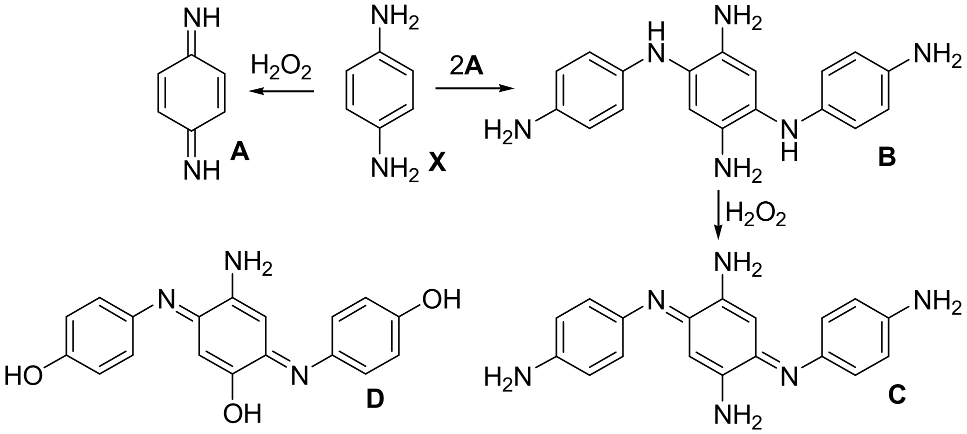
SECTION I. ORGANIC CHEMISTRY

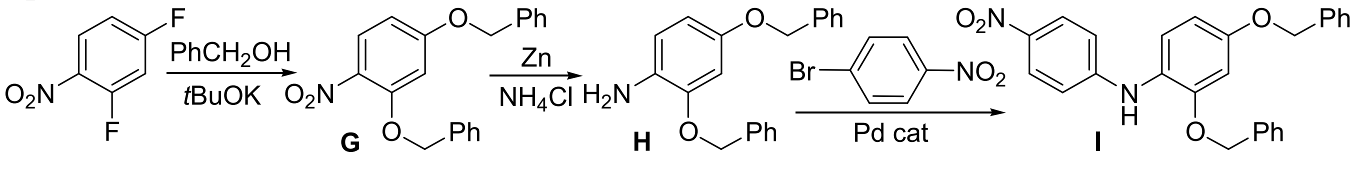
Problem 1 (authors Avramenko N.N., Gorlova A.A.)

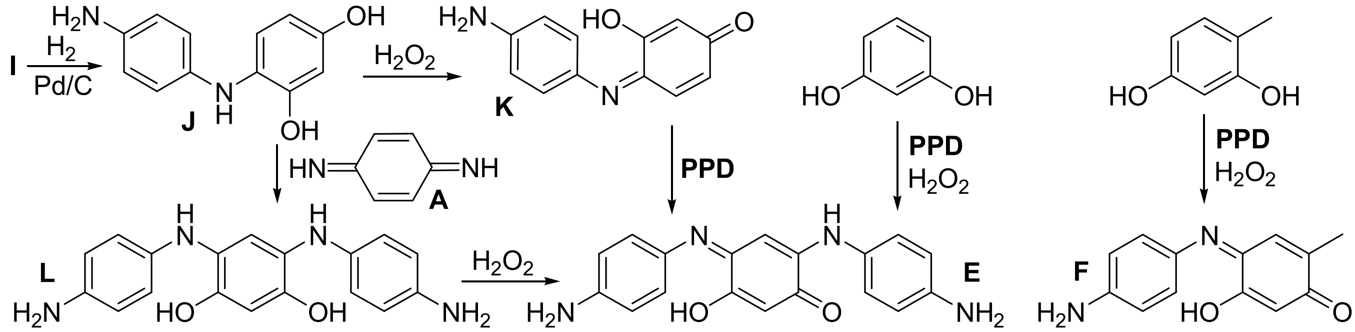
1. Based on the problem statement, it is easy to guess that compound **A** is quinone diimine. You can also come to this logically. Based on the molecular formula, the final compound **C** differs from the starting three molecules by 6 hydrogen atoms (totally 6-electron oxidation). This means that at the first stage, two-electron oxidation occurs and the molecular formula of compound **A** is $C_6H_6N_2$. The only possible compound with such formula is quinone diimine. The next step is aromatic electrophilic substitution in para-aminoaniline. As the final product contains the center of symmetry, the substitution occurs in the 2nd and 5th positions. Compound **C** is a product of two-electron oxidation. Among all possible tautomers, only given tautomer contains two types of exchangeable hydrogen atoms. Structure **D** is an analog of structure **C**. The main thing to take into account is that the nitrogen atom is electrophilic (each structure is 0.75 points, 3 points overall).



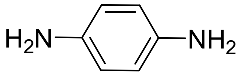
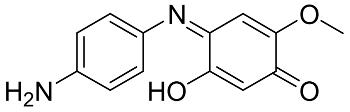
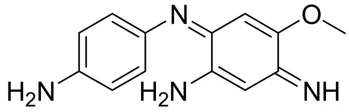
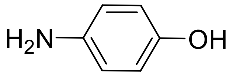
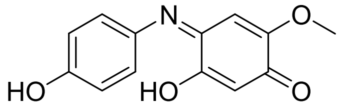
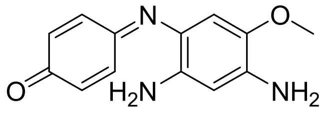
2. The structure of compound **E** is easier to establish if the structure of all compounds in the scheme for the synthesis of compound **J** is determined. The initial compound contains two active fluorine atoms, which are converted into two benzyloxy fragments (compound **G**). Then the nitro group is reduced to give **H**. The next step is Buchwald–Hartwig amination and bisarylamine **I** is formed. At the next stage of catalytic hydrogenation, the nitro group is reduced with simultaneous removal of two benzyl protecting groups from oxygen atoms. The structure of the **J** connection can be checked with molecular formula. Further transformation of **J** into **E** can occur in two ways. In the first case, an electrophilic attack of quinone diimine **A** on compound **J** occurs with the formation of compound **L** (the so-called *leuco-base*), which upon oxidation gives the dye **E**. Alternatively, **J** can be oxidized to quinone imine **K**, which adds the PPD molecule and gives **L**.

After determination of **E** we can understand at which positions substitution occurs and make conclusion about the structure of **F** (one position is blocked by a methyl group). The correctness of the assumption can be verified by molecular formula (each structure is 1 point, 8 points overall).





3,4. It will not be difficult to write the required structures after the solving of task 2 (pay attention that keto-quinoine tautomer is more stable than imino-quinone). First, you need to identify the complementary colors that correspond to the energy that is being absorbed. Thus, one group has colors – purple, green; the second is purple and orange. As you can see, longer wavelengths correspond to the second group. It is known that amino and imino groups contribute to a greater bathochromic shift than the corresponding oxygen-containing groups. Then derivatives of para-aminoaniline absorb purple and orange light, and paraaminophenol – purple and green. For similar reasons, it is possible to determine the colors within each group. A larger number of amino groups in the starting compound promotes a larger bathochromic shift. The structures of the compounds and their colors are shown below (each structure – 0.5 points, correct determination of colors in each series – 1 point, 4 points overall).

	1	**2**
	 Yellow	 Blue
	 Yellow	 Red

References

1. Robbins, Clarence R. (2012). *Chemical and Physical Behavior of Human Hair || Dyeing Human Hair., 10.1007/978-3-642-25611-0(Chapter 7), 445–488.* doi:10.1007/978-3-642-25611-0_7

2. Morel, Olivier J. X.; Christie, Robert M. (2011). *Current Trends in the Chemistry of Permanent Hair Dyeing. , 111(4), 2537–2561.* doi:10.1021/cr1000145

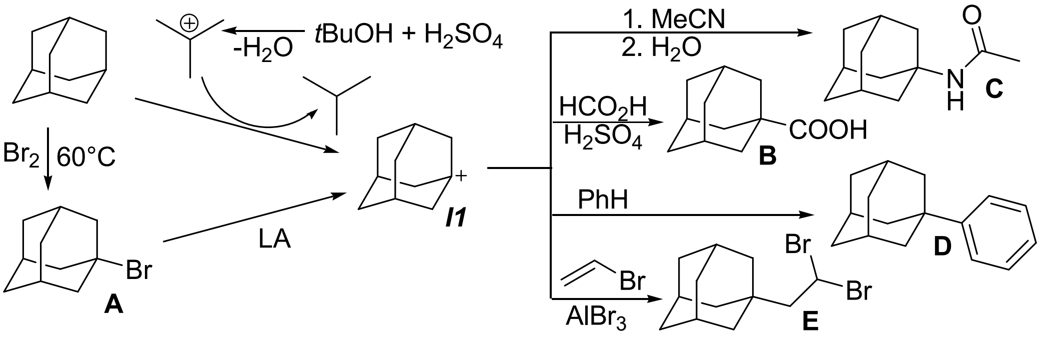
3. Vel Leitner, N. Karpel; Berger, P.; Legube, B. (2002). *Oxidation of Amino Groups by Hydroxyl Radicals in Relation to the Oxidation Degree of the α-Carbon. Environmental Science & Technology, 36(14), 3083–3089.* doi:10.1021/es0101173

4. Bailey, Aaron D.; Murphy, Bryan P.; Guan, Hairong (2016). *Mechanistic Insights into Oxidative Oligomerization of p-Phenylenediamine and Resorcinol. The Journal of Physical Chemistry A, (), acs.jpca.6b08571–.* doi:10.1021/acs.jpca.6b08571

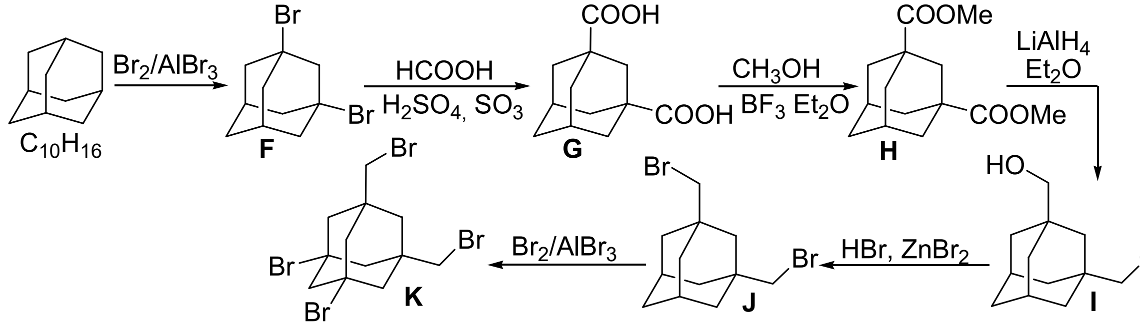
5. Lerner, L. (2011). *Identity of a Purple Dye Formed by Peroxidic Oxidation of p-Aminophenol at Low pH. The Journal of Physical Chemistry A, 115(35), 9901–9910.* doi:10.1021/jp2045806

Problem 2 (author Kandaskalov D.V.)

1. Calculate the number of bromine atoms that “entered” in the adamantane during bromination $C_{10}H_{16–x}Br_x$: $12 \cdot 10 / (12 \cdot 10 + 16 – x + 80x) = 0.5583$, $x = 1$.
So, compound **A** is monobromadamantane. Theoretically, there are two variants, however, based on the symmetry **A** (third-order axis) given in the condition, it is unambiguously determined that **A** is 1-bromadamantane. A further solution to this problem is to determine the intermediate **I1**. Usually, the treatment of bromoderivatives with Lewis acids proceeds through the formation of carbocations. This hypothesis is also confirmed by the fact that the same particle is formed from adamantane in *t*BuOH – H_2SO_4. In this system, *tert*-butyl carbocation is formed due to dehydration and reacts with adamantane to transfer the hydride ion and form isobutane. So ***I1*** is the corresponding carbocation. Then **D** and **E** are easily decoded (see scheme below). Compounds **B** and **C** can cause complexity. To decipher **B** (empirical formula $C_{11}H_{16}O_2$) follows the reaction of the carbocation with the formate anion with the formation of the corresponding formate, the carbon content of which corresponds to the condition. However, formates are readily hydrolyzed. So, **B** – isomer of the corresponding formate $C_{11}H_{16}O_2$. There is only one variant based on adamantane skeleton: 1-adamantane carboxylic acid. Its formation from adamantane occurs *via* adamantyl cation, which subsequently undergoes carbonylation with carbon monoxide generated *in situ* by the interaction of formic and sulfuric acids. Compound **C** is the appropriate acylated 1-adamantyl amine. Its formation occurs through the attack of the cation on the acetonitrile molecule, followed by hydrolysis (1 point for each structure, 6 points in total).

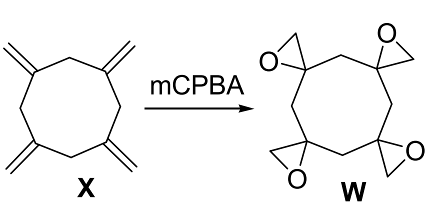


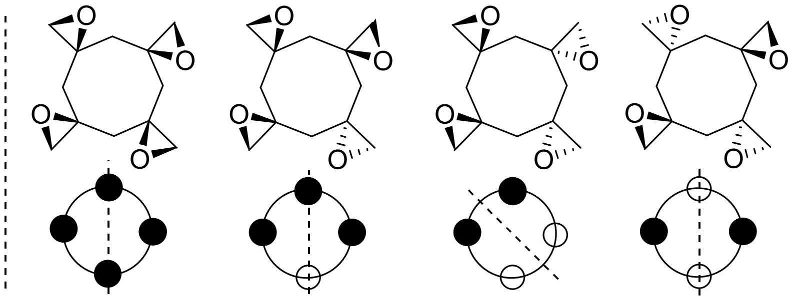
2. The synthesis of **X** starts with the reaction of bromination of adamantane to obtain **F**. Based on the carbon content, we calculate the number of bromine atoms that were introduced into the molecule $C_{10}H_{16–x}Br_x$: $12 \cdot 10 / (12 \cdot 10 + 16 – x + 80x) = 0.4085$, $x = 2$. Despite the fact that there are several dibromo derivatives, only one compound will be formed, where bromine replaces tertiary carbon atoms. Further, bromine atoms are replaced by carboxyl groups (compound **G**). This conclusion can be reached after solving the first block of the problem. Even without knowing the reaction of introduction of the carboxyl function it can be guessed, since then there is the classic process of formation of the ester **H** and its reduction to alcohol **I**. Also it should follow from the fact that this is the stage where molecule could obtain additional 2 carbon atoms. Compound **I** then nucleophilically gives matching dibromo derivative **J**. Subsequent bromination leads to the introduction of 2 bromine atoms to the tertiary carbon atoms affording compound **K**. It matches to the carbon content in it and the symmetry is the same as in **F**.



