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 π-bonds of the olefin molecules are usually used as the catalysts in these processes. Chloroaluminate anions (like $AlCl_4^-$) 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=($TeCl_4$+4$AlCl_3$). The second component B was considered as an analog of Te(IV) chloroaluminate $Te[AlCl_4]_4$ 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 $TeCl_4$ 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 $NaAlCl_4$ showed. The cryoscopic measurements in $NaAlCl_4$ melt enabled to determine the molecular weights of these compounds being equal to 1126±43 g/mole and 867±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 cm^{-1} and is therefore so low in energy that this bond undoubtedly is a kind of Te—Te interaction. The ^{27}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 $AlCl_3$ 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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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
7Te(cryst.) + $2TeCl_4$ + $8AlCl_3$ and the minimum atomic ratio for the composition from which the excess of $TeCl_4$ is not substracted is Te : Al : 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. Substracting one mole of $TeCl_4$ from the obtained ratio and dividing by 2 we obtain 4Te + 4Al + 14Cl and the ratio is Te:Al:Cl=2:2:7, which can be then verified by comparison with the molecular weight given
87.5% of Te(cryst.) corresponds to
7Te(cryst.) + $TeCl_4$ + $4AlCl_3$ = 8Te + 4Al + 16Cl and the ratio is Te:Al:Cl = 2:1:4
91.7% of Te(cryst.) corresponds to
11Te(cryst.) + $TeCl_4$ + $4AlCl_3$ = 12Te + 4Al + 16Cl and the ratio is Te:Al:Cl = 3:1:4

2. The molecular formulae of compounds I and II

Compound I [1]	$Te_4Al_4Cl_{14}$
Compound II [1]	$Te_4Al_2Cl_8$

Molecular formulae can be deduced from the data on molar weights. Both correspond to doubled simplest formula.
for I: $2(Te_2Al_2Cl_7)$ gives calculated m.w. = 1114.7 against experimental value of 1126 ± 43
for II: $2(Te_2AlCl_4)$ gives calculated m.w. = 848 against experimental value of 867 ± 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	$[Te_4]^{2+}$	$[Al_2Cl_7]^-$

	[0.5]	[0.5]
Compound II	$[Te_4]^{2+}$ [0.5]	$[AlCl_4]^-$ [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 $AlCl_4^-$ anions which seems probable for II, which therefore can be formulated as $[Te_4]^{2+}[AlCl_4]_2^-$. As according to similar colouration the cations are likely to be the same in both cases, the structure of I should contain $[Te_4]^{2+}$ cations and $[Al_2Cl_7]^-$ 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:
$AlCl_4^-$ is a single tetrahedron; [1]
$Al_2Cl_7^-$ is two tetrahedra sharing a common vertex (a chlorine atoms) - [1]
The geometry of the cation:
$[Te_4]^{2+}$ 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 $\boxed{<}$ 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 $AlCl_3$. which is a volatile solid and can be relatively easily removed on heating.

6. The reaction equation. Total [1]

$$Te_4[Al_2Cl_7]_2 = Te_4[AlCl_4]_2 + 2AlCl_3$$

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 $[C_9H_6(OH)NH][BiI_4]$ ($M_r = 862.7$).

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 (≈2 *ml*) of cold acidified solution containing trace amounts of Bi^{3+} 50 *mg* of potassium hexathiocyanatochromate(III) ($K_3[Cr(SCN)_6]$) 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 ($(BiO)_2CO_3$) 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 H_2SO_4 solution are added to the mixture. The acidification leads to the reaction of coproportiation 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 BrCN, and iodide is oxidized into 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 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 $Na_2S_2O_3$ 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 $Na_2S_2O_3$ solution) ?

11. By how many times the multiplicative method just described is more sensitive than Berg's gravimetric method ?

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1.a)

The cation	The anion

1.b)

The oxidation state of bismuth in 8-hydroxyquinolinium tetraiodobismuthate:	

2.

The smallest mass of bismuth determined reliable by Berg method, *mg*	

3. Reaction equation

4. Reaction equation

5. Reaction equation

6. Reaction equation

7. Reaction equations

a)

b)

8. Reaction equation

9. Reaction equations

a)

b)

10.

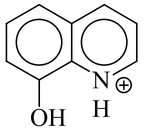
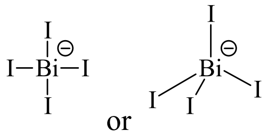
Place for calculations:		
a)	The number of moles of thiosulfate to 1 mole of bismuth	
b)	The least mass of bismuth, *mg*	

11.

	Detection limit of gravimetric method Detection limit of multiplicative method	

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]

2. [1]

The smallest mass of bismuth determined reliably by Berg method, *mg*	12.1

Molar mass of precipitate is 862.7 g, which contain 209.0 g of bismuth. Thus, 0.0500 *g* of precipitate correspond to $1.21 \cdot 10^{-2}$ *g* = 12.1 *mg* of bismuth.

3. Reaction equation - [0.5]

$$Bi^{3+} + [Cr(SCN)_6]^{3-} \longrightarrow Bi[Cr(SCN)_6].$$

4. Reaction equation - [1]

$$2Bi[Cr(SCN)_6] + 6HCO_3^- \longrightarrow (BiO)_2CO_3 + 2[Cr(SCN)_6]^{3-} + 3H_2O + 5CO_2$$

or

$$2Bi[Cr(SCN)_6] + HCO_3^- + 5OH^- \longrightarrow (BiO)_2CO_3 + 2[Cr(SCN)_6]^{3-} + 3H_2O \text{ etc.}$$

(variations are possible)

5. Reaction equation - [1.5]

$$[Cr(SCN)6]3- + 24I_2 + 24H_2O \longrightarrow Cr^{3+} + 6SO_4^{2-} + 6ICN + 42I^- + 48\ H^+$$

6. Reaction equation - [1]

$$ICN + I^- + H^+ \longrightarrow I_2 + HCN$$

7. Reaction equations

a)

$$3Br_2 + I^- + 3H_2O \longrightarrow IO_3^- + 6Br^- + 6H^+$$

[0.5]

b)

$$Br_2 + HCN \longrightarrow BrCN + Br^- + H^+$$

[0.5]

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

8. Reaction equation - [1]

$$Br_2 + HCOOH \longrightarrow 2Br^- + CO_2 + 2H^+.$$

9. Reaction equations - total [1]

a)

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

[0.5]

b)

$$BrCN + 2I^- + H^+ \longrightarrow I_2 + HCN + Br^-$$

[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*	$1.83\cdot10^{-3}$ [1]

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

Solution:

titration of iodine by thiosulfate involves the reaction:

$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$.

