \dots$  instead of  $0.0590 \cdot \log \dots$
- ii) Penalty of [-0.5] - for writing  $\log[\text{Fe}(\text{CN})_6^{4-}]/[\text{Fe}(\text{CN})_6^{3-}]$  instead of  $\log[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]$ ;  $\log[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$  or  $\log[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$  instead of  $\log[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]$ .

### 2.

The units of pre-logarithm factor	$V$ [0.5]
-----------------------------------	-----------

*Penalty points*

[-0.25] if the units are derived from  $RT/nF$  and the resulting units are not  $V$

3.

The ratio of stability constants $\beta\{\text{Fe}(\text{CN})_6^{3-}\}/\beta\{\text{Fe}(\text{CN})_6^{4-}\}$ write only the final result of calculations in the blank cell →	$8.90 \cdot 10^6$  [4]
<p>Calculations:</p> $E_{\text{II}} = E^\circ(\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{4-}) + 0.0590 \lg[\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{4-}] =$ $E^\circ(\text{Fe}^{3+} / \text{Fe}^{2+}) + 0.0590 \lg(\beta_1 / \beta_2) + 0.0590 \lg([\text{CN}^-]^6 / [\text{CN}^-]^6) +$ $+ 0.0590 \lg[\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{4-}] = 0.242$ <p>(where <math>\beta_1</math> and <math>\beta_2</math> are stability constants for <math>\text{Fe}(\text{CN})_6^{4-}</math> and <math>\text{Fe}(\text{CN})_6^{3-}</math>, respectively.)</p> $[\text{Fe}(\text{CN})_6^{3-}] / [\text{Fe}(\text{CN})_6^{4-}] = [\text{Fe}^{3+}] / [\text{Fe}^{2+}], \text{ therefore}$ $\Delta E = E_{\text{II}} - E_{\text{I}} = 0.0590 \cdot \log(\beta_1 / \beta_2), \text{ and } \beta_2 / \beta_1 = 8.90 \cdot 10^6.$	

*Penalty points:*Correct solution lies within  $8.89 \cdot 10^6$  and  $8.91 \cdot 10^6$ 

[-0.25] if less than or more than 3 significant digits are given in the final answer.

[-0.5] if the equations are written correctly, but the result is wrong due to arithmetic mistake

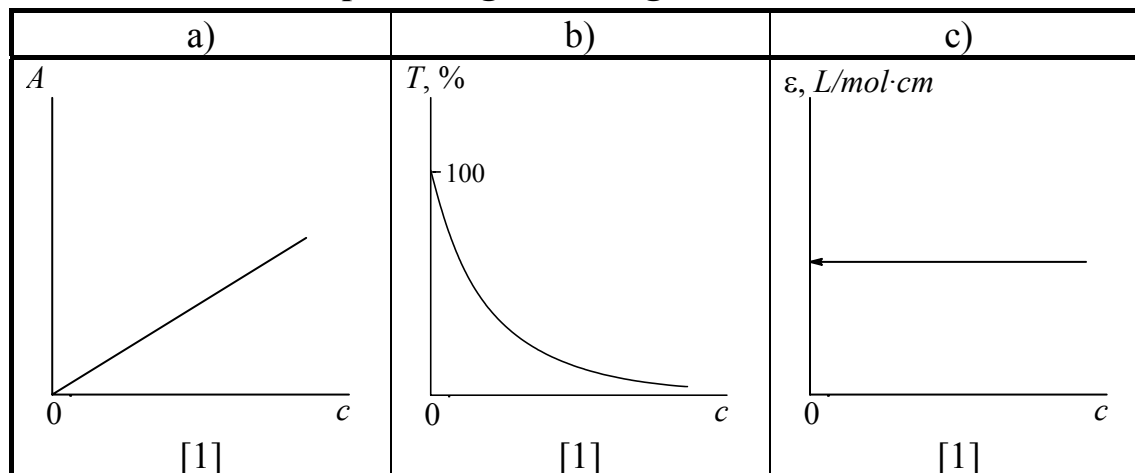
[0] points are given if the equation is incorrect.

**4. The ranges of variation:**

	from	to	
a)	0	100	[0.5]
b)	0	$\infty$	[0.5]

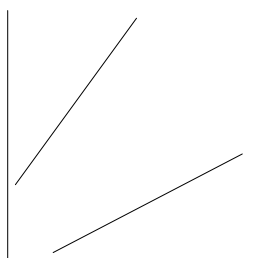
*Penalty points:*

[-0.25] penalty is imposed for each incorrect limit.