The next transformation **K** → **X** is rather nontrivial. It will be optimal to decode compound **X** from its spectral data. The fact that **X** has only two singlets in the ^{1}H NMR spectrum with an integrated intensity ratio of 1 : 1 indicates its high symmetry. From empirical formula $C_{12}H_{16}$ it follows that each singlet contains 8 equivalent protons. Therefore **X** has an axis of symmetry of the 8th order or cuban symmetry (in each group, 1 proton). But, if the protons are two in group, this is the axis of symmetry of the 4th order or the symmetry of the tetrahedron. The second case is impossible due to carbon atom count. But in first case the 12 carbon atoms could de divided in 3 group with 4 carbons in each. Considering that this is a monocyclic compound, we unambiguously get its structure (see figure). Really compound **X** does not have the axis of symmetry of the 4th order due to 3D shape nature. But the conformational lability of the compound leads to this symmetry from spectral point of view. Its oxidation gives the tetraepoxide **W** (1 point for each structure (**C** – **W**), 8 points in total).

3. Theoretically; the formation of 4 diastereomers of substance **W** is possible. They are shown in the figure. For simplicity, you can imagine that the **X** molecule is flat and lies in the plane of the sheet. During epoxidation the oxygen atom could be attached from front side (marked by black circle) or from back side (marked by transparent circle). So, topologically only 4 options are possible. In each case, there are elements of symmetry in the molecule that are incompatible with chirality. In the figure, the dashed line indicates the planes of symmetry (correct number of diastereomers – 0.5 points, number of chiral – 0.5 points).





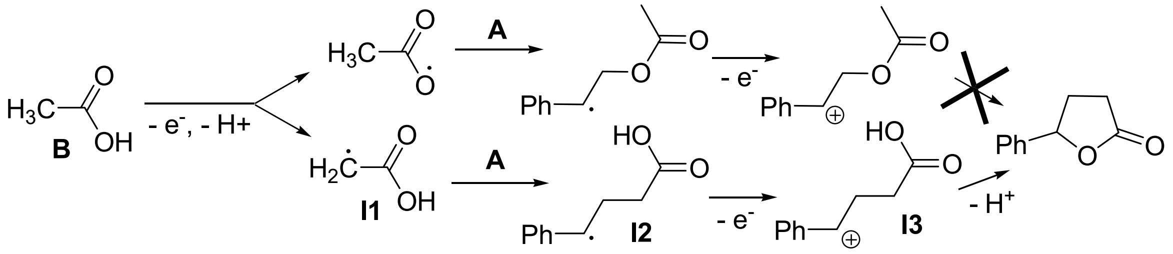
References

1. Averina, 1. Fort, Raymond C.; Schleyer, Paul von R. (1964). Adamantane: Consequences of the Diamondoid Structure. Chemical Reviews, 64(3), 277–300. doi:10.1021/cr60229a004

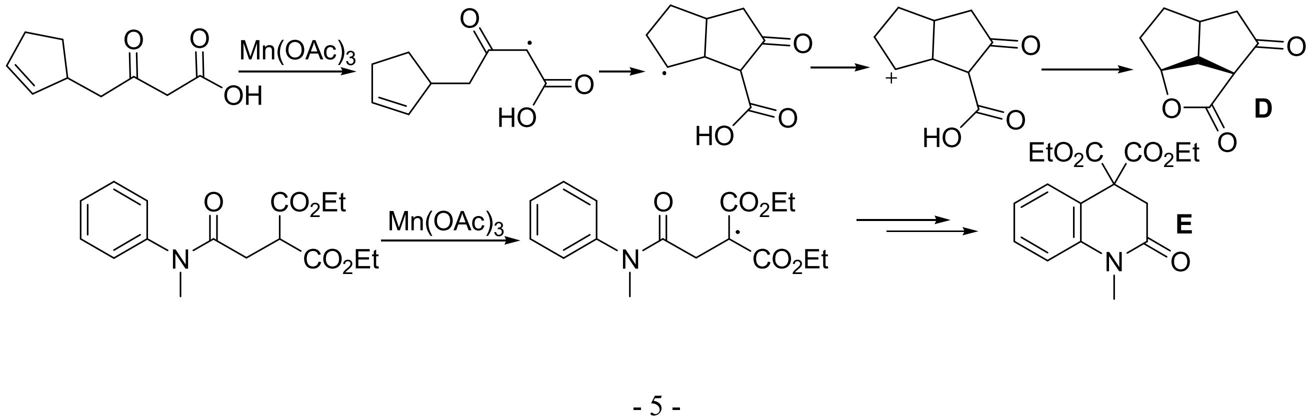
2. Elena B.; Sedenkova, Kseniya N.; Bakhtin, Stanislav G.; Grishin, Yuri K.; Kutateladze, Andrei G.; Roznyatovsky, Vitaly A.; Rybakov, Victor B.; Butov, Gennady M.; Kuznetsova, Tamara S.; Zefirov, Nikolay S. (2014). *symm-Tetramethylenecyclooctane: En Route to Poly-spirocycles. The Journal of Organic Chemistry, 79(17), 8163–8170.* doi:10.1021/jo501380y

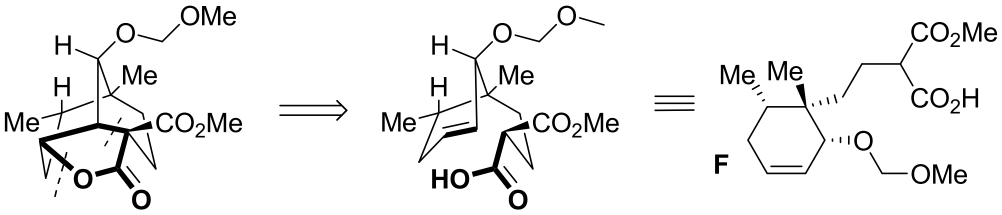
Problem 3 (authors Bahtin S.G., Volochnyuk D.M.)

1,2. From the given dat, we can calculate hydrocarbon **A** composition ($\nu_C : \nu_H =$ $= (92.29/12) : (7.71/1) = 1 : 1$). So the empirical formula of the hydrocarbon is C_xH_x. Based on this, it can be assumed that this can be C_2H_2 (acetylene), C_6H_6 (benzene) or C_8H_8 (styrene). Benzene is not fit, since it is not oxidized by $KMnO_4$. Acetylene is also discarded, since it is oxidized by $KMnO_4$ to CO_2 in an acidic environment. So the substance **A** is styrene, which is oxidized to benzoic acid (PhCOOH), which can be confirmed by calculation ($\nu_C : \nu_H : \nu_O = (68.85/12) : (4.92/1) : (26.23/16) = 7 : 6 : 2$). For the finding of the structure **B** we need to find the fragment which come to molecule during the reaction. This is –CH_2COO–. Taking into account that the reaction occurs as double SET process which leads to acetic acid (compound **B**). **I1** is formed from acetic acid due to the one electron oxidation and detachment of H^+. So **I1** is a radical. Then two structures can be represented for it. The stage of formation of intermediate **I2**, according to the condition, is the addition of the formed radical at the C=C-bond of styrene. This addition should proceed with the formation of a radical in which the radical center is concentrated on the benzyl carbon atom, since this ensures its conjugation with the benzene ring. Removing of an electron from radical will lead to the formation of the corresponding carbocation. Moreover, only one of them will be able to eliminate H^+ with the formation of the target lactone (1 point for each structure (**A**, **B**, **C**), 3 points in total; 0.5 point for each intermediate (**I1**, **I2**, и **I3**) 1.5 points in total).

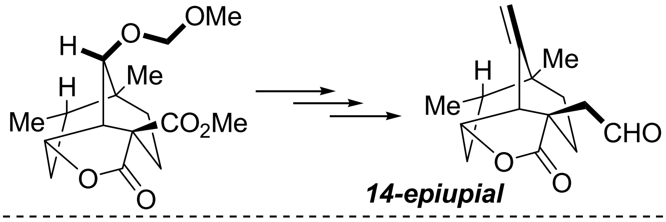


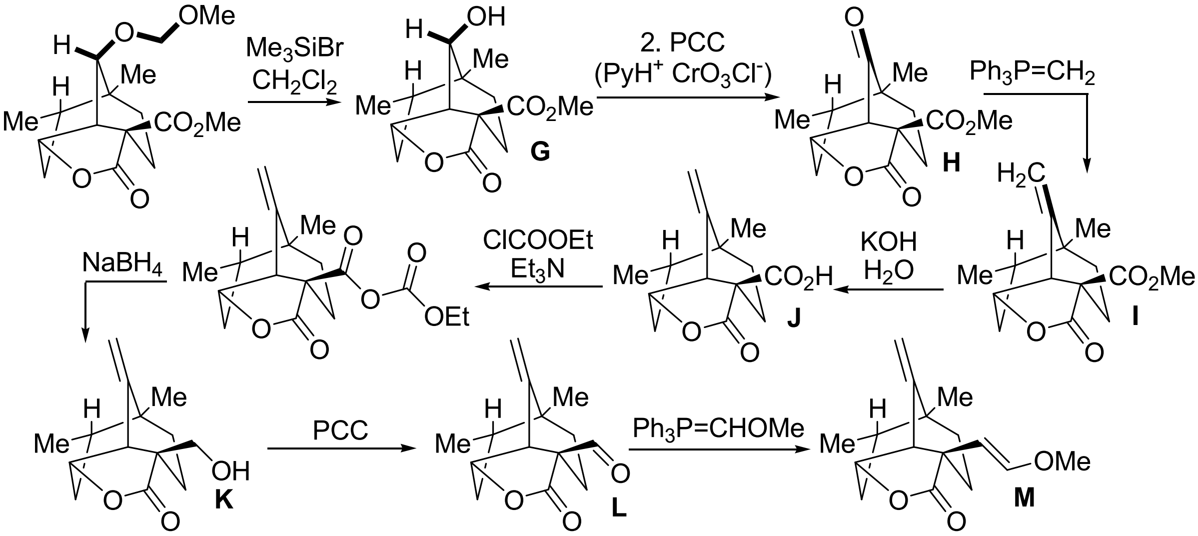
To decipher compounds **D** and **E**, it is also necessary to use mechanistic logic. In the case of derivatives of β-dicarbonyl compounds, the radical is generated between two carbonyl groups (stabilization by double conjugation). These reactions represent the generation of the corresponding radical in the α-position to the carboxyl group, followed by its transformations. In the case of compounds **D** attachment occurs at the double bond with the closure of the lactone ring. In the case of compound **E**, the corresponding radical attacks the aromatic nucleus by analogy with the reaction for the formation of **P2P**. To decipher compound **F**, in addition to the knowledge gained in the previous paragraphs, a retrosynthetic approach must be applied. One should recognize the lactone fragment and bonds those were created during the reaction. After that, the structure of **F** becomes obvious.





The subsequent decoding of the scheme requires a careful analysis of the structure at the beginning of the sequence of transformations and the final one. Here you will notice that there are only two changes occurred. In the first case, the fragment $C(H)OCH_2OMe$ turned into C = CH_2. In the second – the fragment CO_2Me turned into CH_2CHO.





Further, the problem is reduced to knowledge about the transformation of functional groups in organic compounds. **Obtaining G**. Removing of MOM protection from OH function. **The step G → H**. Oxidation of alcohol to the corresponding ketone. **The step H → I**. Wittig olefination. **Step I → J**. Hydrolysis of methyl ester. **The step J → K**. Activation of carboxyl function via mixed anhydride with followed reduction to alcohol with $NaBH_4$. **The step K → L**. Oxidation of alcohol to aldehyde. **The step L → M**. Wittig reaction affords vinyl ester which is further hydrolysed to upial (each structure (**D**, **E**, **G** – **M**) is 1 point, resulting 9 points in total, 1.5 points – structure **F**).

References

1. Melikyan, Gagik G. (2004). *Organic Reactions || Carbon-Carbon Bond-Forming Reactions Promoted by Trivalent Manganese, 10.1002/0471264180.* doi:10.1002/0471264180.or049.03

2. Mondal, Manoj; Bora, Utpal (2013*) RSC Advances,* 3(41), 18716. doi:10.1039/C3RA42480D

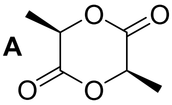
3. Corey, E. J.; Kang, Myung Chol (1984). *J. Am. Chem. Soc. 106(18), 5384.* doi:10.1021/ja00330a076

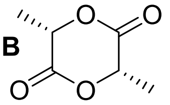
4. Paquette, L. A., Schaefer, A. G., & Springer, J. P. (1987). *Tetrahedron, 43(23), 5567.* doi:10.1016/s0040-4020(01)87738-3

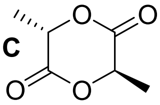
SECTION II. LIFE SCIENCES AND POLYMERS

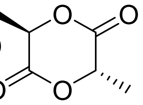
Problem 1 (authors Ilievski F., Karpushkin E.A.)

1. Two chiral carbon atoms give rise to three isomers, since **C** and **D** are identical structures (meso-forms) (0.5 point for the number of isomers and each structure, 2 points in total, 0.5 point penalty for each incorrect structure).

A


B


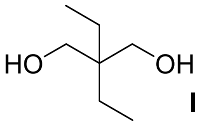
C


D


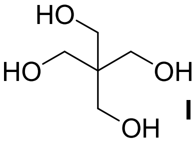
2. Homofermentative conversion of glucose produces two lactic acid molecules per a molecule of the monosaccharide: glucose + 2ADP + 2P_i → 2lactate + 2ATP

Since lactose consists of two monosaccharide units (each being prone to lactic acid fermentation), 1 mole of lactose yields 4 moles of lactic acid further affording 2 moles of lactide **M2**. Hence, 1 kg (1000 / 342.12 = 2.92 mol) of lactose can be converted into 5.85 mol of **M2** (5.85 · 144.13 = 843 g). The reactions of heterofermentative conversion (glucose + ADP + P_i → lactate + ethanol + CO_2 + ATP) and of bifidobacterial fermentation (2glucose + 5ADP + 5P_i → 3acetate + 2lactate + 5ATP) also accepted (1 point for the reaction, 1 point for calculation, 2 points in total).

