53rd International Chemistry Olympiad

Mock Olympiad

Theoretical Tour

Химический факультет МГУ имени М.В. Ломоносова

22 ноября 2020 г.

Translated by Igeru#8910

Click to open the original version

Problem 1. Spinel (10 points)

Question	**1**	**2**	**3**	**4**	**5**	**6**	**Total**
Points	1	2	2	2	1.5	1.5	**10**

Nitrates of metals X and Y were mixed in 1:2 ratio and heated to get a phase with a spinel structure. X nitrate reacts with ammonia, forming a white amorphous hydroxide precipitate, which is dissolved in the excess of the reagent. Y nitrate forms an amethyst-coloured hydrate, which upon dissolution in water forms a yellowish solution that becomes transparent only when strongly acidified with nitric acid.

1. Write down the formula of the spinel.

2. Examine the structure of X and Y hexa-aquo ions from the position of CFT.

3. Calculate the CFSE for two aquo complexes.

4. In the spinel structure, two thirds of the cations have octahedral arrangement and one third has tetrahedral arrangement. Based on CFT, predict the coordination number of each cation in the obtained spinel.

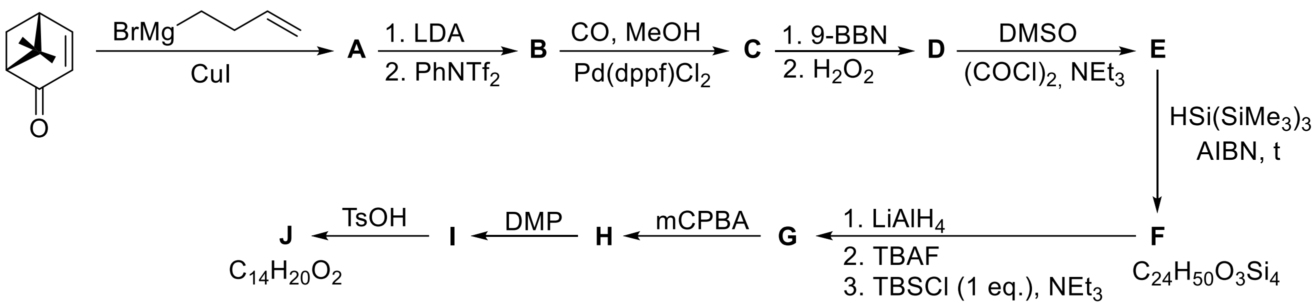
5. Give the structural formula of three different cations that form upon the hydrolysis of X hexa-aquo cation.

6. Propose a method of synthesis of anhydrous X nitrate starting from the metal. Write the reaction equations and specify the conditions.

Problem 2. Total synthesis (10 points)

Question	1	Total:
Points	10	**10**

The fragment of total synthesis of a natural terpenoid is given below:



Draw the structure of compounds A–J, if it's known that:

- a bicyclic compound F doesn't have any bridge carbon atoms;
- the stereoselectivity of G to H conversion is regulated by hydrogen bonding;
- in ^{1}H NMR spectra of compound G there is a singlet around 6,7 ppm.

When drawing structural formulas, show the stereochemistry using wedge and dash projections.

Used abbreviations:

LDA – lithium diisopropylamide

Tf –trifluoromethanesulfonyl

dppf – 1,1'-bis(diphenylphosphino)ferrocene

9-BBN – 9-borabicyclo[3.3.1]nonane

DMSO – dimethylsulfoxide

AIBN – 2,2'-azobis(isobutyronitrile)

TBAF – tetrabutylammonium fluoride

TBS – tert-butyldimethylsilyl

mCPBA – meta-chloroperoxybenzoic acid

DMP – Dess-Martin periodinane

Ts – para-toluenesulfonyl

Answer sheet:

Structural formulas (including stereochemistry)

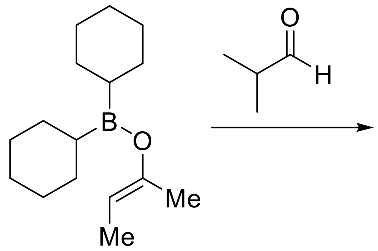
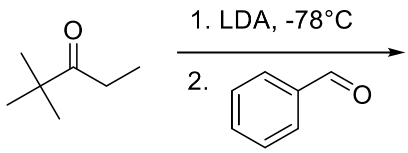
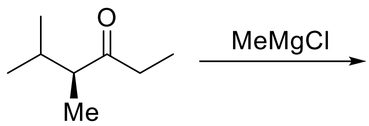
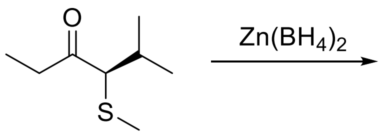
A	**B**
C	**D**
E	**F**
***G**	**H**
I	**J**