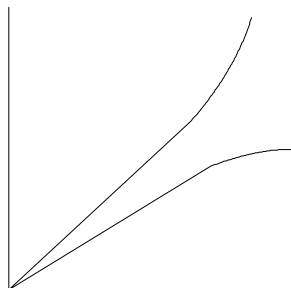
**5. Draw a sketch of plot using the axes given below.**

*Penalty points:*

- a) [-1] if a plot of any decreasing, or constant, or function is drawn.  
 [-0.5] if a line which fails to pass through the origin of coordinates is drawn as shown below



- [-0.25] if a line going from the origin, but changing to a curve at higher concentrations is drawn, as shown below



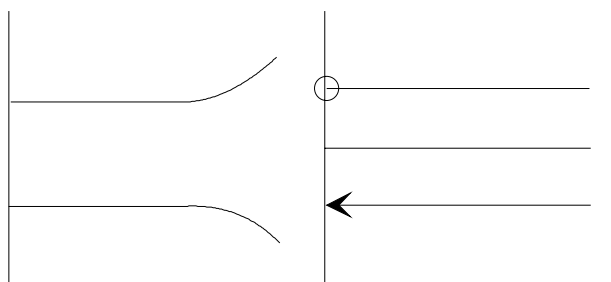
- b) [-1] if any growing function of a function crossing the concentration axis is drawn

[-0.5] if a line with negative slope is drawn

The exponential curve which originates not from 100% mark, or the exclusion of the point  $c = 0$ , are not considered faults.

- c) [-1] for any function which does not have a well defined constant region starting from  $c = 0$ .

[-0.25] if the constant function curves up or down at higher concentrations, as shown below on the left.



drawing any constant function either without exclusion of zero concentration limit, or with an exclusion whatever way is chosen to display this exclusion, e.g. as above on the right.

**6. Fill in only the final results in the cells below. You may use empty space below the cells for calculations.**

a)	b)
$1.76 \cdot 10^{-3} \text{ M}$	$0.183 \text{ M}$
[2]	[2]

Calculations

a) Using Bouger-Lambert-Beer law

$$A = \varepsilon l c = \varepsilon l [\text{Fe}(\text{CN})_6^{3-}] = 0.971;$$

$$[\text{Fe}(\text{CN})_6^{3-}] = 0.971 / (1100 \cdot 0.502) = 1.76 \cdot 10^{-3} \text{ M} = [\text{Fe}^{3+}]_I$$

b) using Nernst's equation

$$E = E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0590 \cdot \log[\text{Fe}^{3+}]_I / [\text{Fe}^{2+}]_I = 0.771 + 0.0590 \cdot \log[\text{Fe}^{3+}]_I / [\text{Fe}^{2+}]_I = 0.652 \text{ V.}$$

hence,

$$[\text{Fe}^{3+}]_I / [\text{Fe}^{2+}]_I = 9.62 \cdot 10^{-3};$$

$$[\text{Fe}^{2+}]_I = 1.76 \cdot 10^{-3} / 9.62 \cdot 10^{-3} = 0.183 \text{ M.}$$

*Penalty points:*

[-0.25] if less than or more than 3 significant digits are given in the final answer.

[-0.5] if the equations are written correctly, but the result is wrong due to an arithmetic mistake.

## Problem 6

Two isomeric hydrocarbons A and B contain 85.7 mass % of carbon.

1. Write a general formula which satisfies this condition.

The hydrocarbons A and B possess the following properties. The reaction of each of the compounds with ozone with subsequent treatment of the product with zinc dust in the presence of acid gives a single organic product C. The oxidation of compound C gives a single product, the carboxylic acid D. According to spectral data all hydrogen atoms in this acid except the one in carboxylic group are contained in methyl groups. The density of vapours of D corrected to normal conditions (0°C, 1 atm) is 9.1 g/l.

Compound A is more reactive than compound B in the reaction with cold neutral potassium permanganate. A single compound F is formed from A, and a 1:1 mixture of isomers G1 and G2 is formed from B.

2. Draw the structural formulae of the compound D both in aqueous solution and in vapour phase.

3. Write the formula of compound C.

4. Draw the structures of isomers A and B.

5. a) Write the reactions of the transformation of A or B into C and D.

b) Write the reactions of the transformation of A and B into F, G1 and G2.

6. Compounds G1 and G2 readily react with acetone in the presence of acids and form compounds H1 and H2. Draw the structures of H1 and H2.

7. Compounds A and B react with bromine. One of the products of these reactions is non-polar (dipole moment of this molecule is practically equal to zero) and optically inactive. Draw the stereochemical formula of this product, and write the reaction of its formation. Determine the absolute configuration of chiral atoms in this molecule (if any) and mark them according to RS nomenclature by *R* or *S* letters.