3. **I2** contains less of carbon atoms and more of hydrogen atoms than **M1** ($C_6H_{10}O_2$), which means that **I2** is a saturated molecule ($C_xH_{2x+2}O_y$). From comparison with **M1** ($C_6H_{10}O_2$), $x \le 5$ and $2x + 2 \ge 12$; hence, $x = 5$. Furthermore, **I1** contains more of carbon and hydrogen atoms than **I2**, yet their masses are close. The difference in the molecular mass (4 g/mol) likely corresponds to the substitution of two O atoms in **I2** with CH_2 fragments in **I1**. Hence, **I2** ($C_5O_yH_{12}$) contains at least 3 O atoms. Since its molecular mass is less than 144 g/mol (that for **M1**), it cannot contain more than 4 O atoms. In view of these constrains and the presence of two types of carbon atoms in its structure, a feasible solution for **I2** is pentaerythritol ($C_5H_{12}O_4$). Then gross formula of **I1** is $C_7H_{16}O_2$. The structure of **I1** which satisfies the condition of four types of carbon atoms in the molecule is 2,2-diethylpropane-1,3-diol (1 point per gross formula, 1 point per structure, 4 points in total).

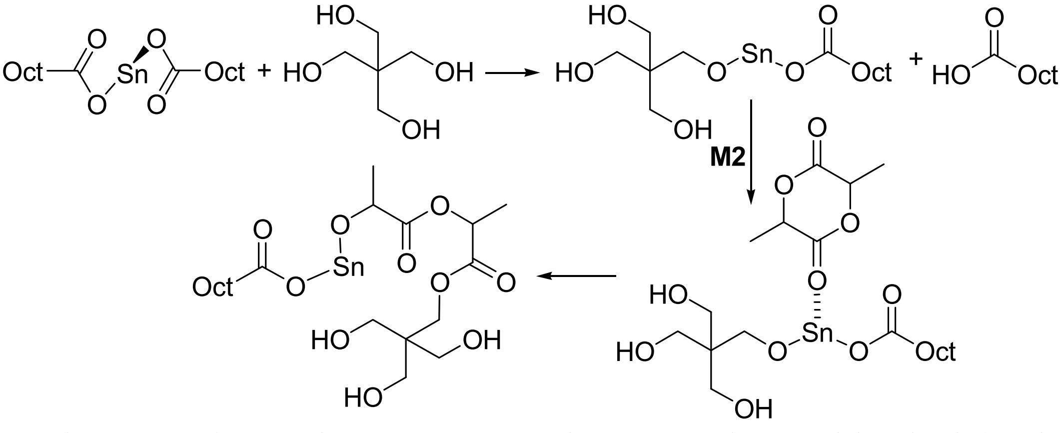


I1

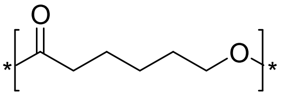


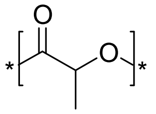
I2

Let us draw the mechanism of **M2** addition (not required but may aid in answering the following questions):



4. a, b) In the case of **M2**, the monomer and repeat units are identical (each monomer molecules produces one repeat unit). Each molecule of **M2** yields two identical repeat units:

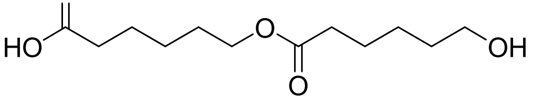

M¹

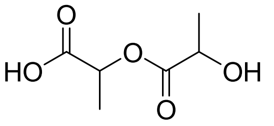

M²

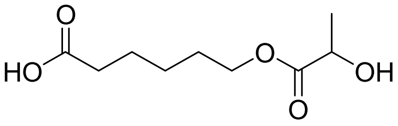
c) Each OH group in **I1** and **I2** can substitute an OctCOO unit in tin octanoate and thus give rise to a propagating chain. Hence, the macromolecules of **P1** and **P2** consist of 2 and 4, respectively, branches. It is reasonable to consider equal reactivities of OH group in the initiators, hence the length of the branches is equal. In the case of **P1**, each branch is built of $n/2$ monomer units ($n/4$ of **M1** and $n/4$ of **M2**, given the equimolar mixture and equal reactivities). Since each molecule of **M2** produces two repeat units, a branch of **P1** consists of $n/4$ repeat units $\mathbf{M^1}$ and $n/2$ repeat units $\mathbf{M^2}$. Given equal reactivities, the monomer units distribution along the polymer chains is random. However, since a pair of repeat units $\mathbf{M^2}$ is produced from a single monomer molecule, single $\mathbf{M^2}$ units cannot be separated by $\mathbf{M^1}$. Overall, a branch structure is $\mathrm{[M^{1}_{\mathit{n}/4}\text{-}\mathit{ran}\text{-}(M^{2}_{2})_{\mathit{n}/4}]}$. The branches are linked via an **I1** residue and capped by hydrogens (due to quenching of the propagating chains with HCl). Finally, **P1** = $\mathrm{H{-}[M^{1}_{\mathit{n}/4}\text{-}\mathit{ran}\text{-}(M^{2}_{2})_{\mathit{n}/4}]{-}O{-}CH_2{-}C(C_2H_5)_2{-}CH_2{-}O{-}[M^{1}_{\mathit{n}/4}\text{-}\mathit{ran}\text{-}(M^{2}_{2})_{\mathit{n}/4}]{-}H}$
Structure of **P2** is similar, yet it contains 4 branches and each branch is thus twice shorter:
P2 = $\mathrm{C\{CH_2{-}O{-}[M^{1}_{\mathit{n}/8}\text{-}\mathit{ran}\text{-}(M^{2}_{2})_{\mathit{n}/8}]{-}H\}_4}$

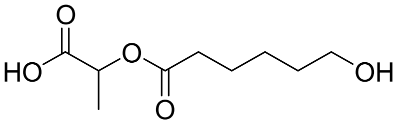
d) According to the structure, each macromolecule of **P2** contains four CH_2 groups originating from the co-initiator (8H), $4 \cdot n/8 = n/2$ repeat units $\mathbf{M^1}$ (10H each, $10 \cdot 160/2 = 800$H in total) and $4 \cdot 2 \cdot n/8 = n$ repeat units $\mathbf{M^2}$ (4H each, $4 \cdot 160 = 640$H in total). Hence, the ratio of integral values of the signals of $\mathbf{M^1}$: $\mathbf{M^2}$: **I2** is 800 : 640 : 8 = 100 : 80 : 1.
Alternative solution: since no side product is released during ring-opening polymerization, the monomer unit composition is the same as that of the monomers. At equal reactivities, a macromolecule with degree of polymerization 160 is built of 80 molecules of **M1** (800H) and 80 molecules of **M2** (640H). They are linked via an **I2** residue containing 4 methylene groups (8H). Hence, the ratio of integral values of the signals of $\mathbf{M^1}$: $\mathbf{M^2}$: **I2** is 800 : 640 : 8 = 100 : 80 : 1.

e) Cleavage of the backbone in the produced polymers occurs via hydrolysis of the ester linkages, and the dimers in question correspond to the dyads of the repeat units in the polymer structure. The repeat units (see i. 4a) are nonsymmetrical. Still, the ionic ring-opening polymerization is a regioselective process, thus no head-tail isomers are possible. Hence, four structures are possible for the dimers (note that the $\mathbf{M^1{-}M^2}$ and $\mathbf{M^2{-}M^1}$ dimers are distinguishable due to the nonsymmetrical structures):


M¹-M¹


M²-M²


M¹-M²


M²-M¹

f) Each unit of $\mathbf{M^2}$ can take one of the two chiral structures (R or S), hence 2 optical isomers are possible for each of $\mathbf{M^1{-}M^2}$ and $\mathbf{M^2{-}M^1}$ dimers, whereas 4 isomers are possible for $\mathbf{M^2{-}M^2}$ (R,R, R,S, S,R, and S,S) due to two chiral atoms in the structure. Overall, 1 + 2 + 2 + 4 = 9 optical isomers are possible for the dimers.

(0.5 point for each number of the repeat units, 0.5 point for each repeat unit, 1 point for each polymer structure, 1 point for the signal ratio, 0.25 point for each dimer structure, 1 point for the number of optical isomers, 7 points in total).

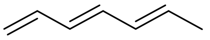
Problem 2 (author Garifullin B.N.)

1. $CH_2=C(CH_3)_2 + O_3 + (CH_3)_2S \rightarrow CH_2O + (CH_3)_2C=O + (CH_3)_2S=O$ (1 point)

2. Neutral ozonolisys of alkenes leads to carbonyl products. If an acyclic polyene enters the reaction. The minimum number of products equals three, at least one product containing two carbonyl groups by contrast to the other two monocarbonyl ones. Thus **B** – **D** are not homologs. Ozonolysis of **A** (C_5H_8) leads to glyoxal (**D**, 58 g/mol), acetaldehyde (**C**, 44 g/mol), and formaldehyde (**B**, 30 g/mol). The molar masses of the consecutive members of the homologous series starting with formaldehyde and glyoxal differ (by definition) by 14 g/mol (the value of *x*). One can suggest the hereunder unbrahched structures with due account for the limit of the molar mass of **A** (1 point for each structure, 3 points in total):

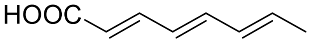
A	B	C	D
$CH_3–CH=CH–CH=CH_2$	$CH_2=O$	$CH_3–CH=O$	$O=CH–CH=O$
$CH_3–CH=CH–CH=CH–CH=CH_2$	$CH_2=O$	$CH_3–CH=O$	$O=CH–CH=O$
$CH_3–CH_2–CH=CH–CH_2–CH=CH–CH_3$	$CH_3–CH=O$	$CH_3–CH_2–CH=O$	$O=CH–CH_2–CH=O$

3. A non-equimolar mixture of organic products of neutral ozonolysis can be obtained only in the case of hepta-1,3,5-triene (1B:1C:2D). Thus (1 point):

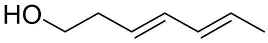


A

4. The **E** → **A** transformation can be either decarboxylation (loss of CO_2) or dehydration (loss of H_2O). Thus, one can propose two structures out of the variety of isomers (any reasonable isomers of **E1** and **E2** accepted) (1 point for each structure, 2 points in total):

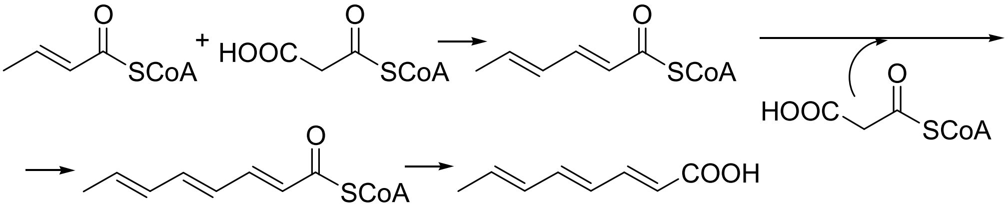


E1

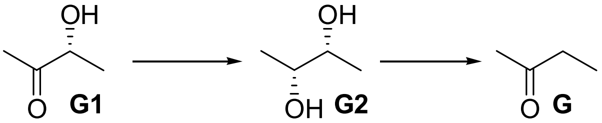


E2

5. The reaction given in the task can be repeated many times with additional molecules of malonyl–CoA, finally leading to the thioester of an unsaturated fatty acid containing 8 C atoms. Enzymatic removal of CoA–SH from the thioester affords **E1** with a sole position of the carboxylic group possible (the leaving co-enzyme A residues not shown) (2 points):



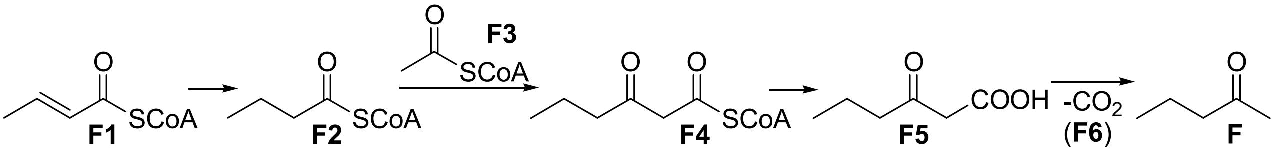
6. With due account for methyl ketone as the final product and the number of asymmetric C atoms, the structures of metabolites are (0.5 points for each structure, 1.5 points in total):



7. Both **F1** and **F3** contain the residue of co-enzyme A, a complicated molecule with a great number of C atoms. Thus, elimination of co-enzyme A occurs at the second and third steps (**F** has a low molar mass and is free of the co-enzyme A residue). **F5** contains a free carboxylic group, thus the **F5** → **F** transition could be decarboxylation leading to the ketone (similar to the biosynthesis of **E**). Taking into account that the molecules of **F2** and

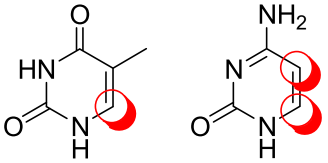
F4 differ by two C atoms, **F3** is deciphered as acetyl-CoA, and **F2** + **F3** is a condensation reaction < which results in elimination of free co-enzyme A containing 19 + 2 = 21 carbon atoms (1 point).

8. **F** contains a CH_3–C(O) fragment, thus **F1** is crotonyl-CoA. Reduction of the double bond leads to butyryl-CoA (**F2**). The further steps are found using the above considerations (0.5 point for each structure, 3.5 points in total):



Problem 3 (author Garifullin B.N.)