Problem 3. Stereoselectivity of nucleophilic addition (10 points)

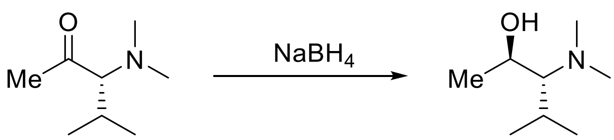
Question	1	1	Total:
Points	8	2	**10**

Stereoselectivity of nucleophilic addition to the carbonyl group is of great importance in synthesis of complicated organic molecules.

1. Provide the major products of the reactions given below. For each product, specify, does it form as an only product or a racemate. For racemates, showing the structure of one enantiomer is sufficient.

	Reaction	Major product	Racemate or one isomer?
A)			
B)			
C)			
D)			

2. Explain the stereoselectivity of the following reaction:

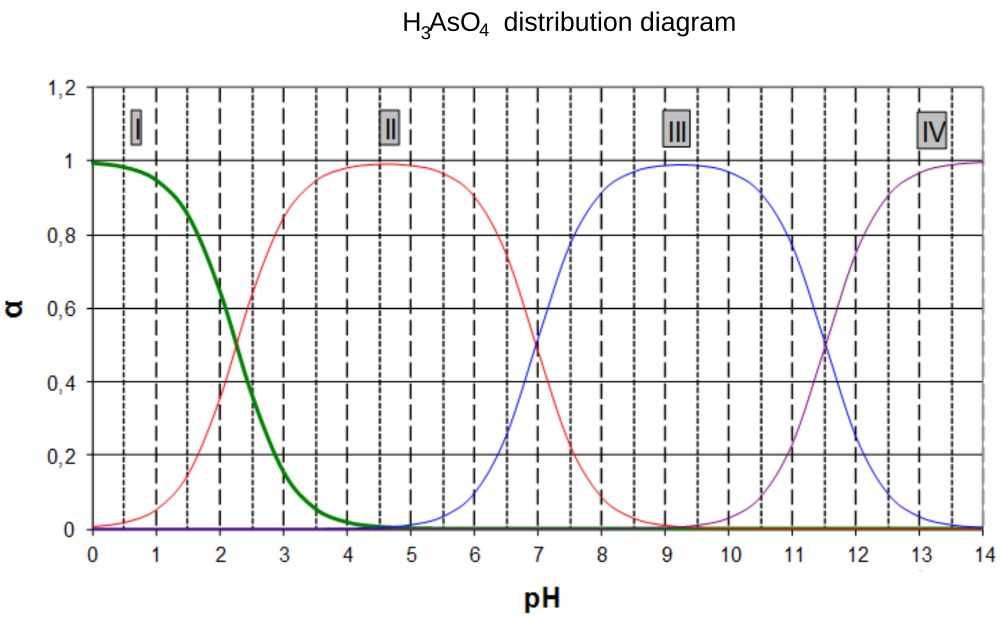


Using the Newman projection draw the reactive conformation and the direction of the nucleophilic attack.

Problem 4. Equilibria in the arsenic acid solutions (10 points)

Question	1	2	3	4	5	6	7	8	9	10	Total:
Points	2	3	4	2	6	1	4	2	2	2	28

A distribution diagram (graph of the dependance of the ratio of As-containing species on the pH) for arsenic acid is given on the graph.



1. Determine, which As-containing species do graphs I, II, III, IV correspond to.

I	II	III	IV

2. Using the graph, estimate all dissociation constants for arsenic acid.

3. Write down the exact mathematical equation (of constants and $[H^+]$) for the curve I (green). How can this equation be simplified at pH=2?

4. At what pH will the concentration of hydroarsenate ions be 2020 times greater then the concentration of dihydroarsenate ions?

5. Calculate the pH of 0,2020M and 10^{-6} M sodium dihydroarsenate aqueous solutions.

pH=_______ at 0.2020M, pH=_______ at 10^{-6} M

6. Will the $H_3AsO_4 - KH_2AsO_4$ solution be a good buffer? Explain.

7. Draw the titration curve of H_3AsO_4 with an alcali (pH = f(V_{alcali})) schematically and show on your graph the pH values that correspond to pK_3 and $(pK_1 + pK_2)/2$.

8. The existence of metaarsenic acid $HAsO_3$ is assumed. Compare pK_1 (H_3AsO_4) and pK_1($HAsO_3$) by estimating their difference.