Alkenes react with peroxyacids with the addition of oxygen to double bond to form a three-membered oxygen-containing ring. This epoxidation reaction is highly stereospecific to retain the relative positions of substituents at the bond to which the oxygen atom is attached.

The epoxidation of compound A by peroxyacetic acid yields a single compound K. Under the same conditions B gives a mixture of isomers L1 and L2 (the ratio is 1:1).

8. Is the compound K optically active? Draw the stereochemical formula of K. Are the individual compounds L1 and L2 optically active? Draw the stereochemical formulae of L1 and L2.

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Personal code \_\_\_\_\_

Team \_\_\_\_\_

## The Solution Report Form

1.

The general formula	
---------------------	--

place for calculations:

2. Compound D

In aqueous solution	In vapours

3.

Compound C	
------------	--

4.

A	B



5. Here and in all other questions you may use any type of stereochemical formulae which you prefer. Note that here and in all other answers the mechanisms of reactions are not required and writing them shall not bring additional points.

$A \longrightarrow C \longrightarrow D$
$A \longrightarrow F$
$B \longrightarrow G1 + G2$

6.

H1	H2

--	--

7. Bromination

--

8. Draw the structures and place a checkmark at the boxes below

K	L1	L2
<input type="checkbox"/> YES, the molecule is optically active	<input type="checkbox"/> YES, the molecule is optically active	<input type="checkbox"/> YES, the molecule is optically active
<input type="checkbox"/> NO the molecule is not optically active	<input type="checkbox"/> NO the molecule is not optically active	<input type="checkbox"/> NO the molecule is not optically active

## Answers and points

(points are given in shaded square brackets)

Grand total - [31]

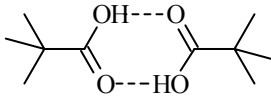
1.

The general formula	$C_nH_{2n}$ [1]
---------------------	-----------------

Answers like  $(CH_2)_n$  ;  $n(CH_2)$  are also accepted

[-0.5] if the answer is  $CH_2$ . All other answers are unacceptable.

2. Compound D - total [3]

In aqueous solution	In vapours
$(CH_3)_3CCOOH$ [2]	 [1]

Dimeric structure in vapour phase is guessed using the value of vapour density.

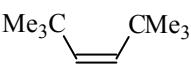
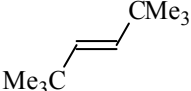
Molar weight in vapour phase is  $9.1 \cdot 22.4 = 204$  which is close to twice the molar weight of  $(CH_3)_3CCOOH$ . Possibly, as other simple fat acids, this acid is also dimerized in vapours.

Indication of  $(CH_3)_3CCOO^-$  as the formula in solution - [-0.5]

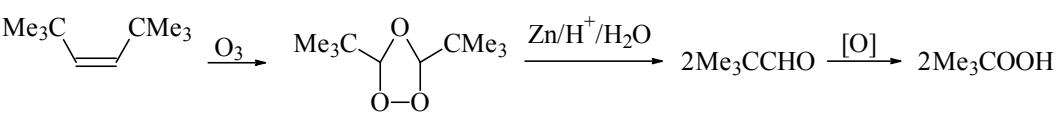
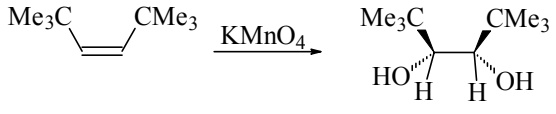
3.

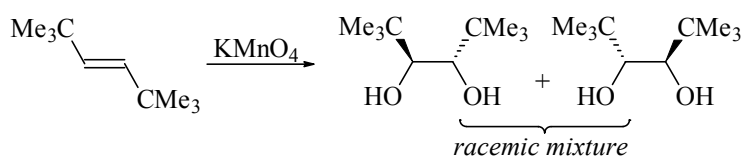
Compound C	$(CH_3)_3CCHO$ [1]
------------	--------------------

4. total [4]

A	B
 [2]	 [2]

5. Total - [5]

A $\longrightarrow$ C $\longrightarrow$ D	
	[1] [1]
<p>Points are given for drawing the reaction of ozonolysis: A <math>\rightarrow</math> aldehyde. Drawing ozonide is not necessary and is not awarded nor penalized.</p>	
A $\longrightarrow$ F	
	[1]



[2]

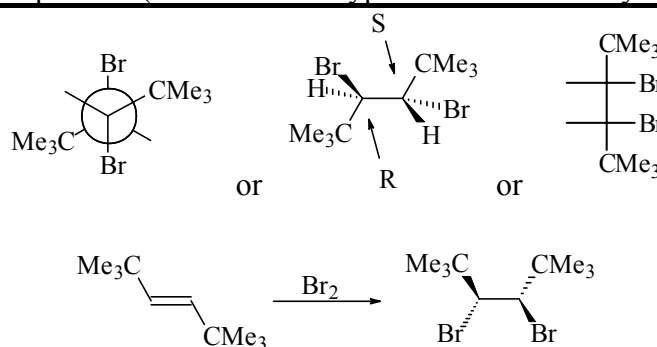
If reactions are written, but the stereochemistry is not indicated in any understandable form, or indicated wrong - [0.25]