1. Cytosine and thymine are the major pyrimidine bases found in DNA. Only C-5 and C-6 atoms can be methylated in these bases without interference with the system of hydrogen bonds forming the DNA duplex (0.25 for the choice of each of T and C, 0.25 point for each correct C atom, 1 point in total; 0.25 penalty for each of the following: incorrect atom, uracil or a purine base):

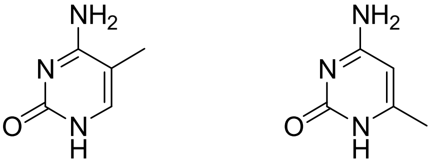


thymine cytosine

2. Since methylation can be considered as a substitution of an H atom by the CH_3 group, CH_2 should be added to the formula of a base to get that of the methylated derivative:

Base	Formula of the base	Formula of the methylated derivative
Adenine	$C_5H_5N_5$	$C_6H_7N_5$
Guanine	$C_5H_5N_5O$	$C_6H_7N_5O$
Thymine	$C_5H_6N_2O_2$	$C_6H_8N_2O_2$
Cytosine (C)	$\mathbf{C_4H_5N_3O}$	$\mathbf{C_5H_7N_3O}$

The four-membered arithmetic progression is true only for methylcytosine (only three-membered for adenine). With an account for the answer in i. 1, only two structures are possible for **Y** (0.5 point for calculation and each structure, 1.5 point in total):



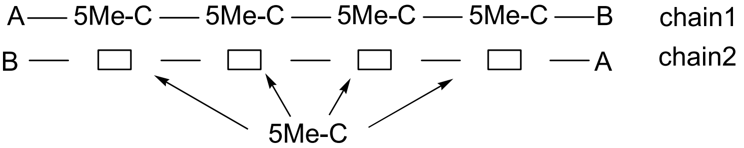
5-methylcytosine 6-methylcytosine

3. With an account for palindromic character of the dinucleotide and possibility of methylation of both DNA chains, the nucleoside **Z** contains guanine as a part of the Watson-Crick C–G pair (with the total molar mass of the residues of these bases of 492.45 g/mol). The C → 5-MeC transfer is accompanied by an increase of the molar mass by 16.03 g/mol. Then:

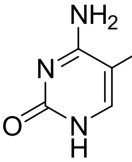
$$\frac{492.45 \cdot n + 16.03 \cdot m}{492.45 \cdot n} = 1.0203$$

$\frac{n}{m} = 1.60$, which corresponds to the ratio of 8 to 5 (or its multiples like 16 to 10). In the simplest case, 5 of 8 dinucleotides contain methyl groups, whereas **Y**/**X** equals 5/3 (3 points).

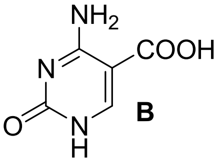
4. We are dealing with a double-stranded DNA, thus there are four cytosines in each chain. Methylation of cytosine at C-5 does not change the number of hydrogen bonds in the duplex with guanine, thus guanine can equivalently form pairs with both– C and 5-MeC. In the case of all four cytosines methylated in one chain and only one in the other, four variants of location of the sole 5-MeC in the second chain (directed 5` → 3`) are possible (2 points).



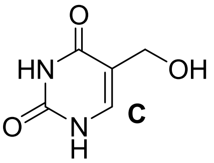
5. Molar O:N ratios can be found as 2:3 (**A**), 1:1 (**B**), and 3:2 (**C**) based on the given mass fractions of the elements. Comparison of the molecular formulae of the major nitrogenous bases with the starting structure (**Y**) allows determining the residual molar masses and thus the number of C and H atoms in the compounds: $C_5H_7N_3O_2$ (**A**), $C_5H_3N_3O_3$ (**B**), and $C_5H_6N_2O_3$ (**C**). Since thymine is one of the products of demethylation of Y, the latter is unambiguously attributed as 5-methylcytosine. The structure of **A** is found from one–step character of the **Y** → **A** transitin and general demethylation vector. **B** is a typical metabolite of the –CH_2–OH group oxidation. **C** differs from **A** by substitution of the NH_2-group with the oxygen atom, which corresponds to deamination to thymine residue (1 point for each structure, 3 points in total; 0.5 point penalty if the calculation missing; 0.25 point for each molecular formulae if structural ones missing)



A



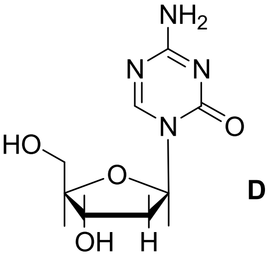
B



C

6. At least three types of enzymatic reactions are needed to form the target metabolites: deamination (metabolite **C**), hydroxylation (all three metabolites) and decarboxylation (logical completion of the demethylation process leading back to cytidine). Combination of these three processes can lead to all three major pyrimidine bases – C, T, and U (0.5 point for each base, 1.5 point in total).

7. **E** is deciphered as deoxyribocytidine. Methylation at C-5 can be prevented by modification of this atom. Attachment of any group to the atom would result in a significant increase in the molar mass of **D** as compared to that of **E**, which is not in agreement with the fact that masses are very close. Thus, the only possible variant is substitution of C-5 (with the attached hydrogen) in the heterocycle by the nitrogen atom (2 points), giving 5-azacytidine:



D

8. The N-glycoside bond of **D** is hydrolyzed in the acidic medium of stomach (1 point).

SECTION III. ANALYTICAL CHEMISTRY

Problem 1 (author Shved A.M.)

1. The simplest base with the oxidation state of nitrogen –3 is ammonia, NH_3 (0.5 points). An oxygen atom can correspond to a molecular weight difference of 16, which really corresponds to a base with the oxidation state of nitrogen -1, hydroxylamine NH_2OH (0.5 points). The basic properties of these compounds are due to the presence of a lone electron pair on the nitrogen atom, which, due to this, is able to attach a proton. The basicity increases in the series $NH_2OH < N_2H_4 < NH_3$ (0.5 points), which is associated with a decrease of acceptor environment of the nitrogen atom and, as a consequence, with an increase in the electron density on the nitrogen atom. (1.5 points in total).

2. The basicity constants of hydrazine are expressed as follows:

$$N_2H_4 + H_2O = N_2H_5^+ + OH^- \qquad K_{b1} = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]}$$

$$N_2H_5^+ + H_2O = N_2H_6^{2+} + OH^- \qquad K_{b2} = \frac{[N_2H_6^{2+}][OH^-]}{[N_2H_5^+]}$$

Then the acidity constant of hydrazonium ion for the first step is (0.5 points):

$$N_2H_6^{2+} = N_2H_5^+ + H^+ \quad K_{a1} = \frac{[N_2H_5^+][H^+]}{[N_2H_6^{2+}]} = \frac{[OH^-][H^+]}{K_{b2}} = \frac{K_w}{K_{b2}}$$

$$pK_{a1} = pK_a(N_2H_6^{2+}) = pK_w - pK_{b2} = 14 - 15.10 = -1.10$$

And similarly, for the second step (0.5 points, 1 point in total):

$$N_2H_5^+ = N_2H_4 + H^+ \quad K_{a2} = \frac{[N_2H_4][H^+]}{[N_2H_5^+]} = \frac{[OH^-][H^+]}{K_{b1}} = \frac{K_w}{K_{b1}}$$

$$pK_{a2} = pK_a(N_2H_5^+) = pK_w - pK_{b1} = 14 - 5.90 = 8.10$$

3. Since the basicity constants of hydrazine differ by almost 9 orders of magnitude, only the first step of dissociation of hydrazine can be taken into account. Moreover, even in the first step hydrazine is a rather weak base and the solution is not very dilute. Then we can assume that the equilibrium concentration of N_2H_4 is equal to its initial concentration. Hence, we can get (2.5 points in total):

$$K_{b1} = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]} \approx \frac{[OH^-]^2}{c} \Rightarrow [OH^-] = \sqrt{K_{b1} \cdot c}$$

$$pH = 14 - pOH = 14 + \lg[OH^-] = 14 + \lg\left(\sqrt{K_{b1} \cdot c}\right) = 14 + \lg\left(\sqrt{10^{-5.90} \cdot 0.30}\right) = 10.8$$

4. a) When a smaller volume of HCl of the same concentration is added to a 0.30M solution of hydrazine, a part of hydrazine reacts with HCl forming the N_2H_5Cl salt. As a result, a mixture of N_2H_4 and N_2H_5Cl is formed with the following concentrations:

$$c(N_2H_4) = \frac{0.30 \cdot V - 0.30 \cdot 0.5V}{V + 0.5V} = 0.10\ (M)$$

$$c(N_2H_5Cl) = \frac{0.30 \cdot 0.5V}{V + 0.5V} = 0.10\ (M)$$

This mixture is a buffer solution (N_2H_4 is a weak base and N_2H_5Cl acts as a conjugate acid). pH of buffer solutions is calculated by the formula (2.5 points in total):

$$pH = pK_a(N_2H_5^+) + \lg\frac{c(N_2H_4)}{c(N_2H_5Cl)} = 8.10 + \lg\frac{0.10}{0.10} = 8.10$$

b) When an acid of the same volume (and hence of the same molar amount) is added to hydrazine solution, N_2H_5Cl is formed with the following concentration:

$$c(\mathrm{N_2H_5Cl}) = \frac{0.30 \cdot V}{V+V} = 0.15\ (\mathrm{M})$$

This solution can be considered as a solution of a weak monoprotic acid with the acidity constant $K_a(N_2H_5^+) = K_{a2}$ since the hydrolysis of $N_2H_5^+$ to $N_2H_6^{2+}$ is characterized by an incomparably lower constant K_{b2}. Since K_{a2} is very small and the solution is not very dilute, the equilibrium concentration of $N_2H_5^+$ can be considered approximately equal to the concentration of N_2H_5Cl. Hence (2.5 points in total):

$$K_a(\mathrm{N_2H_5^+}) = \frac{[\mathrm{N_2H_4}][\mathrm{H^+}]}{[\mathrm{N_2H_5^+}]} \approx \frac{[\mathrm{H^+}]^2}{c} \Rightarrow [\mathrm{H^+}] = \sqrt{K_{a2} \cdot c}$$

$$\mathrm{pH} = -\lg[\mathrm{H^+}] = -\lg\left(\sqrt{K_{a2} \cdot c}\right) = -\lg\left(\sqrt{10^{-8.1} \cdot 0.15}\right) = 4.46$$

c) When twice as much acid is added to hydrazine, we can formally assume that $N_2H_6Cl_2$ is yielded with the concentration:

$$c(\mathrm{N_2H_6Cl_2}) = \frac{0.30 \cdot V}{V+2V} = 0.10\ (\mathrm{M})$$

In reality, the solution contains a mixture of 0.10M N_2H_5Cl and 0.10M HCl, as in the first step $N_2H_6^{2+}$ is a strong acid. Because of a very large difference in the dissociation constants for the first and second steps, the second step can be ignored. In this case we can use the formula to calculate the pH of a strong acid (2.5 points in total):

$$\mathrm{pH} = -\lg[\mathrm{H^+}] = -\lg c = -\lg 0.10 = 1.00$$

5. The reaction equation is as follows:

$$\mathrm{N_2H_5N_3 + H_2SO_4 = N_2H_6SO_4\downarrow + HN_3}$$

The initial quantities of compounds:

$$n(\mathrm{N_2H_5N_3})_0 = \frac{m}{M} = 3.0\ \mathrm{g} / 75\ \mathrm{g/mol} = 0.040\ \mathrm{mol}$$

$$n(\mathrm{H_2SO_4})_0 = cV = 2\mathrm{M} \cdot 0.020\ \mathrm{L} = 0.040\ \mathrm{mol}$$

The amount of precipitated product:

$$n(\mathrm{N_2H_6SO_4}) = \frac{m}{M} = 3.7\ \mathrm{g} / 130\ \mathrm{g/mol} = 0.0285\ \mathrm{mol}$$

The final composition of the solution with a volume of V = 20 mL + 25 mL = 45 mL (0.5 points for each concentration of compounds):

$$c(\mathrm{N_2H_5HSO_4}) = \frac{n(\mathrm{N_2H_5N_3})_0 - n(\mathrm{N_2H_6SO_4})}{V} = \frac{(0.040-0.0285)\ \mathrm{mol}}{0.045\ \mathrm{L}} = 0.256\mathrm{M}$$

$$c(\mathrm{HN_3}) = \frac{n(\mathrm{N_2H_5N_3})_0}{V} = \frac{0.040\ \text{моль}}{0.045\ \text{л}} = 0.889\mathrm{M}$$

The concentrations of HSO_4^- and HN_3 are of the same order of magnitude, but the dissociation constant of hydrosulfate ion is more than 2 orders of magnitude higher than the dissociation constant of hydrazoic acid. Thus, the stronger acid HSO_4^- suppresses the dissociation of the weaker acid HN_3 and the acidity of the solution is mainly determined by the dissociation of hydrosulfate ion (0.5 points):

$$\mathrm{HSO_4^- = H^+ + SO_4^{2-}} \quad K_{a2} = \frac{[\mathrm{H^+}][\mathrm{SO_4^{2-}}]}{[\mathrm{HSO_4^-}]} \approx \frac{[\mathrm{H^+}]^2}{c-[\mathrm{H^+}]}$$

$$[\mathrm{H^+}] = \frac{-K_{a2} + \sqrt{K_{a2}^2 + 4K_{a2}c}}{2} = \frac{-10^{-1.99} + \sqrt{(10^{-1.99})^2 + 4 \cdot 10^{-1.99} \cdot 0.256}}{2} = 0.046\ (\mathrm{M})$$

The solubility product, by definition, corresponds to equilibrium:

$$N_2H_6^{2+}SO_4^{2-}{}_{(s)} = N_2H_6^{2+} + SO_4^{2-} \qquad K_{sp} = [N_2H_6^{2+}][SO_4^{2-}]$$

calculate the equilibrium concentration of $N_2H_6^{2+}$, it can be considered that in an acidic medium partial protonation of $N_2H_5^+$ occurs, while its dissociation is suppressed by the dissociation of a strong acid HSO_4^-. Hence (0.5 points):

$$K_a(\mathrm{N_2H_6^{2+}}) = \frac{[\mathrm{N_2H_5^+}][\mathrm{H^+}]}{[\mathrm{N_2H_6^{2+}}]} = \frac{(c(\mathrm{N_2H_5HSO_4}) - [\mathrm{N_2H_6^{2+}}])[\mathrm{H^+}]}{[\mathrm{N_2H_6^{2+}}]}$$

$$[\mathrm{N_2H_6^{2+}}] = \frac{c(\mathrm{N_2H_5HSO_4})\cdot[\mathrm{H^+}]}{K_a(\mathrm{N_2H_6^{2+}}) + [\mathrm{H^+}]} = \frac{0.256\cdot 0.046}{10^{1.10} + 0.046} = 9.32\cdot 10^{-4}\ (\mathrm{M})$$

The concentration of sulfate ions was previously assumed to be equal to the concentration of H^+ when the dissociation of HSO_4^- was considered, i.e., $[SO_4^{2-}] = [H^+] = 0.046\,M$. Thus, the solubility product is (0.5 points, 2.5 points in total):

$$K_{sp} = [\mathrm{N_2H_6^{2+}}][\mathrm{SO_4^{2-}}] = 9.32\cdot 10^{-4}\cdot 0.046 = 4.29\cdot 10^{-5}$$

Problem 2 (author Kandaskalov D.V.)