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 IO_3^-, which in reaction 9a gave $36\cdot3 = 108$ moles of I_2, which take $108\cdot2 = 216$ moles of thiosulfate for titration. However, that is not all. Indeed, 6 moles of HCN are generated per mole of 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 $2.00\cdot10^{-6}$ mole of $Na_2S_2O_3$, which corresponds to $209.0\cdot2.00\cdot10^{-6}/228 = 1.83\cdot10^{-6}$ *g* = $1.83\cdot10^{-3}$ *mg* = 1.83 μg**.**

11.

Detection limit of gravimetric method Detection limit of multiplicative method	6600 [0.5]

The multiplicative method is more sensitive than the gravimetric method by $12.1\text{mg}/1.83\cdot10^{-3}\text{mg} = 6600$ times.

Problem 3.

In 1908 Rutherford together with H.Geiger measured the rate of emission of α-particles (x) by radium (in the nature this element is represented by a single nuclide $^{226}_{88}\mathrm{Ra}$) and found that 1.00 g of radium emits $x = 3.42\cdot10^{10}$ α - particles per second.

In 1911 Rutherford and American physical chemist B.Boltwood measured the rate of formation of helium from radium. This experiment permits to obtain the most accurate value of Avogadro's number available at that time, given that the value of molar volume of ideal gas was well established. To achieve this goal a sample of radium salt purified from decay products and containing m = 192 *mg* of Ra was put into a device and the volume of the evolved helium was measured.

After 83 days (t = 83.0 days) of the experiment 6.58 mm^3 of He was collected (V_{He} = 6.58 mm^3 corrected to 0^o C and 1 atm).

To understand the results of this experiment we shall need the kinetic scheme of radioactive decay of Ra which is given below (half-lives are over the arrows, the type of decay is below the arrows).

$$\mathrm{Ra} \xrightarrow[\alpha]{>1500\text{ years}} \mathrm{Rn} \xrightarrow[\alpha]{3.83\text{ days}} \mathrm{RaA} \xrightarrow[\alpha]{3.05\text{ min}} \mathrm{RaB} \xrightarrow[\beta]{26.8\text{ min}} \mathrm{RaC} \xrightarrow[\beta]{19.7\text{ min}}$$

$$\longrightarrow \mathrm{RaC'} \xrightarrow[\alpha]{1.63\cdot10^{-4}\text{ s}} \mathrm{RaD} \xrightarrow[\beta]{27.1\text{ years}} \mathrm{RaE} \xrightarrow[\beta]{5\text{ days}} \mathrm{Po} \xrightarrow[\alpha]{138\text{ days}} \mathrm{Pb}\text{ (stable)}$$

(RaA -RaE are intermediate products of radon decay).

1. Write the first six radioactive decays using a modern notation showing atomic and mass numbers of all nuclei involved.

As a rough first approximation half-lives of all radium decay products, except those of RaD and Po, may be assumed to be negligible compared to the time of measurement t. Using this approximation perform the following calculations.

2. a) How many helium atoms were formed from each decayed radium atom after 83 days?

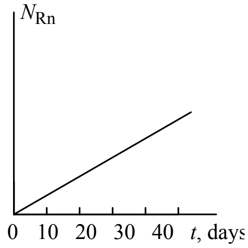
b) How many helium atoms were formed in total during the experiment?

3. Calculate an approximate value of Avogadro's number from the above data.

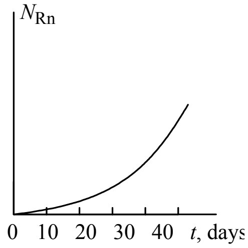
For a more accurate computation of Avogadro's number the half-life of radon $T_{1/2}(\mathrm{Rn})$ = 3.83 days cannot be neglected as it is comparable with the duration of experiment t and not all of radon atoms decayed to the end of experiment.

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

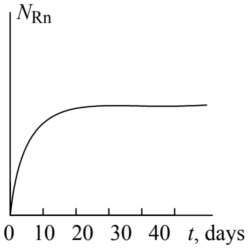
A



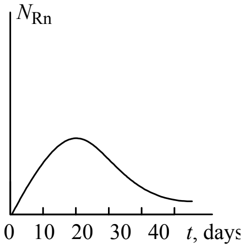
B



C

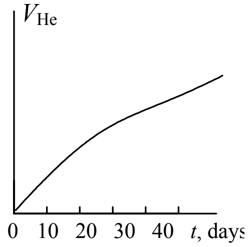


D

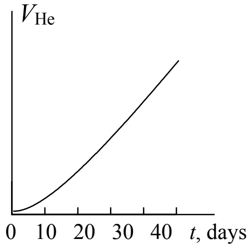


5. Choose which of the plots given below shows the time dependence of the volume of helium in the course of the experiment.

