

# **54 International Olympiad of Schoolchildren in Chemistry**

## **Qualifying Olympiad Theoretical round**

**Department of Chemistry, Lomonosov Moscow State  
University June 17, 2022.**

## General guidelines

- This set of theoretical round tasks contains 8 problems with answer sheets and occupies 32 pages.
- The maximum possible sum of points is 80.
- The Olympiad is held remotely using the proctoring system.
- You have **5 hours** to complete your assignments.
- The task will appear on the server in your Personal Profile at exactly 10:00 Moscow time. You can print the assignment while remaining in the proctor's field of view. Printing time is not included in the 5 hours allotted for the solution.
- Start work after the proctor commands "Start".
- Wherever required, support your answers with calculations.
- Only the worksheets on which you are completing the assignment, pens, ruler, calculator, water, chocolate bars may be present at the workplace. No electronic devices other than those that communicate with the proctor are allowed.
- **Write the solution only on the answer sheets. The back of the answer sheets can be used as a draft. Drafts will not be scanned or graded.**
- You must immediately stop working after the command sounds "Stop." If you do not stop writing within 1 minute, your result for the whole Olympiad will be canceled.
- After the "Stop" command sounds, only after being instructed to do so by the proctor, start taking photos or scans of all pages of the blank copy. Then compile all photos or scans into a single file labeled with your last name and initials and upload the file to the server. Do not leave the conference until the proctor tells you that the file has been successfully uploaded and is readable.

We wish you the best of luck!

# Periodic table

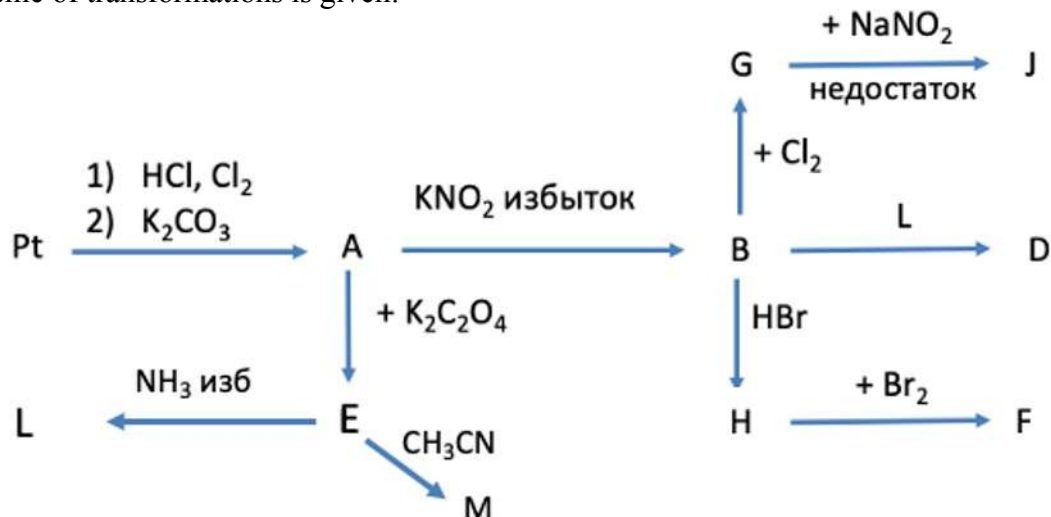
1																								18											
<div>1 H 1.008</div>		2		<div>atomic number</div> <div>Symbol</div> <div>atomic mass</div>														13		14		15		16		17		<div>2 He 4.003</div>							
<div>3 Li 6.94</div>		<div>4 Be 9.01</div>														<div>5 B 10.81</div>		<div>6 C 12.01</div>		<div>7 N 14.01</div>		<div>8 O 16.00</div>		<div>9 F 19.00</div>		<div>10 Ne 20.18</div>									
<div>11 Na 22.99</div>		<div>12 Mg 24.31</div>		3		4		5		6		7		8		9		10		11		12		<div>13 Al 26.98</div>		<div>14 Si 28.09</div>		<div>15 P 30.97</div>		<div>16 S 32.06</div>		<div>17 Cl 35.45</div>		<div>18 Ar 39.95</div>	
<div>19 K 39.10</div>		<div>20 Ca 40.08</div>		<div>21 Sc 44.96</div>		<div>22 Ti 47.87</div>		<div>23 V 50.94</div>		<div>24 Cr 52.00</div>		<div>25 Mn 54.94</div>		<div>26 Fe 55.85</div>		<div>27 Co 58.93</div>		<div>28 Ni 58.69</div>		<div>29 Cu 63.55</div>		<div>30 Zn 65.38</div>		<div>31 Ga 69.72</div>		<div>32 Ge 72.63</div>		<div>33 As 74.92</div>		<div>34 Se 78.97</div>		<div>35 Br 79.90</div>		<div>36 Kr 83.80</div>	
<div>37 Rb 85.47</div>		<div>38 Sr 87.62</div>		<div>39 Y 88.91</div>		<div>40 Zr 91.22</div>		<div>41 Nb 92.91</div>		<div>42 Mo 95.95</div>		<div>43 Tc -</div>		<div>44 Ru 101.1</div>		<div>45 Rh 102.9</div>		<div>46 Pd 106.4</div>		<div>47 Ag 107.9</div>		<div>48 Cd 112.4</div>		<div>49 In 114.8</div>		<div>50 Sn 118.7</div>		<div>51 Sb 121.8</div>		<div>52 Te 127.6</div>		<div>53 I 126.9</div>		<div>54 Xe 131.3</div>	
<div>55 Cs 132.9</div>		<div>56 Ba 137.3</div>		57-71		<div>72 Hf 178.5</div>		<div>73 Ta 180.9</div>		<div>74 W 183.8</div>		<div>75 Re 186.2</div>		<div>76 Os 190.2</div>		<div>77 Ir 192.2</div>		<div>78 Pt 195.1</div>		<div>79 Au 197.0</div>		<div>80 Hg 200.6</div>		<div>81 Tl 204.4</div>		<div>82 Pb 207.2</div>		<div>83 Bi 209.0</div>		<div>84 Po -</div>		<div>85 At -</div>		<div>86 Rn -</div>	
<div>87 Fr -</div>		<div>88 Ra -</div>		89-103		<div>104 Rf -</div>		<div>105 Db -</div>		<div>106 Sg -</div>		<div>107 Bh -</div>		<div>108 Hs -</div>		<div>109 Mt -</div>		<div>110 Ds -</div>		<div>111 Rg -</div>		<div>112 Cn -</div>		<div>113 Nh -</div>		<div>114 Fl -</div>		<div>115 Mc -</div>		<div>116 Lv -</div>		<div>117 Ts -</div>		<div>118 Og -</div>	