1. The graph **1** shows that the solubility of the substance does not depend on pH; graphs **2** and **4** show that solubility (more precisely, concentration logarithms) depends linearly on pH, and graph **3** consists of two segments, it achieves a minimum of solubility. Decrease of pH (increase of "OH^-") should lead to the formation of hydroxide precipitation, which means that the maximum concentration of metal should decrease. So the graph **2** exists, and graph **4** cannot exist. Let's analyze graph **3**: the solubility first decreases, and then grows, which is typical for amphoteric metals. Thus, the graph **3** corresponds to Al^{3+}. Sodium does not form sediment (the solubility constant of NaOH solubility is very high), so its solubility remains about the same (graph **1**). Schedule 2 corresponds to Cu^{2+} (0.5 points for the correct answer, 2 points in all).

2. From the graph we see that before pH 5.0–5.5 and after pH 9.5–10 the solution is not saturated at $c(\mathrm{Al_{aq}})$ = 0.010M, and in this diapasons the precipitation is not occurring (1 point).

3. Let's take any point on the graph **2**, for example pH 8 i.e. $[OH^-] = 10^{-6}$M at this point $c(\mathrm{Cu_{aq}}) = [Cu^{2+}] = 1\cdot 10^{-6}$M. The solution is saturated thus $K_S(Cu(OH)_2) = [Cu^{2+}][OH^-]^2 = (10^{-6})(10^{-6})^2 = 10^{-18}$ (1 point).

4. Knowing K_S we could find solubility s:

$$\mathrm{Fe(OH)_3} \rightarrow \mathrm{Fe^{3+}} + 3\mathrm{OH^-} \quad \mathrm{K_S} = [\mathrm{Fe^{3+}}][\mathrm{OH^-}]^3 = \mathrm{s}\cdot(3\mathrm{s})^3 = 27\mathrm{s}^4$$

$$\mathrm{s} = \sqrt[4]{\frac{\mathrm{K_S}}{27}} = \sqrt[4]{\frac{3.8\cdot 10^{-38}}{27}} = 1.94\cdot 10^{-10}\,\mathrm{mol/L}$$

We obtained s = $1.94\cdot 10^{-10}$M, and it seems to be a correct value, but it is not a case for hydroxides, because according to calculation the concentration of OH^- is $5.8\cdot 10^{-10}$M, which is negligibly low compared to the concentration of hydroxide-ions formed from water autodissociation. So, the autodissociation must be the main source of hydroxide ions, and we can assume that this concentration is 10^{-7}M. In this case, we need to recalculate the solubility (2 points):

$$\mathrm{K_S} = [\mathrm{Fe^{3+}}][\mathrm{OH^-}]^3 = \mathrm{s}\cdot(10^{-7})^3 = 3.8\cdot 10^{-38} \Rightarrow \mathrm{s} = 3.8\cdot 10^{-17}\,\mathrm{mol/L}.$$

5. Let’s write all equilibriums, which are given by stepwise (*K*) and cumulative constants (β):

$$Pb^{2+} + OH^- \rightleftarrows PbOH^+ \qquad K_1 = \frac{[PbOH^+]}{[Pb^{2+}][OH^-]}$$

$$PbOH^+ + OH^- \rightleftarrows Pb(OH)_{2(aq)} \qquad K_2 = \frac{[Pb(OH)_2]}{[PbOH^+][OH^-]}$$

$$Pb(OH)_{2(aq)} + OH^- \rightleftarrows Pb(OH)_3^- \qquad K_3 = \frac{[Pb(OH)_3^-]}{[Pb(OH)_2][OH^-]}$$

$$Pb^{2+} + OH^- \rightleftarrows PbOH^+ \qquad \beta_1 = \frac{[PbOH^+]}{[Pb^{2+}][OH^-]} = K_1$$

$$Pb^{2+} + 2OH^- \rightleftarrows Pb(OH)_{2(aq)} \qquad \beta_2 = \frac{[Pb(OH)_2]}{[Pb^{2+}][OH^-]^2} = K_1 \cdot K_2$$

$$Pb^{2+} + 3OH^- \rightleftarrows Pb(OH)_3^- \qquad \beta_2 = \frac{[Pb(OH)_3^-]}{[Pb^{2+}][OH^-]^3} = K_1 \cdot K_2 \cdot K_3$$

We could directly obtain the values for K_1 and β_1 as $K_1 = \beta_1$ and $K_1K_2 = \beta_2$. We obtain $\beta_1 = K_1 = \beta_2 / K_2 = 10^{7.5}$.

Taking into account that ion concentration of $Pb(OH)^+$ and $Pb(OH)_3^-$ are equal achieving the maximal precipitation, we can write next equations:

$$\left.\begin{aligned} \beta_1 &= \frac{[PbOH^+]}{[Pb^{2+}][OH^-]} \Rightarrow [PbOH^+] = \beta_1 \cdot [Pb^{2+}][OH^-] \\ \beta_3 &= \frac{[Pb(OH)_3^-]}{[Pb^{2+}][OH^-]^3} \Rightarrow [Pb(OH)_3^-] = \beta_3 \cdot [Pb^{2+}][OH^-]^3 \end{aligned}\right\} \beta_1 \cdot [Pb^{2+}][OH^-] = \beta_3 \cdot [Pb^{2+}][OH^-]^3$$

$$\beta_1 = \beta_3[OH^-]^2 \Rightarrow K_1 = K_1K_2K_3[OH^-]^2 \Rightarrow K_2K_3 = \left(\frac{[H^+]}{K_w}\right)^2 = \left(\frac{10^{-10.75}}{10^{-14}}\right)^2 = 10^{6.5}$$

Knowing that $K_2 = 10^3$, we find that $K_3 = 10^{3.5}$. Finally $\beta_3 = K_1K_2K_3 = 10^{14}$ (1 point for the correct constant, 4 points in all):

Specie	logK_n	logβ_n
$Pb(OH)^+$	**7.5**	**7.5**
$Pb(OH)_2$	3.0	**10.5**
$Pb(OH)_3^-$	**3.5**	14.0

6. (2 points)

$$Pb^{2+} + 2OH^- \rightleftarrows Pb(OH)_{2(aq)} \qquad \beta_2 = \frac{[Pb(OH)_2]_{(aq)}}{[Pb^{2+}][OH^-]^2} = K_1 \cdot K_2$$

$$Pb^{2+} + 2OH^- \rightleftarrows Pb(OH)_{2(s)} \qquad \frac{1}{K_S} = \frac{1}{[Pb^{2+}][OH^-]^2}$$

$$Pb(OH)_{2(s)} \rightleftarrows Pb(OH)_{2(aq)} \qquad K_0 = [Pb(OH)_2]_{(aq)}$$

So the constant value is: $K_0 = [Pb(OH)_2]_{(aq)} = \beta_2 \cdot K_S = 10^{10.5} \cdot 5.5 \cdot 10^{-16} = 1.74 \cdot 10^{-5}$

7. Let’s write the material balance for Pb which is in the solution and expressing it as a function of $[Pb^{2+}]$:

$$\begin{aligned} C(Pb_{aq}) &= [Pb^{2+}] + [Pb(OH)^+] + [Pb(OH)_2]_{(aq)} + [Pb(OH)_3^-] = \\ &= [Pb^{2+}] + \beta_1 \cdot [Pb^{2+}][OH^-] + \beta_2 \cdot [Pb^{2+}][OH^-]^2 + \beta_3 \cdot [Pb^{2+}][OH^-]^3 = \\ &= [Pb^{2+}]\left(1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \beta_3[OH^-]^3\right) = \\ &= [Pb^{2+}]\left(1 + 10^{7.5} \cdot 10^{-2.75} + 10^{10.5} \cdot 10^{-5.5} + 10^{14}10^{-8.25}\right) = 7.19 \cdot 10^5 \cdot [Pb^{2+}] \end{aligned}$$

Now, we can find $[Pb^{2+}]$ in solution:

$$K_S = [Pb^{2+}][OH^-]^2 \Rightarrow [Pb^{2+}] = \frac{K_S}{[OH^-]^2} = \frac{5.5 \cdot 10^{-16}}{(10^{-2.75})^2} = 1.74 \cdot 10^{-10} \text{ mol/L}$$

Thus:

$$C(Pb_{aq}) = 7.19\cdot10^5\cdot[Pb^{2+}] = 7.19\cdot10^5\cdot1.74\cdot10^{-10} = 1.25\cdot10^{-4}M$$

The total concentration of Pb is bigger than 10^{-6}M, thus there no complete precipitation (3 points).

Problem 3 (author Beklemishev M.K.)

1. Since x M of the initial substances have reacted, x mol/L of products D and P has formed. Then we can obtain from the expression for the constant:

$$K = \frac{x + x}{(m - x) + (n - x)} = \frac{2x}{m + n - 2x}$$

Substituting $x = K = 0.1$, we can get:

$$0.1 = \frac{0.2}{m + n - 0.2}$$

Hence the requested condition will be: $m + n = 2.2$ mol/L (2 points). For the constant K to be constant, the sum of A and B concentrations of must be equal to this value.

2. Let us transform the expression for the constant from item 1 to the form:

$$\frac{x}{m + n} = 0.5\frac{K}{1 + K}$$

Considering different values of K, we can find that the degree of transformation $\alpha = \frac{x}{m+n}$ increases with an increase in K to 0.5 at $K \to \infty$. Answer: 0.5, which implies that for any values of the constant, the degree of conversion in reaction (1) will not exceed ½ (2 points).

3. a) Dissociation equation: $HA = H^+ + A^-$, $K = ([H^+] + [A^-]) / [HA]$ (1 point).

b) In the solution of acid $[H^+] = [A^-]$ and $K = 2[H^+] / [HA]$, the value of [HA] can be obtained from the expression for the acid material balance: $c(HA) = [A^-] + [HA]$. As a result, we will have: $[H^+] = K\cdot c(HA) / (K + 2)$ (1 point).

c) At $K = 1$ and $c(HA) = 1$, $[H^+] = 0.33$, or pH = 0.48 (1 point). If the expression $c(HA) = [A^-] + [HA]$ is ignored, the values $[H^+] = 0.50$ and pH = 0.30 will be obtained (0.5 point).

d) $K = ([H^+] + [A^-]) / [HA] = ([H^+] + [A^-]) / (c(HA) - [A^-])$; then
$[H^+] = K(c(HA) - [A^-]) - [A^-]$; the concentration of A^- is calculated from the amount of added alkali: $[A^-] = c_0(NaOH)\cdot V(NaOH) / (V_1 + V(NaOH))$, and when calculating $c(HA)$, we should take into account the dilution: $c(HA) = c_0(HA)V_1 / (V_1 + V(NaOH))$ (2 points).

e) The obtained pH values are shown below (0.5 points each, 1.5 points in total):

Volume of NaOH, mL	2	6	12
pH	0.087	0.269	0.602

4. a) Expression for the constant: $K_1 = ([H^+] + [HA^-]) / [H_2A]$. If there are no other particles in solution, $[H^+] = [HA^-]$; assuming for a weak acid that the total acid concentration $c(H_2A)$ is equal to its equilibrium concentration $[H_2A]$, we will obtain: $[H^+] = K_1c(H_2A)/2$, that is, the slope of the $[H^+]$ dependence on $c(H_2A)$ is equal to $K_1/2$, whence $K_1 = 1\cdot10^{-5}$ (2 points).

b) From the above expression for the first acidity constant we have $[H^+] = 5\cdot10^{-6}$, pH 5.3 (1 point). Neglecting the concentration of hydroxide ions, we can write down the electroneutrality equation: $[Na^+] + [H^+] = [HA^-]$. Substituting $[HA^-] = K_1c(H_2A) - [H^+]$, we will obtain $[Na^+] + [H^+] = K_1c(H_2A) - [H^+]$. Substituting the known values: $[Na^+] = (5\cdot10^{-5}) / 25 = 2\cdot10^{-6}$M and $c(H_2A) = 1\cdot\frac{20}{25} = 0.8$M, we can calculate $[H^+] = 3\cdot10^{-6}$M, pH 5.5 (1.5 points).

SECTION IV. PHYSICAL CHEMISTRY

Problem 1 (authors Rozantsev G.M., Shved E.N.)

1. The data from the table is substituted into the equation $k_{obs} = k_s + k_{NO2-}[NO_2^-]$: $1.404\cdot10^{-5} = k_s + 10^{-3}\cdot k_{NO2-}$ and $1.506\cdot10^{-5} = k_s + 1.5\cdot10^{-3}\ k_{NO2-}$. Solving the system of equations, we get $k_{NO2-} = (1.506 - 1.404)\cdot10^{-5}/(1.5 - 1.0)\cdot10^{-3} = 2.04\cdot10^{-3}$ $L\cdot mol^{-1}s^{-1}$ (1 point), $k_s = 1.404\cdot10^{-5} - 2.04\cdot10^{-3}\cdot10^{-3} = 1.20\cdot10^{-5}$ s^{-1} (1 point, 2 points in total).

2. From the Van't-Hoff equation $\ln(k_2/k_1) = E_a/R(1/T_1 - 1/T_2)$ we find $E_a = RT_1T_2\ln(k_2/k_1)/(T_2 - T_1)$. For a route that goes through a solvent S: $E_a = 8.314\cdot303\cdot318\cdot\ln(5\cdot10^{-5}/1.2\cdot10^{-5})/(318 - 303) = 76216$ J/mol (1 point). For the route that goes through the nucleophile NO_2^-: $E_a = 8.314\cdot303\cdot318\ \ln(6.25\cdot10^{-3}/2.04\cdot10^{-3})/(318 - 303) = 59795$ J/mol (1 point, 2 points in total).