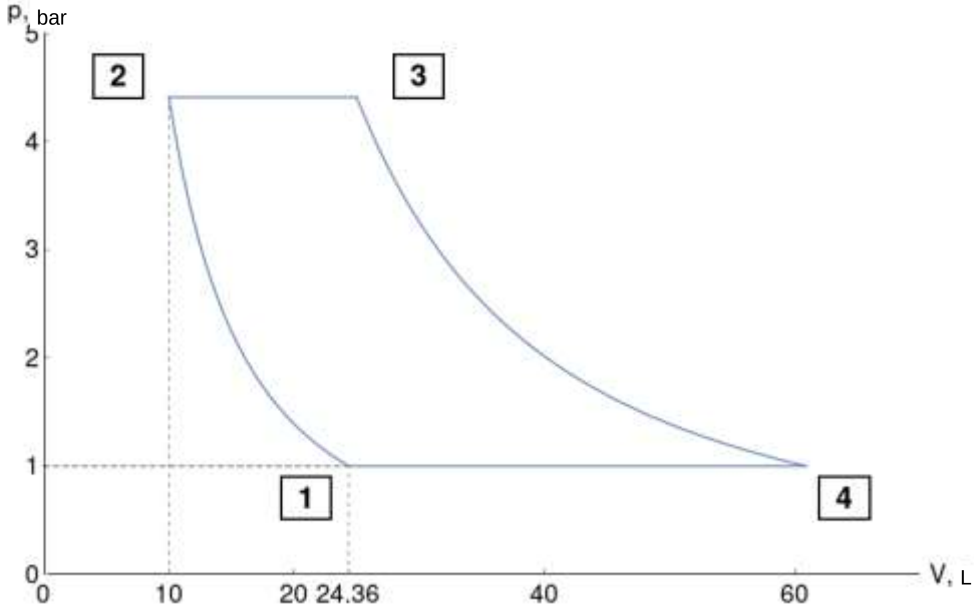
9. Consider liquid ammonia as a solvent. What particles act as an acid and a base in this substance?

10. How will H_3AsO_4 acidity change in ammonia in comparison to water? Explain.

Problem 5. Brayton cycle (10 points)

Question	1	2	3	4	5	Total:
Points	1	2	4	1	2	10

A Brayton cycle for 1 mole of helium is given on the picture. Transitions 1 → 2 and 3 → 4 are adiabatic, 2 → 3 and 4 → 1 are isobaric. All processes are reversible.



1. Choose a direction (clockwise or anticlockwise) in which the cycle functions as a heat engine (produces work).

2. Draw the cycle (qualitatively) in T – S coordinates.

3. Energy conversion efficiency of the Brayton cycle is $\eta = 1 - (p_1/p_2)^x$. Calculate x, if p_1 is the pressure of the gas in point 1 and p_2 is the pressure of the gas in point 2.

Hint: use the adiabatic equation in the form of f(p, T) = const

4. Calculate the energy conversion efficiency of the cycle shown on the picture above.

5. A similar cycle was launched in the opposite direction so that it functions as a heat pump. Calculate the coefficient of performance of such a heat pump.

Important formulas:

Adiabatic equation: pV^{γ} = const, $\gamma = C_p/C_V$

Energy conversion efficiency of a heat engine: $\eta = W/Q_h$, where W is produced work, Q_h is heat transferred from the hot reservoir;

Coefficient of performance of a heat pump: Q_c/W, W is required work, Q_c is heat transferred from the cold reservoir.

Problem 6. Kinetics of infection (10 points)

Question	1	2	3	4	5	6	7	Total
Points	2	3	3	6	2	2	2	20

Biological and biochemical processes often involve an autocatalytic step. For example, the simplest model of spreading of an infectious disease contains an autocatalytic step. in this model there is an infection step:

$$S + I \rightarrow I + I, \qquad k_I;$$

where S is healthy population, I are the infected ones. After that, the infected ones either recover and get the immunity (R), or die (D):

$$I \rightarrow R, \qquad k_R;$$
$$I \rightarrow D, \qquad k_D.$$

1. Write the system of differential equations that corresponds to the suggested scheme, using the ratio of healthy population S, the ratio of the infected ones I, the ratio of those who have immunity R and the ratio of lethal cases D as variables.

2. How will the following events affect the suggested scheme? (Will the rate constants change? How? Will new equations appear?)

a) Quarantine measures are introduced
b) The production of a drug that had shown high anti-infective activity has started
c) Mass vaccination of the population has started.