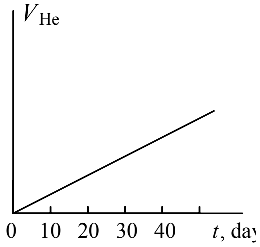
E



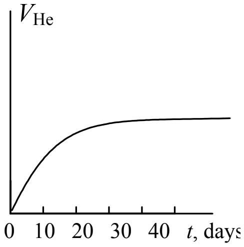
F



G



H



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

$$\mathrm{Ra} \xrightarrow{k_1} \mathrm{Rn} \xrightarrow{k_2} \mathrm{RaA}$$

(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'_{Rn} and the number of radium atoms N_{Ra}.

b) Evaluate N'_{Rn} using the rate of radium decay given above ($x = 3.42 \cdot 10^{10}$ α-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'_{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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Team ____________________________

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:

$${}^{\boxed{}}_{\boxed{}}\boxed{} \longrightarrow {}^{\boxed{}}_{\boxed{}}\boxed{} + {}^{\boxed{}}_{\boxed{}}\boxed{}$$

$${}^{\boxed{}}_{\boxed{}}\boxed{} \longrightarrow {}^{\boxed{}}_{\boxed{}}\boxed{} + {}^{\boxed{}}_{\boxed{}}\boxed{}$$

$${}^{\boxed{}}_{\boxed{}}\boxed{} \longrightarrow {}^{\boxed{}}_{\boxed{}}\boxed{} + {}^{\boxed{}}_{\boxed{}}\boxed{}$$

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$${}^{\boxed{}}_{\boxed{}}\boxed{} \longrightarrow {}^{\boxed{}}_{\boxed{}}\boxed{} + {}^{\boxed{}}_{\boxed{}}\boxed{}$$

2. a) circle the correct answer

1	2	3	4	5

b)

Number of helium atoms (rough estimate)	

3.

Avogadro's number (rough estimate)	

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
☐	☐	☐	☐

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
☐	☐	☐	☐

6. Underline the correct answer

$k = 1/T_{1/2}$	$k = ln2/T_{1/2}$	$k = ln2 \cdot T_{1/2}$	$k = \pi/T_{1/2}$

7.

a) Underline the correct answer

$N'_{\mathrm{Rn}} = k_1 \cdot N_{\mathrm{Ra}} / k_2$	$N'_{\mathrm{Rn}} = k_2 \cdot N_{\mathrm{Ra}} / k_1$	$N'_{\mathrm{Rn}} = k_1 \cdot N_{\mathrm{Ra}} / 2k_2$	$N'_{\mathrm{Rn}} = k_1 \cdot N_{\mathrm{Ra}} / 3k_2$

b) Insert the calculated value

N'_{Rn}	

8.

Underline the correct answer

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

9. a)

A more accurate estimate of the number of helium atoms	

b)

A more accurate estimate of Avogadro's number (mol^{-1})	

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

1.

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

$$^{226}_{88}\mathrm{Ra} \longrightarrow {}^{222}_{86}\mathrm{Rn} + {}^{4}_{2}\mathrm{He}$$

$$^{222}_{86}\mathrm{Rn} \longrightarrow {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\mathrm{He}$$

$$^{218}_{84}\mathrm{Po} \longrightarrow {}^{214}_{82}\mathrm{Pb} + {}^{4}_{2}\mathrm{He}$$

$$^{214}_{82}\mathrm{Pb} \longrightarrow {}^{214}_{83}\mathrm{Bi} + \mathrm{e}$$

$$^{214}_{83}\mathrm{Bi} \longrightarrow {}^{214}_{84}\mathrm{Po} + \mathrm{e}$$

$$^{214}_{84}\mathrm{Po} \longrightarrow {}^{210}_{82}\mathrm{Pb} + {}^{4}_{2}\mathrm{He}$$

2. Total [1.5]

a) circle the correct answer

1	2	3	④ [0.5]	5

b)

Number of helium atoms (rough estimate) $N_{\mathrm{He}} = 4xmt = 1.9\cdot10^{17}$	$1.9\cdot10^{17}$ [1]

3.

The first estimate of Avogadro's number	$6.4\cdot10^{23}$ mol^{-1} [1]

Solution. The Avogadro's number N_{A} is the number of particles in one mole. $N_{\mathrm{A}} = N_{\mathrm{He}}/\nu_{\mathrm{He}}$, where N_{He} is number of helium atoms, and ν_{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 $N_{\mathrm{He}} = 4xmt$, and

$N_{\mathrm{A}} = 4xmt/\nu_{\mathrm{He}} = 4\cdot3.42\cdot10^{10}\cdot0.192\cdot(83\cdot24\cdot3600)/(6.58\cdot10^{-6}/22.4) = 6.4\cdot10^{23}$ 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 α-particles emitted by radium, but to the end of the experiment α-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]

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

7. Total [5]

a) Underline the correct answer [2]

$N'_{\text{Rn}} = k_1\cdot N_{\text{ra}}/k_2$	$N'_{\text{Rn}} = k_2\cdot N_{\text{Ra}}/k_1$	$N'_{\text{Rn}} = k_1\cdot N_{\text{Ra}}/2k_2$	$N'_{\text{Rn}} = k_1\cdot N_{\text{Ra}}/3k_2$

The number of radon atoms reaches a quasi-stationary state, at which the rate of formation is equal to the rate of decay $k_2N'_{\text{Rn}} = k_1N_{\text{Ra}}$, whence $N'_{\text{Rn}} = k_1\cdot N_{\text{Ra}}/k_2$

b) [3]

N'_{Rn}	$3.14\cdot10^{15}$

The rate of radium decay is $k_1N_{\text{Ra}} = xm$, whence

$N'_{\text{Rn}} = xm/(ln2/T_{1/2(\text{Rn})}) = 3.42\cdot10^{10}\cdot0.192/(0.693/3.83\cdot24\cdot3600)) = 3.14\cdot10^{15}$

8.