6. Total [4]

H1	H2
[2]	[2]

7. Total [6]

Non-polar bromination product (either of three types of structures may be given)



[6]

Only the reaction without any indication of the stereochemistry in any form [0.25]

Reaction with incorrect stereochemistry (any other vic-dibromide in place of meso-form)

[2]

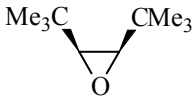
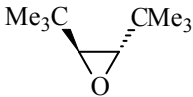
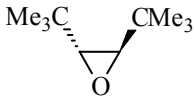
Everything correct, but RS not given [4]

Both centers are R or S [4]

R and S centers are confused with each other (R in place of S, and vice versa) [4.5]

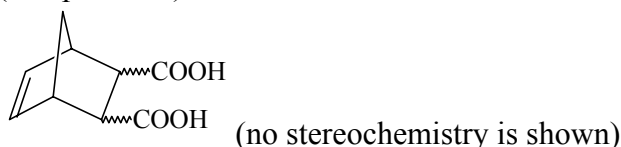
Wrong products are given, but R and S are assigned correctly on a wrong molecule [2]

## 8. Total - [7]

K	L1	L2
 <p style="text-align: right;">[2]</p>	 <p style="text-align: right;">[1]</p>	 <p style="text-align: right;">[1]</p>
<input type="checkbox"/> YES, the molecule is optically active <input checked="" type="checkbox"/> NO the molecule is not optically active <p style="text-align: right;">[1]</p>	<input checked="" type="checkbox"/> YES, the molecule is optically active <input type="checkbox"/> NO the molecule is not optically active <p style="text-align: right;">[1]</p>	<input checked="" type="checkbox"/> YES, the molecule is optically active <input type="checkbox"/> NO the molecule is not optically active <p style="text-align: right;">[1]</p>

## Problem 7

Stereochemistry of organic compounds can sometimes be determined by studying their chemical behavior. The stereochemical configuration of one of the isomers of 5-norbornene-2,3-dicarboxylic acids (compound **X**)



was established by the following experiments.

On heating this substance decomposes producing water and a new compound **Y**. Compound **Y** slowly dissolves in excess of aqueous NaOH with the formation of product **X<sub>1</sub>** same to that is formed in the reaction of **X** with NaOH. The resulting solution of **X<sub>1</sub>** is treated by I<sub>2</sub> to give compounds containing iodine. Acidification of the solution leads to a mixture of two isomeric compounds, **A** and **B** in the 3:1 ratio. The titration of 0.3913 g of compound **A** by 0.1000 M aqueous solution of NaOH in the presence of phenolphthalein takes 12.70 ml of alkali. The same amount of 0.1000 M solution of NaOH is required for the titration of 0.3913 g of compound **B**. On heating compound **A** slowly transforms into compound **C**, which contains no iodine and is able to react with water. Under the same conditions compound **B** does not undergo this transformation, but on heating with hydrochloric acid slowly transforms into **A**.

*All reactions must be written as balance equations. No mechanisms required.*

*Additional sheets of The Solution Report Form are available from supervisor.*

1. Mark by asterisks (\*) the asymmetric carbon atoms in the structure of 5-norbornene-2,3-dicarboxylic acids.
2. Draw the stereochemical formulas of all stereoisomers of compound **X**, and the structures of products of their dehydration in those cases when it is possible.
3. Write the reactions of NaOH with a stereoisomer of **X** and a stereoisomer of **Y**.
4. Calculate the molar mass of compound **A**. Write the reactions leading from **X<sub>1</sub>** to **A**.
5. Write the reaction of the formation of **C** from **A** and the reaction of **C** with water.
6. Draw the stereochemical formula of compound **X** which satisfies all of the data given in the problem.
7. Write the reactions leading from **B** to **A**.
8. Are the compounds **A** and **B** diastereomers?