3. Express the rate of change of the ratio of the infected population dI/dt from I and a rate constant. Consider that in the beginning stages R and D are much less than S and I.

The solution of the differential equation from the last question is the function:

$$\ln\frac{I}{1-I} = at + C.$$

In the table the data on the amount of infected per 1 million is given:

N	0.76	1.52	2.46	4.04	6.74	10.29	16.03	24.68
t, days	0	2	4	6	8	10	12	14

4. Calculate the parameters a and C.

5. According to this model, after how many days the number of ill people will double in comparison to day 14?

6. According to this model, after how many days every 1000th will be infected?

The disadvantage of the suggested model is that, according to this model only one epidemic "wave" is possible. The second and other "waves" appear if the time-dependent rate constants are used. For example, if $k_I = k/t^h$, two "waves" are possible.

7. Explain qualitatively, why does the second "wave" appear using this description.

Problem 7. Labels in primary metabolism (10 points)

Question	1	2	3	4	5	6	7	8	9	Total
Points	3	1	2	1	2	2	3	4	2	**20**

Labeled compounds are widely used by researchers for establishing the sequence of steps in metabolic pathways and clarifying the mechanism of the occurring reactions. In this problem you are asked to analyze the results of such a research related to primary metabolism.

D-glucose completely labeled at the third carbon atom was involved in the glycolysis. Glycolysis was conducted in anaerobic conditions by a culture doing alcoholic fermentation.

1. Draw the product in which the label will be found. If applicable, show the position of the label.

2. What is the ratio of the labelled product?

In another experiment the citric acid cycle was researched. For this purpose, acetyl-CoA labelled at the carboxylic carbon atom was fed into it. Based on the structure of the citrate that was forming upon the reaction of acetyl-CoA with oxaloacetate, researchers expected to get a mixture of 2-ketoglutarate molecules, labelled at the 1st and 5th carbon atoms. However, it was found that 2-ketoglutarate contains a label only at the position 5.

3. Explain the reason that lead to the unexpected result. A reminder: all steps of the cycle are catalyzed by enzymes.

Sodium fluoroacetate is used as a rodent control agent. It's extremely toxic and event small quantities of this compound getting into the organism can be fatal. Having gotten into the cells, the fluoroacetate-anion turns into fluoroacetyl-CoA and incorporates into the citric acid cycle in this form, which leads to the accumulation of iso-citrate in the cells and decrease in concentration of other intermediates.

4. At which step does the cycle "stall"?

5. How many full turns can the cycle do before halting after the fluoroacetyl-CoA molecule incorporation into the cycle?

6. Draw the final product of the fluoroacetyl-CoA transformation in the cycle. Mark the 1st carbon atom.

7. What compound present in a variety of fruits should be introduced into the organism after the ingestion of fluoroacetate-anion to "restart" the citric acid cycle? Explain the mechanism of its action.

Gluconeogenesis, catalyzed by rat liver slices, occurs in the $^{14}CO_2$ atmosphere. Gluconeogenesis process starts from the piruvate, and the first pathway involves the following steps:

A) piruvate transfer from the cytosol to the mitochondrial matrix;
B) carboxylation of piruvate with the formation of oxaloacetate;
C) reduction of oxaloacetate to malate;
D) transfer of malate from the mitochondrial matrix to the cytosol;
E) oxidation of malate to oxaloacetate;
F) decarboxylation of oxaloacetate with the formation of phosphoenolpiruvate, after which the same intermediates are involved in the pathway to glucose as in glycolysis.

It was found that upon the oxaloacetate decarboxylation, the atom that leaves the carbon atom is the one that was introduced to the piruvate in the carboxylation step, but some ammount of label is found in the synthesized glucose.

8. Because of conjugation of gluconeogenesis with which process is the label found in glucose? Explain the mechanism of the label migration.

9. At which position(s) will the label be found?

Problem 8. Simple questions on polymers (10 баллов)

Question	**1**	**2**	**3**	**4**	**5**	**Total**
Points	2	2	2	2	2	**10**

A sample of polyethylene with a mass of 28.0 g contains $3.01 \cdot 10^{20}$ methyl groups.

1. Calculate the average degree of polymerization and molecular mass of of polyethylene.
If it is impossible, try to give an estimate (more or less of some value) and explain, what additional information is needed for a precise calculation.

A sample of acrilonitrile, butadiene and styrene copolymer contains 85.48% of carbon (mass ratio), 7.92% of hydrogen and nitrogen.