[0.5]

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

9. Total [2.5]

a)

A more accurate estimate of the number of helium atoms	$1.79\cdot10^{17}$ [1.5]

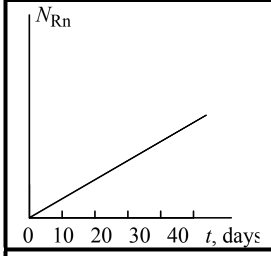
$N_{\text{He}} = 4xmt - 3\,N'_{Rn} = 1.9\cdot10^{17} - 3\cdot3.14\cdot10^{15} = 1.79\cdot10^{17}$

b)

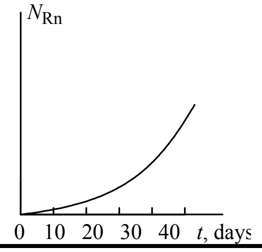
A more accurate estimate of Avogadro's number (mol^{-1})	$6.09\cdot10^{23}$ [1]

$N_{\text{À}} = N_{\text{He}}/\nu(\text{He}) = 1.79\cdot10^{17}/(6.58\cdot10^{-6}/22.4) = 6.09\cdot10^{23}$

Total: 16.20


N_{Rn}
0 10 20 30 40 t, days

☐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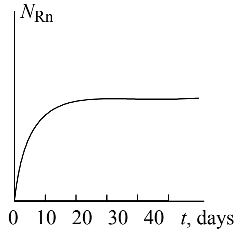
N_{Rn}
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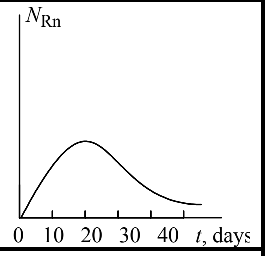
N_{Rn}
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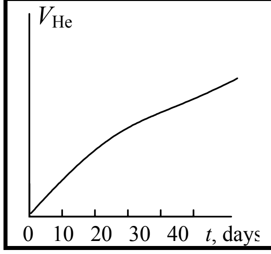
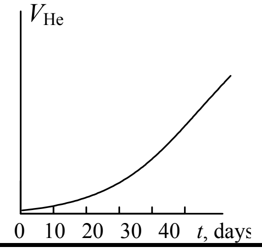

V_{He}
0 10 20 30 40 t, days


V_{He}
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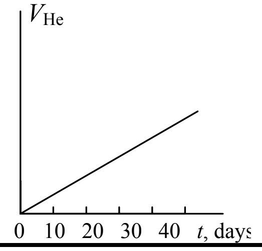
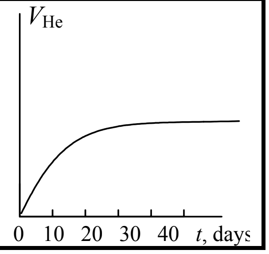

V_{He}
0 10 20 30 40 t, days


V_{He}
0 10 20 30 40 t, days

Problem 4.

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

$HCrO_4^- + H_2O = CrO_4^{2-} + H_3O^+$ pK$_1$ = 6.50

$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$ pK$_2$ = -1.36

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

1. The ionic product of water $K_W = 1.0\cdot10^{-14}$.
Evaluate the equilibrium constants

a) $CrO_4^{2-} + H_2O = HCrO_4^- + OH^-$

b) $Cr_2O_7^{2-} + 2OH^- = 2CrO_4^{2-} + H_2O$

2. The solubility product of $BaCrO_4$ $K_s = 1.2\cdot10^{-10}$. $BaCr_2O_7$ 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?

a) KOH
b) HCl
c) $BaCl_2$
d) H_2O (consider all the above equilibria)

3. Dissociation constant of acetic acid $K_a = 1.8\cdot10^{-5}$. Calculate the pH value of the following solutions

a) 0.010 M K_2CrO_4
b) 0.010 M $K_2Cr_2O_7$
c) 0.010 M $K_2Cr_2O_7$ + 0.10 M CH_3COOH

4. Calculate the equilibrium concentrations of the following ions in a solution of 0.010 M $K_2Cr_2O_7$ + 0.10 M CH_3COOH

a) CrO_4^{2-}

b) $Cr_2O_7^{2-}$

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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 comon errors in solutions. In the case of non-standard solutions, the evaluation will be done in a similar unified manner as the described scheme. Is 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	$3.2\cdot10^{-8}$ [3] (1,3)
Place for calculations $[HCrO_4^-][OH^-]/[CrO_4^{2-}] = [H^+][OH^-]/([H^+][CrO_4^{2-}]/[HCrO_4^-]) = K_W/K_1 = 1.0\cdot10^{-14}/3.16\cdot10^{-7} = 3.2\cdot10^{-8}$ [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	$4.4\cdot10^{13}$ [3] (1, 4)
Place for calculations $K = ([CrO_4^{2-}][H^+]/[HCrO_4^-])^2/([HCrO_4^-]^2/[Cr_2O_7^{2-}])/([H^+][OH^-])^2 = K_1^2/(K_2K_w^2) = 10^{-2\cdot6.50}/(10^{1.36}\cdot10^{-2\cdot14.00}) = 10^{13.64} = 4.4\cdot10^{13}$. [5] (2)	

2. Place a checkmark at the correct answer

The equilibrium will	shift to left	shift to right	not shift
a) [1]		☑	
b) [1]	☑		
c) [1]		☑	
d) [2]		☑	

calculations:

a) and b) the answer is self-evident

c) $BaCl_2$ shifts the equilibrium to the right due to the binding of chromate ion into a poorly soluble compound

$Ba^{2+} + CrO_4^{2-} = BaCrO_4$

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:

a) $CrO_4^{2-} + H_2O = HCrO_4^- + OH^-$ $K = 3.16\cdot10^{-8}$ (*)

$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}] \approx [CrO_4^{2-}]$,

$[HCrO_4^-] \approx [OH^-]$ (**)

$[OH^-]^2/c_{Cr} = K$, $[OH^-] = \sqrt{Kc_{Cr}} = \sqrt{3.16\cdot10^{-8}\cdot0.01} = 1.78\cdot10^{-5}$

$[H^+] = 5.65\cdot10^{-10}$, pH = 9.25

[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)

$Cr_2O_7^{2-} + H_2O = 2HCrO_4^-$ $K = 1/K_2 = 4.37\cdot10^{-2}$

$HCrO_4^- = H^+ + CrO_4^{2-}$ $K = K_1 = 3.16\cdot10^{-7}$

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

$[HCrO_4^-] = ?$

$c_{Cr} = 2.0\cdot10^{-2}$ M (**) $= [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}] \approx [HCrO_4^-] + 2[Cr_2O_7^{2-}]$ (***)

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

$x = (-1+\sqrt{1+8K_2c_{Cr}})/4K_2 = (-1+\sqrt{1+8\cdot22.9\cdot0.02})/4\cdot22.9 = 1.27\cdot10^{-2}\,M$ (****)

hence $[H^+] = (3.16\cdot10^{-7}\cdot1.27\cdot10^{-2})^{1/2} = 6.33\cdot10^{-5}$; 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 $c_{Cr} = 2\cdot0.010 = 0.020$ M (!!)