3. For hydrolysis $NaNO_2$: $NO_2^- + H_2O \rightleftarrows HNO_2 + OH^-$ the hydrolysis constant is $K_b = K_w/K_a = 1.961\cdot10^{-11} = [HNO_2][OH^-]/[NO_2^-]$. From the material balance equation $[NO_2^-] = C^0 - [HNO_2] = C^0 - [OH^-]$, since $[HNO_2] = [OH^-]$ (1 point). Then $1.961\cdot10^{-11} = [OH^-]^2/(2.0\cdot10^{-3} - [OH^-])$. Solving the quadratic equation $[OH^-]^2 + 1.961\cdot10^{-11}[OH^-] - 3.922\cdot10^{-14} = 0$, we find $[OH^-] = 1.98\cdot10^{-7}$; pOH = 6.70; pH = 7.30 (1 point); $[NO_2^-] = 2.0\cdot10^{-3} - 1.98\cdot10^{-7} = 2.0\cdot10^{-3}$ mol/L (1 point, 3 points in total).

The solution medium is close to neutral, so the more accurate pH value can be obtained taking into account the dissociation of water: $[OH^-] = K_w/[OH^-] + C^0K_b/(K_b + [OH^-])$ and $[OH^-] = 2.22\cdot10^{-7}$ mol/L, $pH = 14 + \lg(2.22\cdot10^{-7}) = 7.34$.

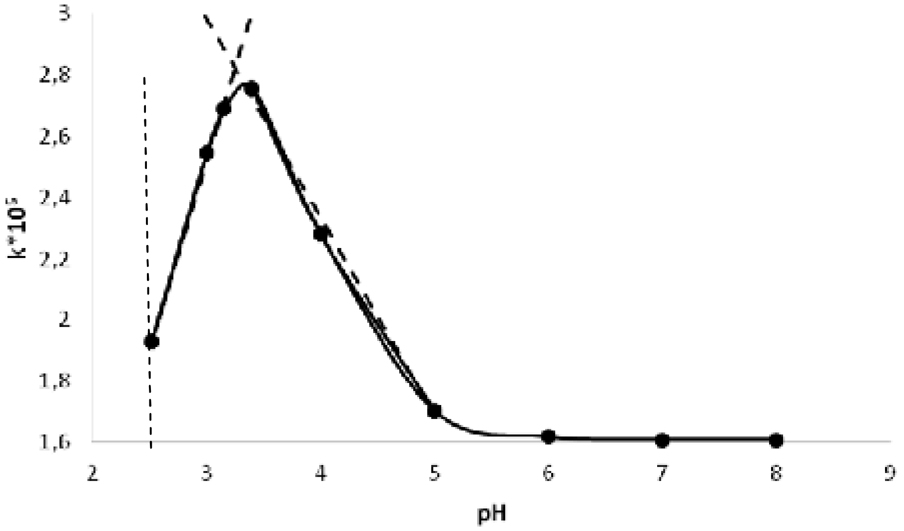
4. When deriving the kinetic equation, the method of stationary approximation is convenient: $r = k_2[Pt(pip)_2Cl_2(NO_2^-)] = k_1[Pt(pip)_2Cl_2(HNO_2)S][NO_2^-] = k_1K[Pt(pip)_2Cl_2S_2][NO_2^-][HNO_2] = k_{cat}[Pt(pip)_2Cl_2S_2][NO_2^-][HNO_2]$ (1 point). The observed rate constant, considering the three routes, includes k_s, k_{NO2-}, k_{cat} and equals to $k_{obs} = k_s + k_{NO2-}[NO_2^-] + k_{cat}[NO_2^-][HNO_2]$ (1 point) $k_{obs} = 1.20\cdot10^{-5} + 2.04\cdot10^{-3}\cdot2.0\cdot10^{-3} + 2.0\cdot10^{-3}\ k_{cat}[HNO_2] = 1.608\cdot10^{-5} + 2.0\cdot10^{-3}k_{cat}[HNO_2]$. Belluco gives the same equation $k_{obs} = 1.608\cdot10^{-5} + 0.027[HNO_2]$, then $2.0\cdot10^{-3}k_{cat} = 0.027$ and $k_{cat} = 0.027/2.0\cdot10^{-3} = 13.5$ $L^2mol^{-2}s^{-1}$ (1 point, 3 points in total).

5. In buffer solution $C_N = [NO_2^-] + [HNO_2] = [NO_2^-] + [H^+][NO_2^-]/K_a$; mole fraction of NO_2^-: $\alpha_{NO2-} = [NO_2^-]/C_N = K_a/([H^+] + K_a)$ (1 point). Considering that $[NO_2^-] = \alpha_{NO2-}C_N$ and $[HNO_2] = C_N - [NO_2^-] = (1 - \alpha_{NO2-})C_N$, for $k_{obs} = k_s + k_{NO2-}[NO_2^-] + k_{cat}[NO_2^-][HNO_2]$ we obtain $k_{obs} = k_s + k_{NO2-}C_N\alpha_{NO2-} + k_{cat}C_N^2\alpha_{NO2-}(1 - \alpha_{NO2-})$ (1 point, 2 points in total).

6. To calculate k_{obs} at different $[H^+]$, two methods are available: to calculate α_{NO2-} according to the formula $\alpha_{NO2-} = [NO_2^-]/C_N = K_a/([H^+] + K_a) = 5.1\cdot10^{-4}/([H^+] + 5.1\cdot10^{-4})$ and substitute it into $k_{obs} = k_s + k_{NO2-}C_N\alpha_{NO2-} + k_{cat}C_N^2\alpha_{NO2-}(1 - \alpha_{NO2-}) = 1.20\cdot10^{-5} + 2.0\cdot10^{-3}\ \alpha_{NO2-}[2.04\cdot10^{-3} + 13.5\cdot2.0\cdot10^{-3}(1 - \alpha_{NO2-})]$; to calculate concentrations according to the formulas $[NO_2^-] = C_NK_a/([H^+] + K_a)$ and $[HNO_2] = C_N - [NO_2^-]$ and substitute them into $k_{obs} = k_s + k_{NO2-}\ [NO_2^-] + k_{cat}[NO_2^-][HNO_2] = 1.20\cdot10^{-5} + 2.0\cdot10^{-3}[NO_2^-] + 13.5[NO_2^-][HNO_2]$. As a result, we get the values k_{obs} depending on $[H^+]$ and pH (2 points):

$[H^+]$, mol/L	$3\cdot10^{-3}$	$1\cdot10^{-3}$	$7\cdot10^{-4}$	$4\cdot10^{-4}$	$1\cdot10^{-4}$	$1\cdot10^{-5}$	$1\cdot10^{-6}$
pH	2.52	3.00	3.15	3.40	4.00	5.00	6.00
$k_{obs}\cdot10^5$, s^{-1}	1.930	2.546	2.689	2.759	2.281	1.702	1.617

7. On the plot $k_{obs} = f([\mathrm{pH}])$ (0.5 points) we find the maximum as the point of intersection of two straight lines: pH ≈ 3.25 (0.5 points, 1 point in total).



The more accurate value can be found by solving the extremum problem by equating the derivative to zero: $d(k_{obs})/d(\alpha_{NO2-}) = 0$. From $d(k_s + k_{NO2-}C_N\alpha_{NO2-} + k_{cat}C_N^2\alpha_{NO2-} - k_{cat}C_N^2\alpha^2_{NO2-})/d(\alpha_{NO2-}) = 0$ we get the quadratic equation $k_{NO2-}C_N + k_{cat}C_N^2 - 2k_{cat}C_N^2\alpha_{NO2-} = 0$, from which we find the mole fraction $\alpha_{NO2-} = (k_{NO2-} + k_{cat}C_N)/2k_{cat}C_N = (2.04\cdot10^{-3} + 13.5\cdot2.0\cdot10^{-3})/2\cdot13.5\cdot2.0\cdot10^{-3} = 0.5378$. From $\alpha_{NO2-} = K_a/([\mathrm{H}^+] + K_a)$ $[\mathrm{H}^+] = K_a/\alpha_{NO2-} - K_a = 5.1\cdot10^{-4}/0.5378 - 5.1\cdot10^{-4} = 4.83\cdot10^{-4}$ mol/L and pH = 3.36.

Problem 2 (author Karpushkin E.A.)

1. (1 point for each equation, 2 points in total)

$C_2H_6 + 2H_2O \rightarrow 2CO + 5H_2$

$CO + H_2O \rightarrow CO_2 + H_2$

2. Since the catalytic activity is due to the surface metal atoms, specific catalytic activity is proportional to the specific surface area of the particles. Let us consider 1 g of the samples, their total volume being 1/8.9 = 0.112 cm^3. Then radius r of the disc with thickness $h = 0.1$ cm is $r = \sqrt{\frac{V}{\pi h}} = \sqrt{\frac{0.11\ \text{см}^2}{0.1\ \text{см}\cdot\pi}} = 0.592$ cm hence, the surface area is $S = 2\cdot\pi r^2 + 2\pi rh = 2.57$ cm^2.

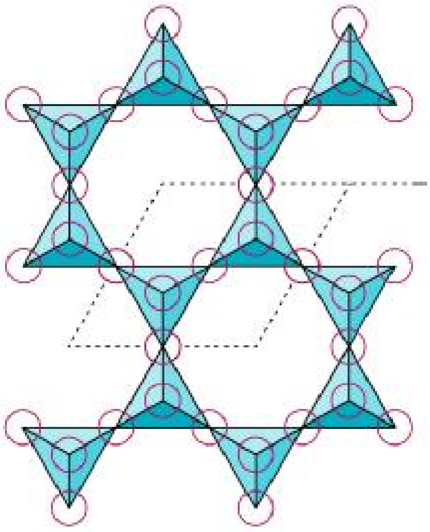
For the nickel chips, the surface area of each particle equals $2\cdot(0.1\cdot0.01 + 0.1\cdot0.005 + 0.01\cdot0.005) = 3.1\cdot10^{-3}$ cm^2, the volume being $0.1\cdot0.01\cdot0.005 = 5\cdot10^{-6}$ cm^3. In view of the total volume of the sample, 1 g of the chips contains 22400 particles, and their total surface area is 69.44 cm^2.

A similar calculation for the spherical nanoparticles gives the surface area per particle $4\pi(5\cdot10^{-7})^2 = 3.142\cdot10^{-12}$ cm^2, and volume per particle $4/3\pi(5\cdot10^{-7})^3 = 5.236\cdot10^{-19}$ cm^3; the sample contains $2.14\cdot10^{17}$ of the particles, their total surface area being $6.72\cdot10^5$ cm^2. Hence, activities of the three samples are $2.57:69.44:6.72\cdot10^5 = 1:27:2.6\cdot10^5$ (1 point for calculation of each surface area, 1 point for the ratio, 4 points in total).

3. Threefold increase in the particle volume leads to increase in its radius by $\sqrt[3]{3}$ times, whereas the surface area is increased by $\sqrt[3]{3^2}$ times, the particles number being down by

3 times. Overall surface area of the formed larger particles is $\sqrt[3]{3^2} / 3 = 0.693$ of that of the initial particles, hence the catalyst activity is decreased by 1/0.693 = 1.44 times (1 point).

4. The smallest fragment, translation of which in the plane gives the required lattice, is shown in dashed lines (image source: https://cdn.britannica.com/42/2642-050-AC18536C/silicon-tetrahedron-silicate-minerals-atom-corner-oxygen.jpg). It contains two SiO_4 tetrahedrons, with one of the oxygen atoms being shared and located inside the cell, and four other oxygen atoms shared between the tetrahedrons being also shared between the adjacent cells. Hence, each cell contains 4·2 – 1 – 4·1/2 = 5 oxygen atoms, the gross formula being Si_2O_5 ($Na_2Si_2O_5$ is accepted as well). Since the nanotube is formed via rolling of the planar phyllosilicate sheet, the nanotube specific surface area equals that of the planar phyllosilicate. The area of the selected cell can be easily calculated (for example, as area of eight regular triangles with side 0.26 nm or area of rhomb with sides 0.52 nm and angle between them 60°): $0.234\ \text{nm}^2 = 2.34 \cdot 10^{-19}\ \text{m}^2$. This area corresponds to the mass of the repeat unit $Na_2Si_2O_5$ (the amount of sodium is determined by electric neutrality or from the number of unshared oxygen atoms): $182.15\ \text{g/mol} / 6.02 \cdot 10^{23}\ \text{mol}^{-1} = 3.03 \cdot 10^{-22}\ \text{g}$. Hence, specific surface area is $2.34 \cdot 10^{-19}\ \text{m}^2 / 3.03 \cdot 10^{-22}\ \text{g} = 772\ \text{m}^2/\text{g}$. This calculation considers only the outer surface of the nanotube; if the inner surface is counted as well, the specific area is twice higher – accepted as correct answer (1 point for the cell, 1 point for gross formula, 1 point for specific surface area, 3 points in total).



5. Let us determine the ratio of nickel to silicon in the reaction mixture. Nickel amount: 2.375 g/238.69 g/mol = 9.95 mmol, silicon amount 0.5 mol/L·0.04 L = 20 mmol, hence Ni : Si = 1 : 2. Formal charge of the repeat unit of the phyllosilicate (Si_2O_5) equals −2 and is exactly compensated by Ni^{2+}. Hence, the product of the hydrothermal treatment can be assigned to $NiSi_2O_5$. However, this compound contains only three elements, and nickel fraction in it is 30.11%, less than that given in the task. The missing for the element can be sodium or hydrogen. Introduction of sodium would decrease the fraction of nickel in the product, which is already below the required one. For the same reason, hydrogen cannot be incorporate as hydrate water. A reasonable assumption is partial substitution of silicate ions with hydroxide ones. In view of the electric neutrality, the formula per a nickel atom can be written at $Ni(Si_2O_5)_x(OH)_{2-2x}$. Mass ratio of Ni in this compound is ($0.463 = \frac{58.69}{58.69 + 136.17x + 17.008(2-2x)}$) solution of the equation yields $x = 0.333$, and the product formula

$$Ni(Si_2O_5)_{0.333}(OH)_{1.333} \text{ or } Ni(Si_2O_5)\cdot 2Ni(OH)_2.$$

The overall reaction equation is as follows:

$$3NiCl_2 + 2Na_2SiO_3 + 2NaOH + H_2O \rightarrow Ni(Si_2O_5)\cdot 2Ni(OH)_2 + 6NaCl$$

It turns out that silicate was taken in excess with respect to the phyllosilicate composition.(1 point for the qualitative composition, 1 point for the formula, 1 point for the equation, 3 points in total; no penalty for the $xNi(Si_2O_5)\cdot yNi(OH)_2\cdot zNiO$ formula if the x, y, z correspond to correct nickel fraction).