2. Calculate the molar and mass ratio of each of the monomers in the polymer.

3. Write all equations of the chain growth reactions (radical polymerization) which lead to the formation of acrilonitrile-styrene diades. In the equations give the structure of a monomeric unit that contains an active centre (growth radical) and a structure of a monomeric unit obtained as a result of addition, other parts of the macromolecule can be marked as R.

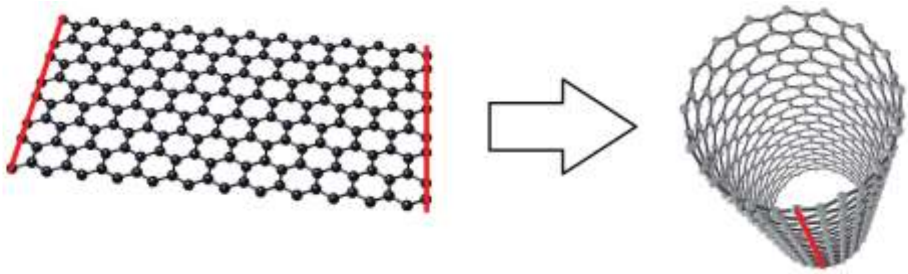
4. What is the molar ratio of acrilonitrile-styrene diades in the copolymer?

5. How many structurally distinct diades (couples of sequential units) can exist in the described copolymer? You don't have to consider optical isomers.

Problem 9. Quantum mechanics of a nanotube (10 points)

Question	1	2	3	4	Total
Points	3	5	5	7	**20**

A rectangular sheet of graphene with the sides ratio of 1:2 was glued to itself along the short side to get a cylindrical nanotube, as shown on the picture:



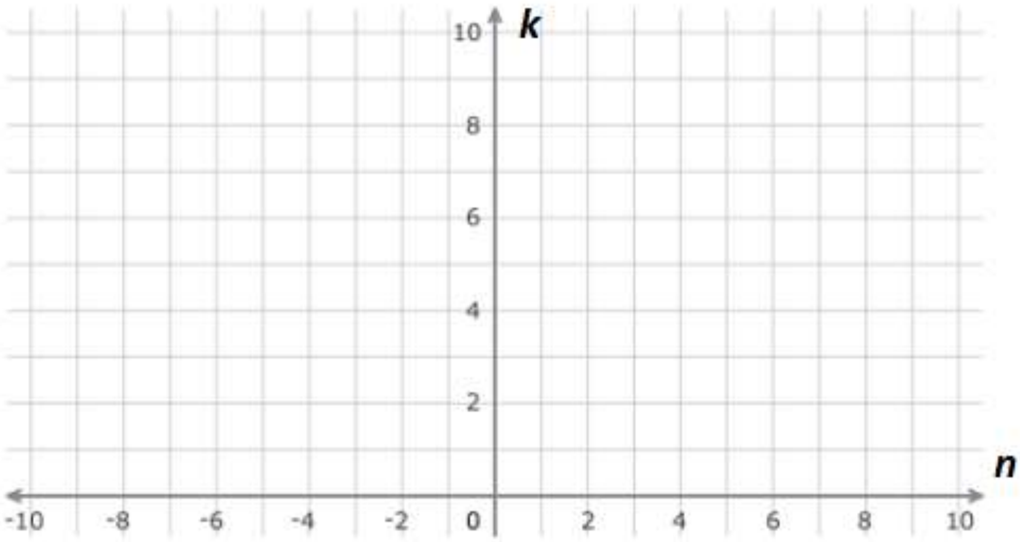
1. Estimate the number of carbon atoms in a nanotube obtained from a 15x30 Å graphene sheet. The length of the C–C bond in a graphene sheet is 1.42 Å.

According to the "particle in a box-particle on a circle" model, π-electrons energy levels in a nanotube having the length L and the radius R is determined by the following expression:

$$E = \frac{\hbar^2}{2m_e R^2} n^2 + \frac{\hbar^2 \pi^2}{2m_e L^2} k^2; \quad n = 0, \pm 1, \pm 2, ...; \quad k = 1, 2, 3, ...$$

where $\hbar$ = $1.055 \cdot 10^{-34}$ J/s, m = $9.109 * 10^{-31}$ kg).

2. Considering that every carbon atom provides one π-electron, mark the quantum numbers of the occupied orbitals in the nanotube described above with dots on the graph below. If you couldn't determine the number of π-electrons in the nanotube, consider it equal to 100.



3. What is the energy of the highest occupied level in this nanotube?

4. Estimate the energy of the highest occupied leven in a nanotube obtained in a similar way from a 1x2 micrometers graphene sheet.