(***) As the dissociation constant of $HCrO_4^-$ is very small, the assumption that $[CrO_4^{2-}]$ can be neglected is fair. pH << 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 << $pK_1 = 6.50$. Therefore, the assumption (***) is indeed fair.

c)
In 0.10 M CH_3COOH $[H^+] = (K_ac)^{1/2/}$ (*) $= (1.8\cdot10^{-5}\cdot0.10)^{1/2} = 1.34\cdot10^{-3}$
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 $K_2Cr_2O_7$ on pH can be safely neglected.

4. Equilibrium concentrations

a)	$3.0\cdot10^{-6}$ [3] (1, 11)
b)	$3.7\cdot10^{-3}$ [3] (1, 11)

calculations:
Tho different methods can be used.

Method 1.

a)
$[HCrO_4^-] = 1.3\cdot10^{-2}$ (*)
$[CrO_4^{2-}] = K_1[HCrO_4^-]/[H^+] = 3.16\cdot10^{-7}\cdot1.3\cdot10^{-2}/1.34\cdot10^{-3} = 3.0\cdot10^{-6}$ M
[10] (2, 12)

b)
$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}]$
$[Cr_2O_7^{2-}] = ½(c_{Cr} - [CrO_4^{2-}] - [HCrO_4^-]) = ½(2.0\cdot10^{-2} - 3.0\cdot10^{-6} - 1.3\cdot10^{-2}) = 3.7\cdot10^{-3}$ M
or otherwise
$[Cr_2O_7^{2-}] = K_2[HCrO_4^-]^2 = 22.9\cdot(1.3\cdot10^{-2})^2 = 3.9\cdot10^{-3}$ M
[10] (2, 12)
comments:
(*) from the calculation of $[HCrO_4^-]$ (cf. 3b) it is evident that if pH << pK, $[HCrO_4^-]$ is independent on pH. In our case pH = 2.87 is indeed << pK = 6.50, and therefore this value of $[HCrO_4^-]$ is equal to that obtained in 3b.

Method 2

a)
$[CrO_4^{2-}] = x$; $[HCrO_4^-] = x[H^+]/K_1$
$[Cr_2O_7^{2-}] = K_2[HCrO_4^-] = x^2K_2[H^+]^2/K_1^2$
$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}] = 2K_2\,[H^+]^2/K_1^2x^2 + (1 + [H^+]/K_1)x$
$K_1 = 3.16\cdot10^{-7}$; $K_2 = 22.9$; $[H^+] = 1.34\cdot10^{-3}$
$8.24\cdot10^8x^2 + 4.24\cdot10^3x - 2.0\cdot10^{-2} = 0$
$x = 3.0\cdot10^{-6}$ M
[10] (2, 12)

b)

$[Cr_2O_7^{2-}] = K_2[HCrO_4^-] = K_2\,[H^+]^2/\,K_1^2[CrO_4^{2-}]^2 = 4.12\cdot10^8\cdot(3.0\cdot10^{-6})^2 = 3.7\cdot10^{-3}$ 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 $K \le 0$ [0]
If $K > 1$
[0.5]

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

(5) If $pH < 0$ or $pH > 14$ [0]
If $0 \le pH < 7$ [0.5]

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

(7) If $pH < 0$ or $pH > 14$ [0]
If $7 < pH \le 14$ [0.5]

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

i) correct expression $[H^+] = \sqrt{K_1[HCrO_4^-]}$ [5]

ii) correct value c(Cr) = $2.0\cdot10^{-2}$ M (and not $1.0\cdot10^{-2}$ M) [5]

iii) correctly written full square equation for the calculation of $[HCrO_4^-]$
[10]

iv) reduced square equation used [5]

v) chemically meaningless assumptions (as e.g. $[HCrO_4^-] \approx c_{Cr}$ etc.) [0]

(9) If pH < 0 or pH ≥ 7 [0]
If pH ≤ 2 [1]

(10) Attempts to treat the effect of $Cr_2O_7^{2-}$ 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 CH_3COOH and $K_2Cr_2O_7$ solutions) [5]
Neglect of the contribution of CH_3COOH into pH value [0]

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

(12) [10] points are given to the correct calculation performed by any method. If the
calculation uses the material balance ($c_{Cr} = 2[Cr_2O_7^{2-}] + [CrO_4^{2-}] + [HCrO_4^-]$) which is written wrongly, e.g. as $c_{Cr} = [Cr_2O_7^{2-}] + [CrO_4^{2-}] + [HCrO_4^-]$ [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 $FeSO_4$ and $Fe_2(SO_4)_3$, and aqueous solution II contains a mixture of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. The concentrations of iron-containing species satisfy the relations $[Fe^{2+}]_I = [Fe(CN)_6^{4-}]_{II}$ and $[Fe^{3+}]_I = [Fe(CN)_6^{3-}]_{II}$. 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 $Fe(CN)_6^{4-}$, $Fe^{3+}\cdot aq$, $Fe^{2+}\cdot aq$, do not absorb light at 420 nm. Molar absorptivity $\varepsilon(Fe(CN)_6^{3-})$=1100 L/mol·cm at this wavelength. Standard redox potential for Fe^{3+}/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.