6. Let us determine the mass fraction of nickel in the obtained product. The reduction reaction is

$$Ni(Si_2O_5)\cdot 2Ni(OH)_2 + 2H_2 \rightarrow Ni(Si_2O_5) + 2Ni + 4H_2O$$

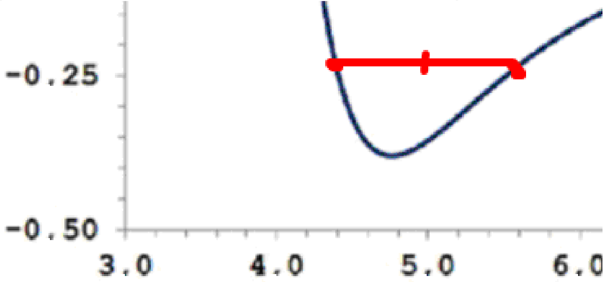
This equation assumes that nickel in the phyllosilicate structure is not reduced (this would disrupt the compound structure, and it is stated that the product contains phyllosilicate nanotubes) and accounts for the fact that nickel hydroxide is decomposed into oxide at heating. Since nickel reduction occurs with yield of 20%, the final product formula is $Ni(Si_2O_5)\cdot NiO_{1.6}\cdot Ni_{0.4}$. The mass fraction of Ni(0) in the product is $0.4\cdot 58.69/(194.86 + 1.6\cdot 74.69 + 0.4\cdot 58.69) = 0.0695$.

Since specific acidity of the semispherical Ni(0) fragments equals that of the spherical nanoparticles (the planar sections are linked to the nanotubes and are not involved in the catalytic reaction), the decrease in the specific catalytic activity is due to the fraction of Ni(0) in the catalyst which is below 100%. Hence, specific activity of the obtained catalyst is decreased with respect to the spherical nanoparticles by 1/0.0695 = 14.4 times (2 points for correct calculation; 1 point penalty if dehydration is not considered, no penalty for reduction of Ni in the phyllosilicate part).

Problem 3 (author Kandaskalov D.V.)

1. a) The bond length corresponds to the minimum on the potential curve i. e. 4.8 Å for Cs_2 (0.5 points) and 5.0 Å for Cs_2^+ (0.5 points); b) The binding energy in the Cs_2 molecule is approximately (excluding the zero-point vibration energy) equal to the depth of the potential well, i. e. 0.40 eV according to the scale on the vertical axis (0.5 points, 1.5 points in total).

2. It is seen from the figure that at –0.25 eV the average bond length is 5.0 Å (1 point)



3. The equilibrium bond length is 4.8 Å, which means that the *covalent* radius of the atom is 2.4 Å. The Cs atom has one *weakly bound* electron in an open outer shell. Removing an electron should sharply reduce the particle size, therefore for Cs^+ only option d) is correct (1 point).

4. (0.25 points for each correct answer, 1.5 points in total).

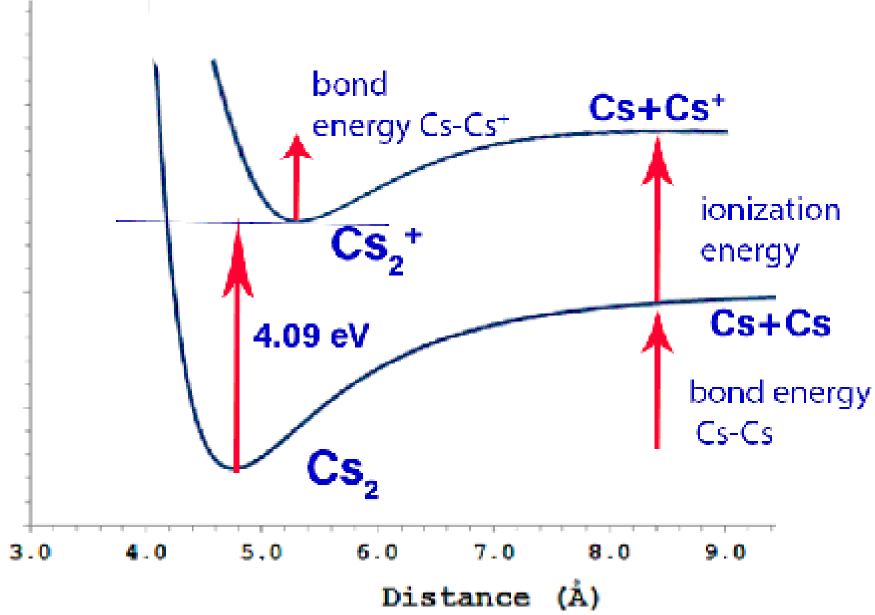
1 f) Formation enthalpy of a compound	4 e) Dissociation energy
2 b) Sublimation enthalpy	5 a) Electron affinity
3 d) Ionization energy	6 c) Crystal lattice energy

5. a) Based on the data in item 3, we can represent reaction (3) in the form of a combination of reactions for which the enthalpies are known, which coincide at $T = 0$ with the reaction energies (2.5 points):

$$\Delta H_3 = \Delta H_1 - \Delta H_2 - 0.5\Delta H_4 - \Delta H_5 + \Delta H_6,$$

$$\Delta H_3 = -553.5 - 76.5 - 0.5\times 159.2 - (-328.2) + 756.9 = 375.5 \text{ kJ/mol } = 3.89 \text{ eV}.$$

b) To calculate the cohesion energy of Cs_2^+ ion let us draw the following scheme:



It is seen that the Cs–Cs$^+$ bond energy can be found by knowing the ionization energy of the atom, the bond energy in the Cs_2 molecule. This sought energy 0.40 + 3.89 – 4.09 = 0.20 eV (2 points, 4.5 points in total).

6. To compare the stability of clusters that have different numbers of atoms, it is necessary to compare the binding energy per particle. Therefore, the most stable cation is Cs_5^+ (0.5 points), and the most stable neutral cluster is – Cs_{10} (0.5 points, 1 point in total).

7. According to Fig. 2 the binding energy per atom in Cs_{10} cluster is $E_0 = 0.258$ eV, and for the Cs_{10}^+ cluster similar energy is $E_+ = 0.323$ eV. It is necessary to find the difference between the energies of Cs_{10}^+ and Cs_{10}. Let's compose the following thermodynamic cycle with participation of Cs_n and Cs_n^+ clusters (all participants are gases):

(1) $Cs_{10} = Cs_9 + Cs$ E_0
(2) $Cs_{10}^+ = Cs_9 + Cs^+$ E_+
(3) $Cs = Cs^+ + e^-$ $I_1 = 3.89$ eV – the known value
(X) $Cs_{10} = Cs_{10}^+ + e^-$ $I_n = x$ – the sought value

It is easy to verify that the reaction (X) is a linear combination of the remaining reactions: (X) = (1) – (2) + (3). From here we find the required value (4.5 points):

$$x = E_0 + I_1 - E_+ = 0.258 - 0.323 + 3.89 = 3.83 \text{ eV}.$$

SECTION V. INORGANIC CHEMISTRY

Problem 1 (author Likhanov M.S.)

1. Let us determine the number of each type atoms in one unit cell (UC) of A. M – is an unknown transition metal. We take into account that the atom located at the vertex belongs to the UC by 1/8, on the edge – by 1/4, on the face – by 1/2, inside the UC – entirely. Then the number of M atoms in one UC = $8·1/8 + 18·1/2 + 14·1 = 24$
O atoms = $24·1/4 + 24·1/2 + 14·1 = 32$ (0.5 points for calculations).
The total formula of the oxide is $M_{24}O_{32}$, taking into account Z = 8, the formula unit (empirical formula) has the composition – M_3O_4 (0.5 points for formula).
Oxides of this composition belong to the spinel family (0.5 points, 1.5 points in total).

2. According to the absorption spectrum of the complex ion **C**, the maximum of the absorption lies in the green region (~ 510 nm), therefore, the colour of coordination complex **C** solution will be red. In reality, the $[Co(H_2O)_6]^{2+}$ solution has a red-pink colour (0.5 points).

3. According to the Henderson-Hasselbach equation:
$pH = 14 + lg(K_b(NH_3·H_2O)) + lg([NH_3·H_2O]) – lg([NH_4Cl])$.
$lg([NH_4Cl]) = 14 – pH + lg(K_b(NH_3·H_2O)) + lg([NH_3·H_2O])$,
$[NH_4Cl]$ = 0.2846M. Thus it is necessary to add 0.02846 mole NH_4Cl to 100 mL of solution. Therefore, $m(NH_4Cl) = 0.02846·53.5 = 1.5226$ g (1 point).

4. Calculate the molar mass of the unit cell of **A**:
$M_{U.C.} = V_{U.C.}dN_A = a^3dN_A = (8.08·10^{-10})^3 · 6.07·10^6 · 6.02·10^{23} = 1927.6$ g/mol, then $M(M_3O_4) = M_{U.C.}/Z = 240.95$ g/mol, thus M(M) = 58.98 g/mol. Therefore, unknown metal is Co. **A** – Co_3O_4. Since the molar masses of cobalt and nickel are close, the oxide Ni_3O_4 can be assumed as an alternative answer; however, this answer is incorrect, since the colour of nickel salts' solutions cannot be pink, and the ammonia complexes for Ni^{+3} are unknown. According to the strong oxidizing properties of Co_3O_4 under the action of HCl, a redox process occurs with the emitting of chlorine:

$$Co_3O_4 + 14HCl = 3H_2[CoCl_4] + Cl_2 + 4H_2O;\ \mathbf{B} – [CoCl_4]^{2–}$$

A blue coordination complex $[CoCl_4]^{2–}$ is formed in excess of chloride ions. In this complex cobalt is in a tetrahedral environment of chloride ions. It is the tetrahedral coordination of cobalt defines the blue coloration. However, upon dilution with water, both the type of ligands and the coordination polyhedron – tetrahedron $[CoCl_4]^{2–}$ – are transformed into the cation $[Co(H_2O)_6]^{2+}$, which gives the solution a red-pink colour:

$$H_2[CoCl_4] + 6H_2O = [Co(H_2O)_6]Cl_2 + 2HCl;\ \mathbf{C} – [Co(H_2O)_6]^{2+}$$

When an excess of ammonia is added, it is reasonable to assume competition between water and ammonia molecules in the coordination environment of the cobalt ion. Since the molar mass of the coordination complex ion **D** is 6 g/mol less than the molar mass of $[Co(H_2O)_6]^{2+}$, and the molar mass of NH_3 is 1 g/mol less than the molar mass of H_2O, we can conclude that all 6 water molecules are replaced by ammonia molecules:

$$[Co(H_2O)_6]Cl_2 + 6NH_3·H_2O = [Co(NH_3)_6]Cl_2 + 12H_2O;\ \mathbf{D} – [Co(NH_3)_6]^{2+}$$

When air is passed into the $[Co(NH_3)_6]Cl_2$ solution, cobalt is oxidized by oxygen to the oxidation state +3. The presence of activated carbon affects the qualitative composition of the resulting coordination complex. Since the molar mass of **F** is 35.5 g/mol more than the molar mass of chloride **D** ($[Co(NH_3)_6]Cl_2$) and taking into account the increase in the oxidation state of cobalt, we assume that coordination complex compound **F** contains one more chloride ion. Then the formula of **F** is $[Co(NH_3)_6]Cl_3$. The molar masses of **E** and **F** differ by 17 g/mol – this is the molar mass of an ammonia molecule, therefore, one of the ammonia molecules was replaced by a chloride ion in the nearest coordination environment of cobalt, then the composition of **E** is $[Co(NH_3)_5Cl]Cl_2$. Reactions equations for the oxidation of the ammonia complex of cobalt(+2) (0.75 points for each compound and equation of the reaction, 8.25 points in total):

$$4[Co(NH_3)_6]Cl_2 + O_2 + 4NH_4Cl = 4[Co(NH_3)_5Cl]Cl_2 + 8NH_3 + 2H_2O;$$

E – $[Co(NH_3)_5Cl]Cl_2$

(или $4[Co(NH_3)_6]Cl_2 + O_2 + 4NH_4Cl + 6H_2O = 4[Co(NH_3)_5Cl]Cl_2 + 8NH_3{\cdot}H_2O$)

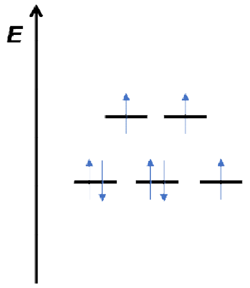
$$4[Co(NH_3)_6]Cl_2 + O_2 + 4NH_4Cl = \text{С}_{\text{акт}} = 4[Co(NH_3)_6]Cl_3 + 4NH_3 + 2H_2O;$$

F – $[Co(NH_3)_6]Cl_3$

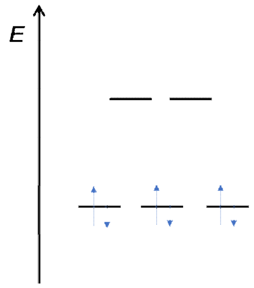
(или $4[Co(NH_3)_6]Cl_2 + O_2 + 4NH_4Cl + 2H_2O = \text{С}_{\text{акт}} = 4[Co(NH_3)_6]Cl_3 + 4NH_3{\cdot}H_2O$)

5. In **D**, cobalt has the +2 oxidation state and contains 7 electrons at the *d*-orbitals. According to the given value of μ_{eff} = 3.87 mB, S = 3/2, therefore, 3 of 7 *d*-electrons are unpaired, which determines the paramagnetic properties of the compound. **F** is a diamagnetic, i.e. does not contain unpaired electrons. The oxidation state of cobalt is +3 in **F**, hence all 6 *d*-electrons are paired. The distributions of electrons are shown below (0.75 points for each diagram).