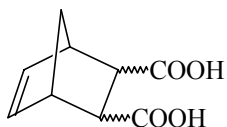
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## The Solution Report Form

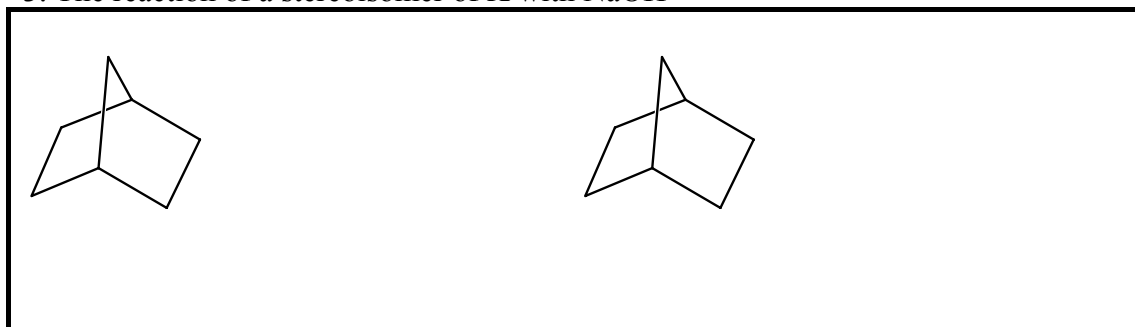
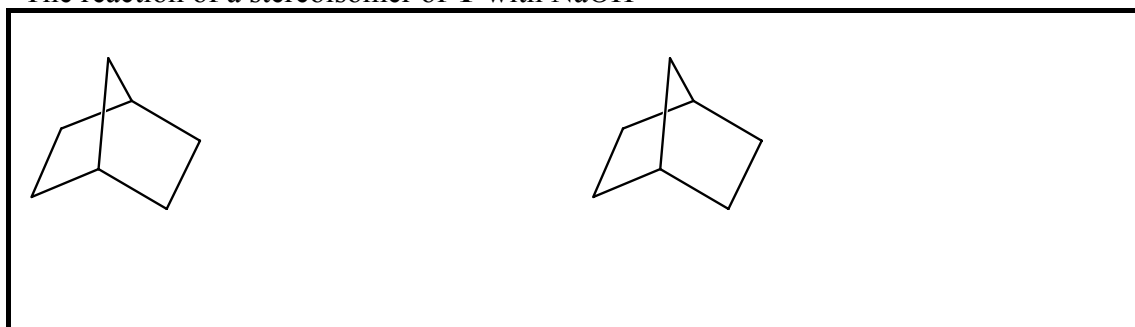
1. Mark the asymmetric carbon atoms on the structure below



2. Fill in left column with the structures of stereoisomers of X, and the right column with the corresponding structures of dehydration products (when such structure does not exist write a minus sign there).

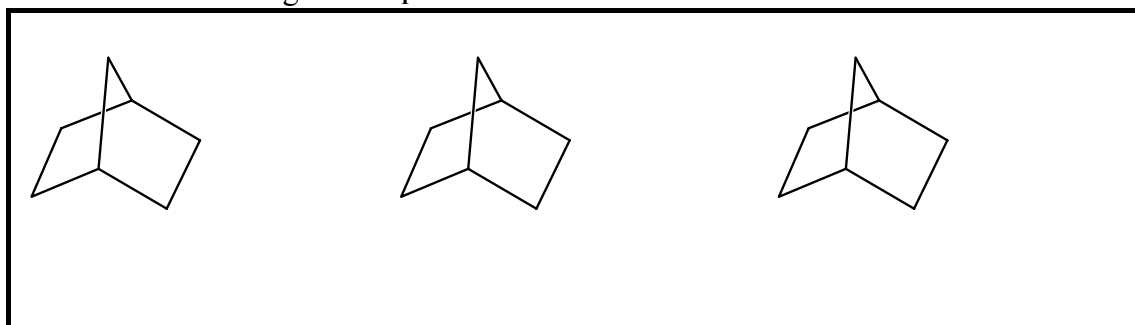
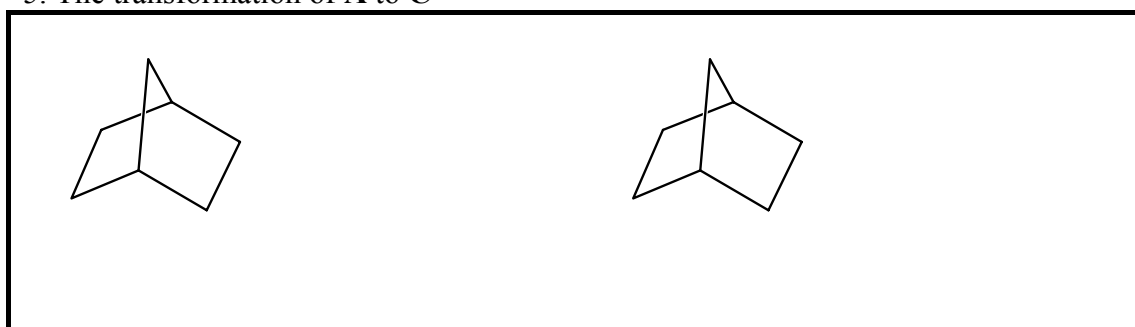