1. Write Nernst's equations for redox systems of

a) the solution I

b) the solution II (in the solution the presence of any forms except cyano-complexes should be ignored)

2. What is the units of pre-logarithm factor in the Nernst's equation?

3. Calculate the ratio of the stability constants $\beta\{Fe(CN)_6^{3-}\}/\beta\{Fe(CN)_6^{4-}\}$

4. What is the absolute range of variation for the following physical magnitudes

a) transmittance *T*; %

b) absorbance *A*.

5. Draw a schematic view of plots of concentration dependencies satisfying Bouger-Lambert-Beer law for

a) absorbance *A*;

b) transmittance *T*; %

c) molar absorptivity ε.

6. Calculate the concentrations of

a) Fe^{3+} in solution I;

b) Fe^{2+} in solution I.

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Personal code ______________________________

Team ______________________________

The Solution Report Form

1. Nernst’s equations

a)	
b)	

2.

The units of pre-logarithm factor	

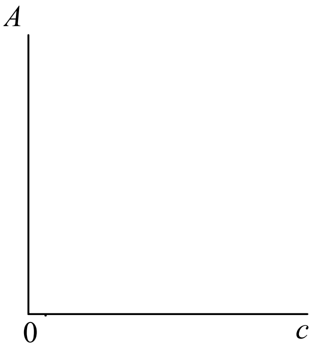
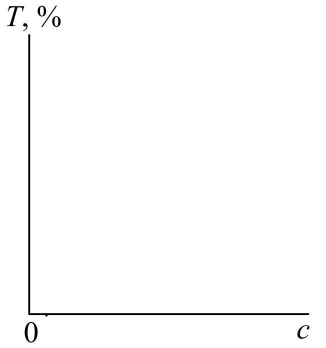
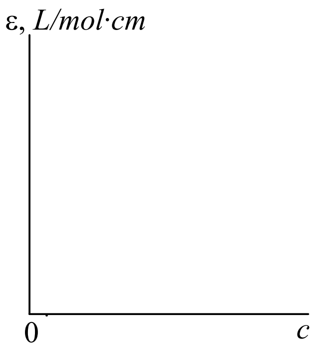
3.

The ratio of stability constants $\beta\{Fe(CN)_6^{3-}\}/\beta\{Fe(CN)_6^{4-}\}$ 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.

a)	b)	c)
		

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

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

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

1. Nernst's equations

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

Penalty points:

Equation a)

i) No penalty is imposed if Nernst's equation was written with E° instead of $E°(Fe^{3+}/Fe^{2+})$ or RT/nF ln… instead of 0.0590 log…

ii) Penalty of [-0.5] – for writing $\log[Fe^{2+}]/[Fe^{3+}]$ instead of $\log[Fe^{3+}]/[Fe^{2+}]$

Equation b)

i) no penalty is imposed if Nernst equation was written with E° instead of $E°(Fe(CN)_6^{3-}/Fe(CN)_6^{4-})$ or RT/nF·ln… instead of 0.0590·log…

ii) Penalty of [-0.5] - for writing $\log[Fe(CN)_6^{4-}]/[Fe(CN)_6^{3-}]$ instead of $\log[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$;
$\log[Fe^{3+}]/[Fe^{2+}]$ or $\log[Fe^{2+}]/[Fe^{3+}]$ instead of $\log[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$.

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 $\beta\{Fe(CN)_6^{3-}\}/\beta\{Fe(CN)_6^{4-}\}$ write only the final result of calculations in the blank cell →	$8.90 \cdot 10^6$ [4]

Calculations:

$$E_{II} = E°(Fe(CN)_6^{3-} / Fe(CN)_6^{4-}) + 0.0590 lg[Fe(CN)_6^{3-} / Fe(CN)_6^{4-}] =$$

$$E°(Fe^{3+} / Fe^{2+}) + 0.0590 lg(\beta_1 / \beta_2) + 0.0590 lg([CN^-]^6 / [CN^-]^6) +$$

$$+ 0.0590 lg[Fe(CN)_6^{3-} / Fe(CN)_6^{4-}] = 0.242$$

(where β_1 and β_2 are stability constants for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$, respectively.)

$[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}] = [Fe^{3+}]/[Fe^{2+}]$, therefore

$\Delta E = E_{II} - E_I = 0.0590 \cdot \log(\beta_1/\beta_2)$, 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.

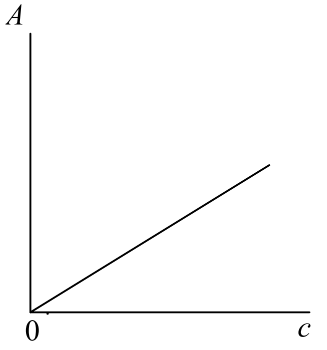
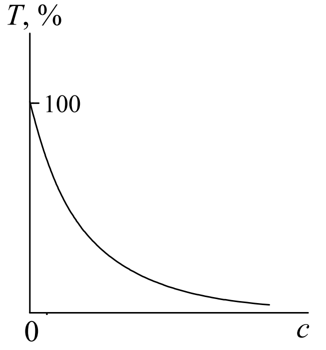
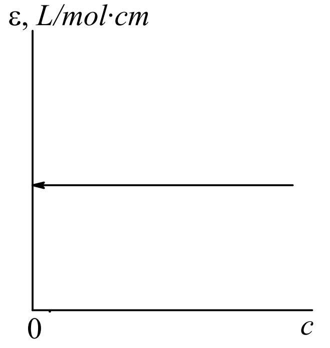
4. The ranges of variation:

	from	to
a)	0	100 [0.5]
b)	0	∞ [0.5]

Penalty points:

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

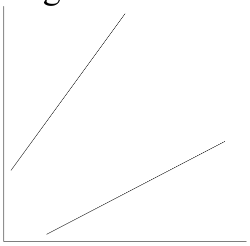
5. Draw a sketch of plot using the axes given below.

a)	b)	c)
		
[1]	[1]	[1]

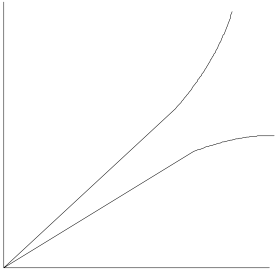
Penalty points:

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



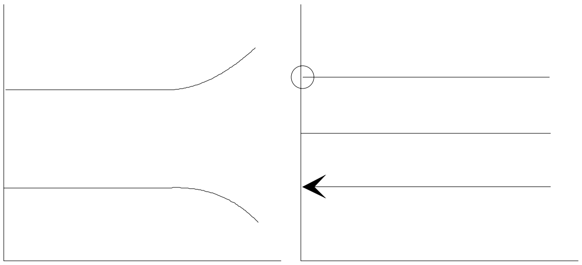
b) [-1] if any growing function of a function crossing the concentration axis is drawn

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

Calculations

a) Using Bouger-Lambert-Beer law

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

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

b) using Nernst's equation

$E=E°(Fe^{3+}/Fe^{2+}) + 0.0590 \cdot \log[Fe^{3+}]_I/[Fe^{2+}]_I =$

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

hence,

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

$[Fe^{2+}]_I = 1.76 \cdot 10^{-3}/9.62 \cdot 10^{-3} = 0.183$ 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 a 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 zink 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 peroxoacids 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 peroxoacetic 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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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 <u>not</u> required and writing them shall <u>not</u> 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
☐ YES, the molecule is optically active ☐ NO the molecule is not optically active	☐ YES, the molecule is optically active ☐ NO the molecule is not optically active	☐ YES, the molecule is optically active ☐ NO the molecule is not optically active

Answers and points

(points are given in shaded square brackets)

Grand total - [31]

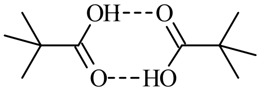
1.

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.

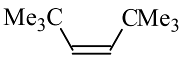
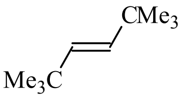
Molar weight in vapour phase is 9.1·22.4 = 204 which is close to twice the molar weight of $(CH_3)_3CCOOH$. Possibly, as other simple fat acids, this acid is also dimerized in vapours.

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

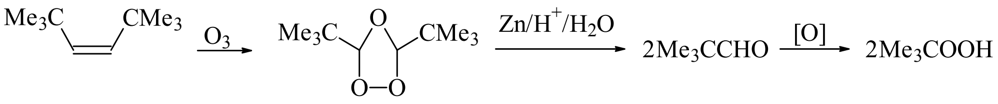
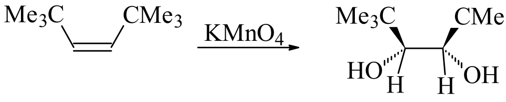
3.

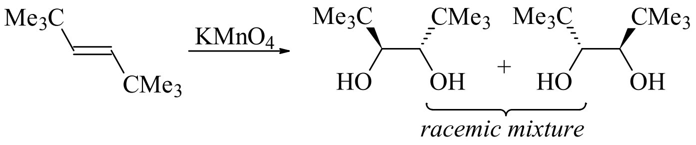
Compound C	$(CH_3)_3CCHO$ [1]

4. total [4]

A	B
 [2]	 [2]

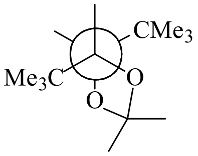
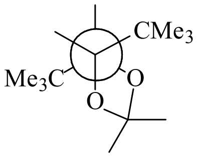
5. Total - [5]

$A \longrightarrow C \longrightarrow D$
 [1] [1] Pints are given for drawing the reaction of ozonolyzis: A -> aldehyde. Drawing ozonide is not necessary and is nor awarded nor penalized.
$A \longrightarrow F$
 [1]

B ⟶ G1 + G2
 [2]

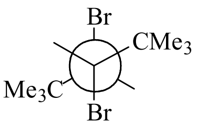
If reactions are written, but the stereochemistry is not indicated in any understandable form, or indicated wrong - [0.25]

6. Total [4]

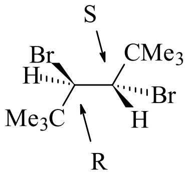
H1	H2
 [2]	 [2]

7. Total [6]

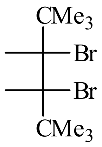
Non-polar bromination product (either of three types of structures may be given)

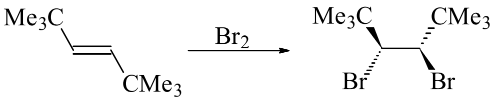


or



or





[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]

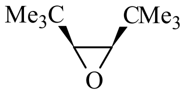
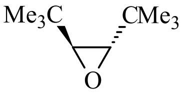
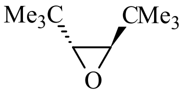
Both centers are R or S [4]

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]

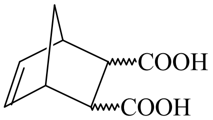
8. Total - [7]

K	L1	L2

 [2]	 [1]	 [1]
☐ YES, the molecule is optically active ☑ NO the molecule is not optically active [1]	☑ YES, the molecule is optically active ☐ NO the molecule is not optically active [1]	☑ YES, the molecule is optically active ☐ NO the molecule is not optically active [1]

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**)



(no stereochemistry is shown)

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_1** same to that is formed in the reaction of **X** with NaOH. The resulting solution of **X_1** is treated by I_2 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. 1. Mark by asterisks (*) the asymmetric carbon atoms in the structure of 5-norbornene-2,3-dicarboxylic acids.
2. 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. 3. Write the reactions of NaOH with a stereoisomer of **X** and a stereoisomer of **Y**.
4. 4. Calculate the molar mass of compound **A**. Write the reactions leading from **X_1** to **A**.
5. 5. Write the reaction of the formation of **C** from **A** and the reaction of **C** with water.
6. 6. Draw the stereochemical formula of compound **X** which satisfies all of the data given in the problem.
7. 7. Write the reactions leading from **B** to **A**.
8. 8. Are the compounds **A** and **B** diastereomers?