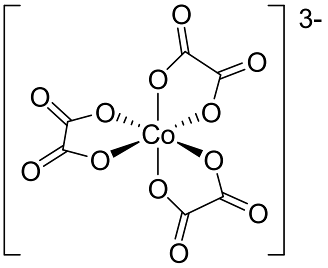
For **D**:

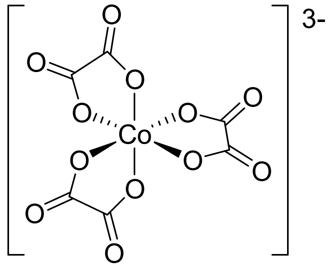


For **F**:



6. When potassium oxalate and hydrogen peroxide are added to a solution of Co^{2+} salts, potassium oxalatocobaltate(+3) can be obtained – a substance of dark green colour. Let's calculate the amount of crystallization water. Suppose the composition is $K_3[Co(C_2O_4)_3]{\cdot}nH_2O$, then $\omega(H_2O) = n{\cdot}18/(440 + n{\cdot}18) = 0.0756$, whence $n = 2$. Thus, **G** is $K_3[Co(C_2O_4)_3]{\cdot}2H_2O$ (0.75 points). Coordination complex ion $[Co(C_2O_4)_3]^{3-}$ contains three identical bidendate ligands – oxalate anions – the relative arrangement of which in the octahedral complex is possible in the only way, therefore, there will be no geometric isomers. However, in such a particle there is no center or plane of symmetry, and the cobalt atom is chiral. Therefore, there will be 2 optical isomers – enantiomers, which are mirror image of each other (0.75 points for each isomer, 2.25 points in total):





Problem 2 (author Kandaskalov D.V.)

1. Knowing the ratio of the mass fractions of the metal in the corresponding fluorides, one can determine the metal: M_M / (M_M + 4·19) = 1.14·M_M / (M_M + 6·19). Solving this equation, we find M_M = 195.4 g/mol (calculation 0.25 points), the unknown metal is platinum **M** = **Pt** (**M** 0.25 points).

Since the same salt **H** can be obtained by the reaction of unknown substances with PtF_4 and PtF_6, it can be assumed that the binary compound **J** contains fluorine. If the mass fraction of fluorine is 45.7%, we find the equivalent of the second element (denote it by ε):

$$\frac{\omega(F)}{\omega(\varepsilon)}=\frac{M_{eq}(F)}{M_{eq}(\varepsilon)}\Rightarrow\frac{45.7}{54.3}=\frac{19}{M_{eq}(\varepsilon)}\Rightarrow M_{eq}(\varepsilon)=22.5\text{ g/mol}$$

which does not match any element.

Assuming that the mass fraction of fluorine 54.3%:

$$\frac{54.3}{45.7}=\frac{19}{M_{eq}(\varepsilon)}\Rightarrow M_{eq}(\varepsilon)=16\text{ g/mol}$$

We find the equivalent of 16 g/mol, which corresponds to S^{2+}, Mo^{6+} or O_2^{2+}. The left side of the transformation scheme (hydrolysis, ozonolysis) suggests that one of the elements should still be oxygen, not sulfur or molybdenum. Oxygen is a substance **Y**. Variant **Y** – O_3 is not suitable, since in many reactions **Y** is one of the products. So **J** is O_2F_2 (for **J** and **Y**, 0.75 points each). Let us now study in detail the substances **C**, **D** and **G**. They are oxygen compounds of the element to which the simple substance **X** corresponds. The condition of the problem indicates that when **C** is formed from **D**, the amount of **C** is one third less than the amount of **D**. If we designate oxide **C** as XO_n, and oxide **D** as XO_m, the reaction can be schematically written:

$${}^{n}\!/_{m}\,XO_m\rightarrow 1XO_n+\frac{{}^{n}\!/_{m}-1}{a}X_a\Rightarrow\frac{n}{m}=1.5$$

We can see from the reaction that if **D** is one third less than **C**, then n/m = 1.5. Therefore, **D** is XO_2, and **C** is XO_3 (0.75 points each for **D** and **C**). **G** can be X_2O_7 or XO_4 in turn. If barium salts have only one **X** atom, then **X** must necessarily have an even oxidation state, then the oxide **G** = XO_4. (**G** 0.75 points).

We now turn to a quantitative analysis of the problem.

Let's analyze barium salts **E** and **F**. Each salt we can write in the form of oxides: **E**: kBaO·XO_3 and **F**: pBaO·XO_4. Assuming that the structure of the anions of both salts is the same, then the number of oxygen atoms should be the same. We can now write the salt **F** as: (k – 1)BaO·XO_4. The ratio of masses is proportional to the ratio of molecular masses, since salts have the same number of **X** atoms. Let's denote the atomic mass of **X** by x. We get the following equation:

$$\frac{M(E)}{M(F)}=\frac{153\cdot k+x+16\cdot 3}{153\cdot(k-1)+x+16\cdot 4}=1.273\Rightarrow x=\frac{161.3-41.77k}{0.273}$$

We can analyze the possible values of k (k is the number of formula units of barium oxide in the salt); k is at least 2, but based on the obtained equation, it cannot be more than 3. If k=2, then x = 285 g/mol (element is not exist), if k = 3, then x = 131.8 g/mol, it corresponds to xenon.

E – Ba_3XeO_6, **F** – Ba_2XeO_6. As a result we find the remaining substances: **X** – Xe, **A** – XeF_4, **B** – XeF_6 (0.75 point for each **E**, **F**, **A**, **B**, **X**, 7 points in total).

2. Based on the reaction with equimolar amounts of the starting materials O_2F_2 and PtF_4, the molecular formula of the salt is $O_2[PtF_6]$. Taking into account the proportions, the formula of substance **I** is $XePt_2F_{12}$.

In $O_2[PtF_6]$ the O_2^+ cation has a charge of +1 (based on the problem statement), then platinum has an oxidation state of +5 in both complexes. The presence of only one signal in the ^{19}F-NMR spectrum of **H** indicates that there is no formation of oligonuclear complexes of the $[Pt_nF_m]$ type, in which nonequivalent fluorine atoms are present. One signal in the NMR spectrum shows that no complexes are formed, such as PtF_5^{x-}, where there are 2 non-equivalent positions of fluorine atoms. Taking into account that the cations in the salts have the same number of atoms (2), the cation in **I** should be XeF^+, and the anion $[Pt_2F_{11}]^-$.

H – $O_2[PtF_6]$, **I** – $XeF[Pt_2F_{11}]$ (0.75 points for each correct structure, 1.5 points in total).

3. (the reaction with ozone is 0.5 points, the remaining 12 reactions are 0.25 points each, 3.5 points in total)

$Xe + 2F_2 \rightarrow XeF_4$

$XeF_4 + F_2 \rightarrow XeF_6$

$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

$XeF_4 + 2H_2SO_4 \rightarrow XeO_2 + 2SO_3 + 4HF$

$3XeO_2 \rightarrow 2XeO_3 + Xe$

$XeO_2 \rightarrow Xe + O_2$

$XeO_3 + 3Ba(OH)_2 \rightarrow Ba_3XeO_6 + 3H_2O$

$XeO_3 + 2Ba(OH)_2 + O_3 \rightarrow Ba_2XeO_6 + 2H_2O + O_2$

$Ba_2XeO_6 + 2H_2SO_4 \rightarrow XeO_4 + 2BaSO_4 + 2H_2O$

$XeO_4 \rightarrow Xe + 2O_2$

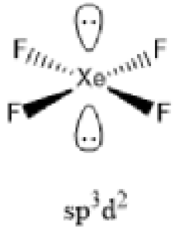
$O_2F_2 + PtF_4 \rightarrow O_2[PtF_6]$

$O_2 + PtF_6 \rightarrow O_2[PtF_6]$

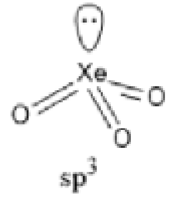
$Xe + 2PtF_6 \rightarrow XeF[Pt_2F_{11}]$

4. (0.5 point for structure with hybridization, 2 points in total)

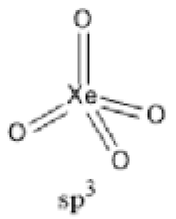
A



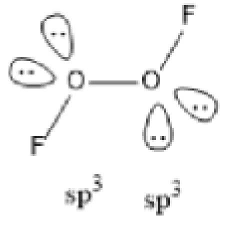
C



G



J



Problem 3 (authors Rozatzev G.M., Shwarzman V.E.)

1. We denote the complex Vaska $[Me(CO)_a(PPh_3)_bCl_c]$, then Me content in it is: $A_{Me}/M_{CV} = 0.2463$, and $M_{CV} = A_{Me}/0.2463$. If **CV** is mononuclear, then the scheme of its production is $MeCl_n \rightarrow [Me(CO)_a(PPh_3)_bCl_c]$ and $5.97/(A_{Me}+35.5n) = 13.1/(0.84M_{CV})$. After substitution in the resulting equation of the expression for M_{CV} we have $5.97/(A_{Me} + 35.5n) = 13.1\cdot0.2463/(0.84A_{Me})$ and $A_{Me} = 64n$ (2.5 points). Considering yellow colour of **CV** $n = 1$ (Cu) is not suitable, but when $n = 3$ A_{Me}=192 g/mol and Me – Ir, and $MeCl_n$ – $IrCl_3$ (1 point). $M_{CV} = 192/0.2463 = 779.5$ (g/mol). Based on the formula of **CV**, $779.5 = 28a + 262b + 35.5c + 192$ or $28a + 35.5c = 587.5 - 262b$. If P is in trans-position, therefore there are at least two of them (b = 2) and $28a + 35.5c = 63.5$, which corresponds to $a = c = 1$ (0.5 points), **CV** – $[Ir(CO)(PPh_3)_2Cl]$ (1 point). The reaction equation (1 point, 6 points overall):

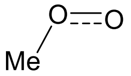
$$IrCl_3 + 2PPh_3 + CH_3OCH_2CH_2OH = [Ir(CO)(PPh_3)_2Cl] + CH_3OCH_3 + 2HCl$$

2. If molar mass **I** more on 4.10% than **CV**, then it is equal $M_I = 779.5\cdot104.1/100 = 811.5$ (g/mol); $\Delta M = 811.5 - 779.5 = 32$ (g/mol), which corresponds to 1 mol O_2 (1 point). Then **I** – $[Ir(CO)(PPh_3)_2Cl(O_2)]$ (0.5 points, 1.5 points in total).

3. O_2 transfer reaction: $[Ir(CO)(PPh_3)_2Cl] + O_2 \rightleftarrows [Ir(CO)(PPh_3)_2Cl(O_2)]$.
Then $K = [Ir(CO)(PPh_3)_2Cl(O_2)] / [Ir(CO)(PPh_3)_2Cl]P_{O2}$ (atm^{-1}). Considering with the yield the equilibrium concentrations are: $[Ir(CO)(PPh_3)_2Cl(O_2)] = 0.7 \cdot 10^{-2} = 7 \cdot 10^{-3}$ (mol/L) (0.5 points); $[Ir(CO)(PPh_3)_2Cl] = 10^{-2} - 7 \cdot 10^{-3} = 3 \cdot 10^{-3}$ (mol/L) (0.5 points); pressure $P_{O2} = 0.171$ atm and $K = 7 \cdot 10^{-3} / 3 \cdot 10^{-3} \cdot 0.171 = 13.6$ (atm^{-1}) (0.5 points, 1.5 points in total).

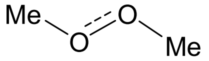
4. (0.5 points for each structure and form of dioxygen, 2 points in total)

1a



O_2^-

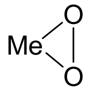
1b



O_2^-

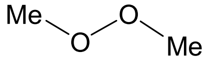
(bond distance l_{o-o} and ν as for superoxide)

2a



O_2^{2-}

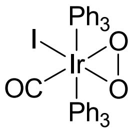
2b



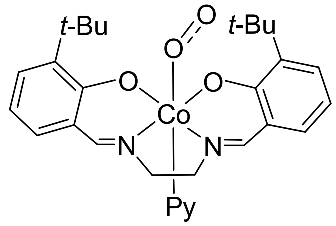
O_2^{2-}

(bond distance l_{o-o} and ν as for peroxide)

5. Characteristics of dioxygen in **II** are close to O_2^{2-} (type **2a**); PPh_3 in trans-positions, as in **CV**. One bond $Co–O_2$ in **III** has characteristics as for type **1a**, the molar ratio complex : pyridine is equimolar (1 : 1). Considering with that the structures **II** and **III** are:



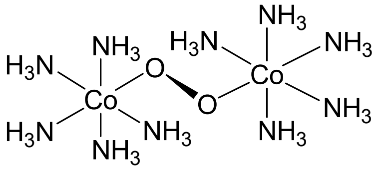
(type **2a**; Ir^{3+}) (0.5 points)



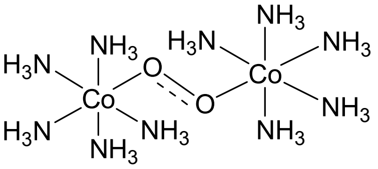
(type **1a**; Co^{3+}) (0.5 points)

The cation **IV** – $[Co_x(NH_3)_yO_2]^{m+}$ with $M = 59x + 17y + 32$; $W_{Co} = 59x \cdot 100 / M = 36.9$; $W_O = 32 \cdot 100 / M = 10.0$; $59x / 0.369 = 320$; $x = 2$ and $M = 320$ g/mol. Then considering with x and molar mass of M we find y: $320 = 118 + 17y + 32$; $y = 10$ (quantity of ammonia).

Cations: **IV** – $[Co_2(NH_3)_{10}O_2]^{4+}$ (1 point) и **V** – $[Co_2(NH_3)_{10}O_2]^{5+}$ (1 point) have structures:



(type **2b**; Co^{3+}) (0.5 points)



(type **1b**; Co^{3+}) (0.5 points)

In complex **V** EPR data refute the possible combination Co^{2+} and Co^{4+}, and magnetic moment indicates one unpaired electron in O_2^- (4 points in total)