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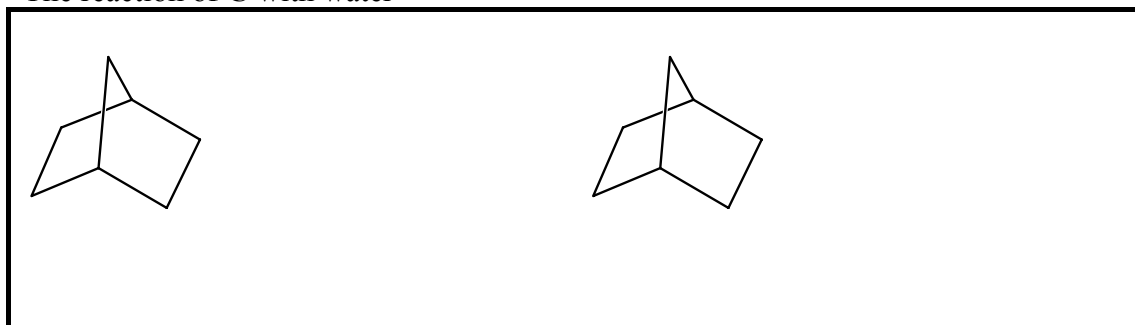
3. The reaction of a stereoisomer of **X** with NaOHThe reaction of a stereoisomer of **Y** with NaOH

## 4.

The molar mass of <b>A</b> , g/mol		Calculations:
------------------------------------	--	---------------

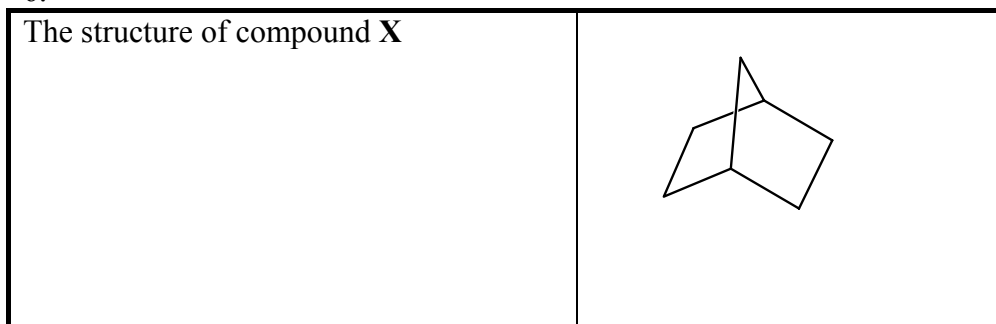
The reactions leading from **X<sub>1</sub>** to **A**5. The transformation of **A** to **C**

The reaction of **C** with water

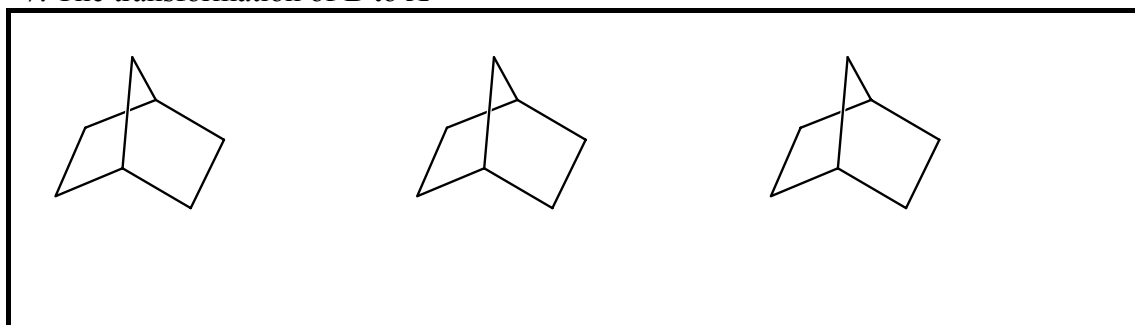


6.