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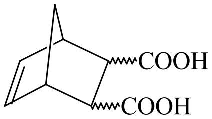
Personal code ______________________________

Team ______________________________

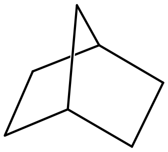
The Solution Report Form

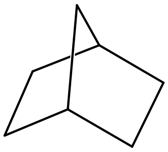
1. Mark the asymmetric carbon atoms on the structure below



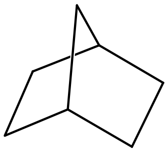
2. Fill in left column with the structures of stereoisomers of X, and the right column with the corresponding structures of dehydration products (when such structure does not exist write a minus sign there).

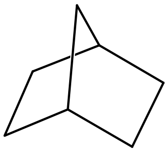
3. The reaction of a stereoisomer of **X** with NaOH





The reaction of a stereoisomer of **Y** with NaOH

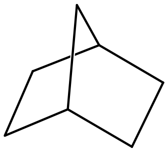


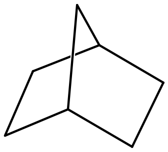


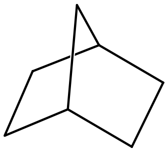
4.

The molar mass of **A, g/mol**		Calculations:

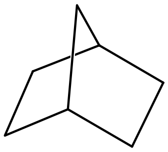
The reactions leading from $\mathbf{X_1}$ to **A**

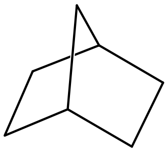




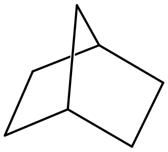


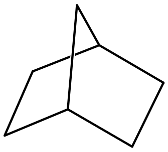
5. The transformation of **A** to **C**



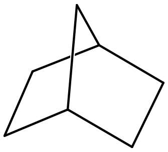


The reaction of **C** with water

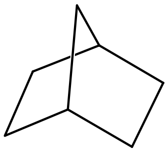


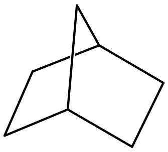


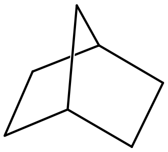
6.

The structure of compound **X**	

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







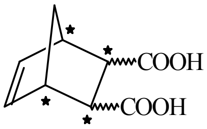
8. Place a checkmark into the box near the correct statement

☐ Yes, **A** and **B** are diastereomers

☐ No, **A** and **B** are not diastereomers

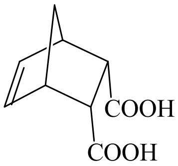
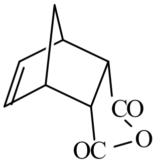
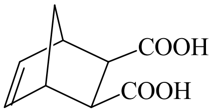
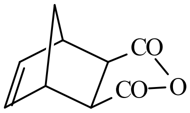
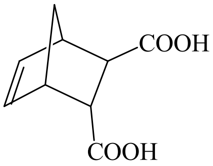
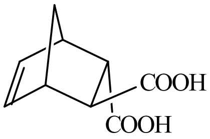
Answers and points (points are given in shaded square brackets)

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



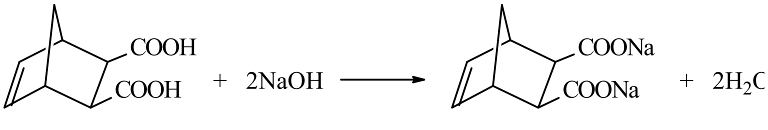
2. Total [6]

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.

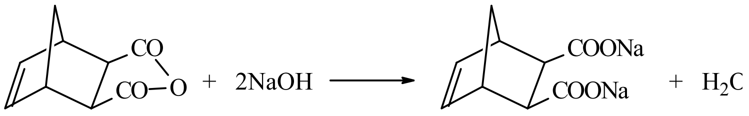
	
	
	—
	—

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

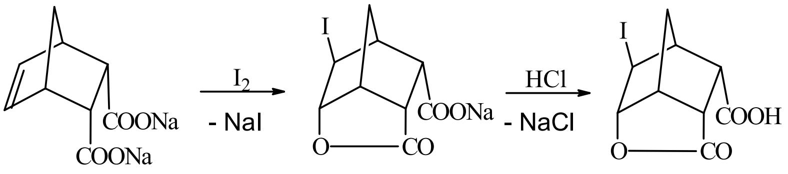


4. Total [7]

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.

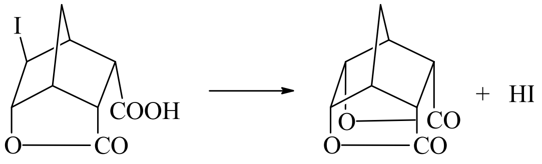
The reactions leading from X_1 to A - [5] points



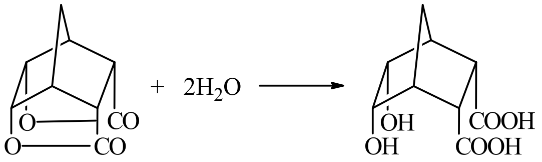
[4] [1]

5. Total [4]

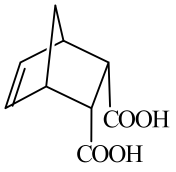
The transformation of A to C - [2] points



The reaction of C with water - [2] points

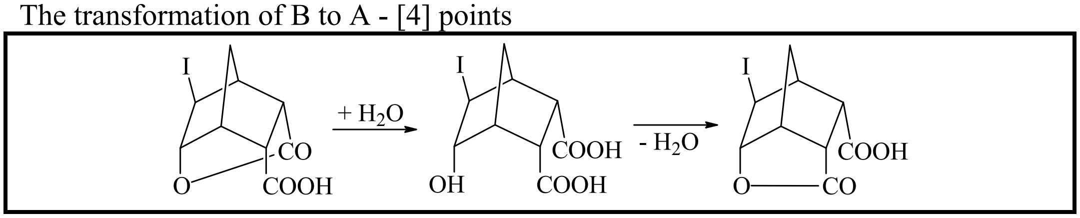


6. Total [4].

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