The structure of compound **X**



7. The transformation of **B** to **A**

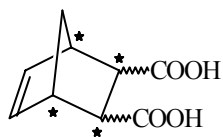


8. Place a checkmark into the box near the correct statement

- Yes, **A** and **B** are diastereomers
- No, **A** and **B** are not diastereomers

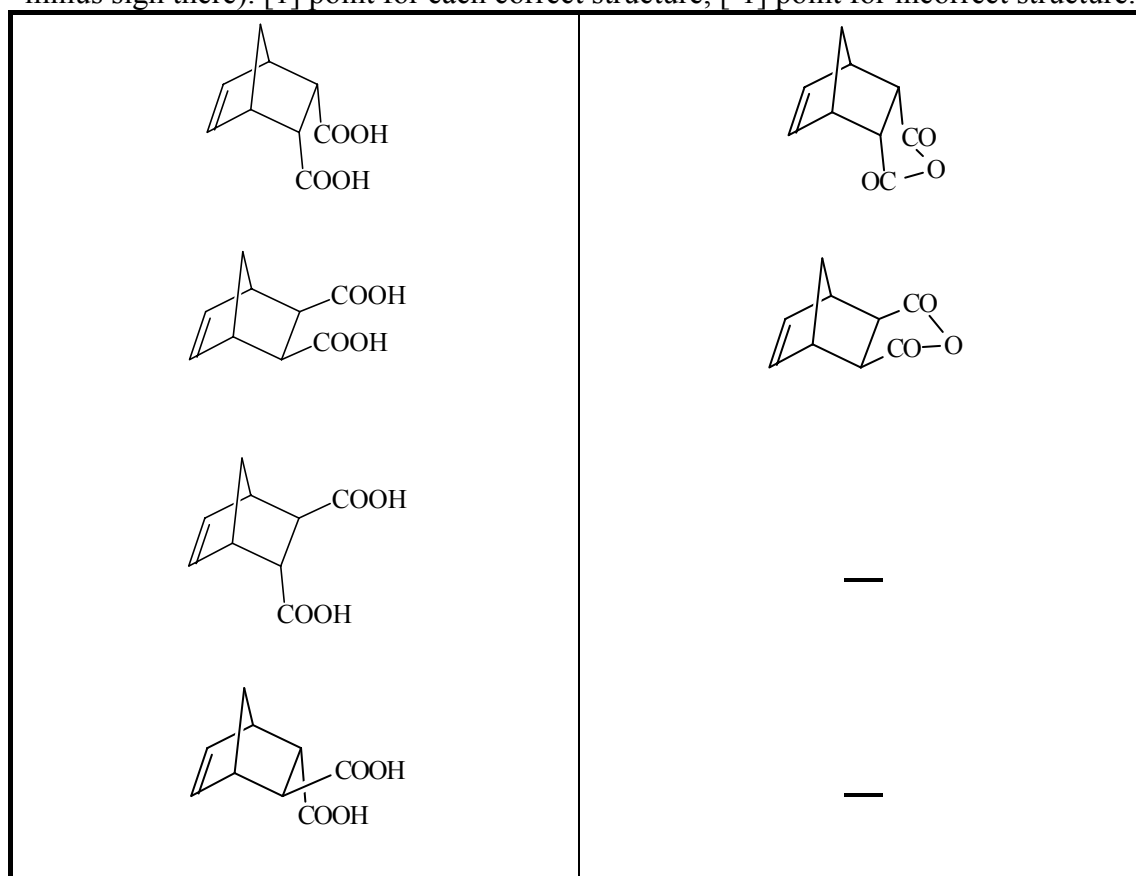
## Answers and points (points are given in shaded square brackets)

1. [1] point for each correct atom, [-1] for each wrong choice. Maximum value [4]



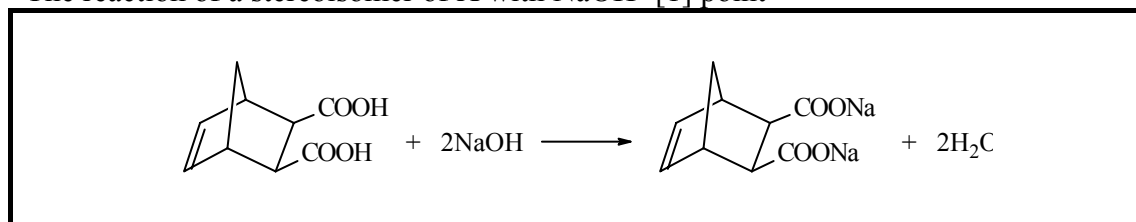
2. Total [6]

Fill in left column with the structures of stereoisomers of X, and the right column with the corresponding structures of dehydration products (when such structure does not exist write a minus sign there). [1] point for each correct structure, [-1] point for incorrect structure.

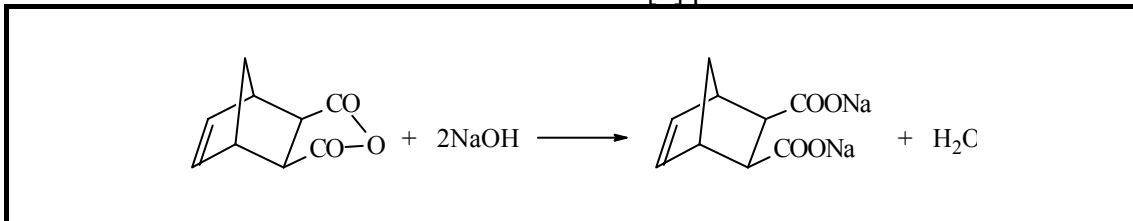


3. Total [2]

The reaction of a stereoisomer of X with NaOH- [1] point



The reaction of a stereoisomer of Y with alkali - [1] point

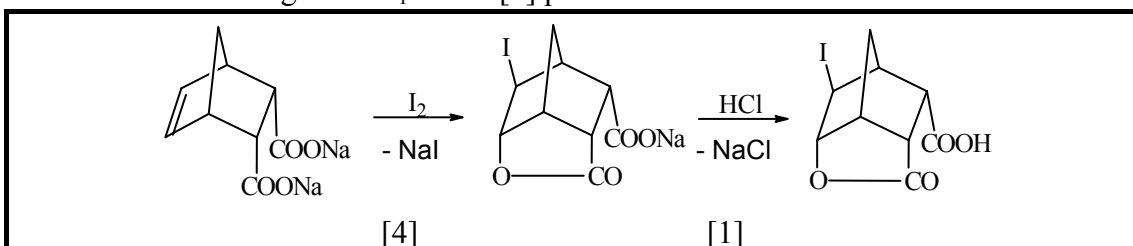


4. Total [7]

The molar mass of A, g/mol	308 [2]	Calculations
----------------------------	------------	--------------

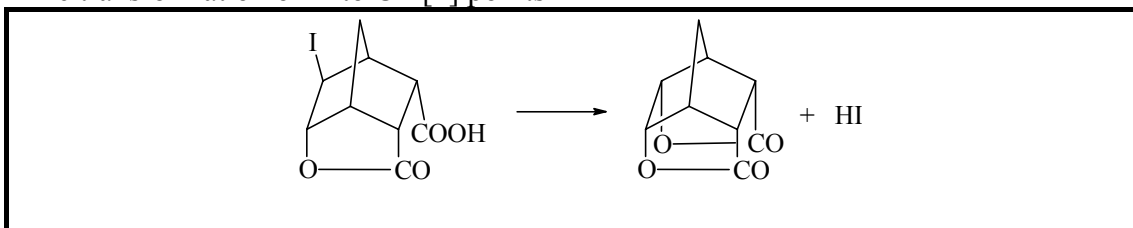
[1] point will be given if right calculations are written, but wrong answer is obtained.

The reactions leading from X<sub>1</sub> to A - [5] points

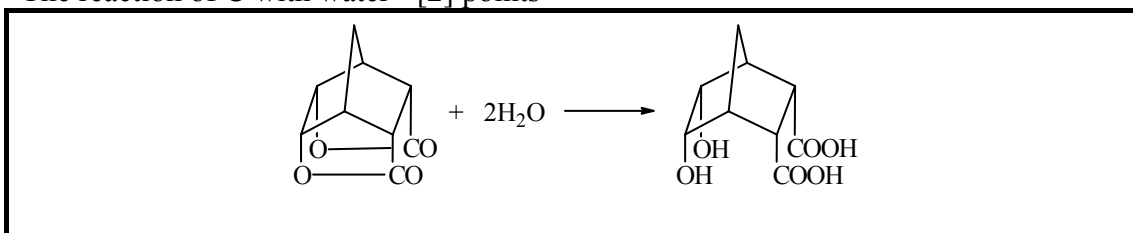


5. Total [4]

The transformation of A to C - [2] points



The reaction of C with water - [2] points

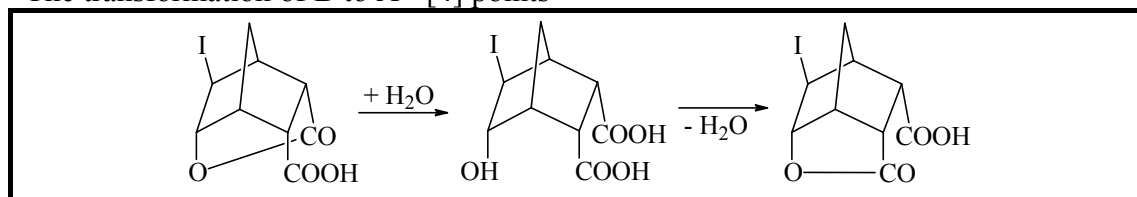


6. Total [4].

The structure of compound X - [4] points	
--	--

7. Total [4]

The transformation of B to A - [4] points



9. Total [1]

Place a checkmark into the square near the correct statement

- Yes, A and B are diastereomers
- No, A and B are not diastereomers - [1] points