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

### Task 1: Platinum transformations (10 points)

Question	1	Total:
Glasses	10	<b>10</b>
Assessment		

A scheme of transformations is given:



It is known that:

**A** - yellow precipitate formed when cooling the solution obtained by interaction of platinum with hydrochloric acid and chlorine and neutralization of the resulting solution with potash.

**B** - colorless crystals formed by evaporation of the solution obtained by boiling **A** with excess potassium nitrite.

**D** is a yellow precipitate formed when the two solutions are mixed.

**E** - red crystals, well soluble in water. They are formed by boiling a solution of substance **A** with potassium oxalate. The solution is evaporated and crystallized.

**F** is orange-red crystals formed when a few drops of bromine are added to a solution of **H**.

**G** - yellow crystals formed when chlorine is passed through solution **B**.

**H** - yellow crystals formed by the action of aqueous HBr solution on solution **B**.

**J** is a pale yellow crystal formed when sodium nitrite is added to a solution of substance **G**. **The filtrate gives a white precipitate with silver nitrate.** The filtrate gives a white precipitate with silver nitrate. There is no inversion center in the anion.

**L** - colorless crystals, well soluble in water. They are formed when the solution is exposed to **E** of a concentrated solution of ammonia.

**M** is a bright yellow precipitate formed when acetonitrile is added to a saturated solution of **E**.

The molecular conductivities of all complexes measured under the same conditions are summarized in the table.

complex	<b>A</b>	<b>E</b>	<b>L</b>	<b>J</b>	<b>D</b>	<b>M</b>	<b>F</b>	<b>G</b>
$\mu$ , Ohm <sup>-1</sup> cm <sup>2</sup>	258.3	262.2	260.8	254.5	165.4	5.0	252.8	260.1

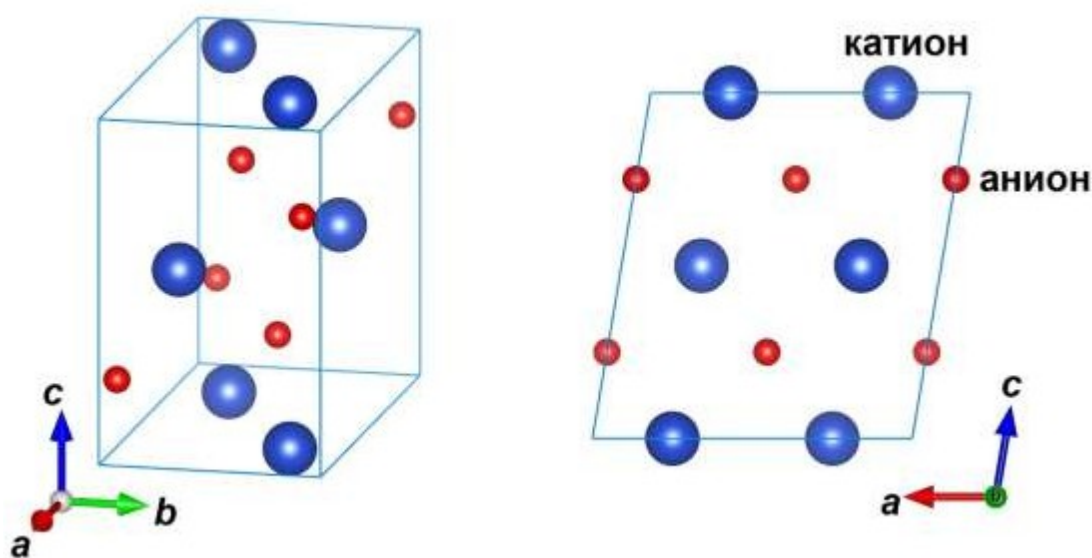
1. depict the structural formulas of the complexes.

<b>A</b>	<b>B</b>	<b>D</b>
<b>E</b>	<b>F</b>	<b>G</b>
<b>H</b>	<b>J</b>	<b>L</b>
<b>M</b>		

## Task 2: Crystallochemistry and TCP (10 points)

Question	1	2	3	4	5	6	7	8	9	10	11	12	13	Total:
Glasses	1	2	1	2	1	3	6	1	3	1	1	1	3	26

**X** - transition metal oxide - crystallizes in a monoclinic unit cell, the general view of which and the projection on the *ac* plane are shown in the figure.



1. Determine the gross composition of the oxide.

Composition X \_\_\_\_\_

2. Determine the coordination numbers and polyhedra for the cation and anion in **X**.

EC (cation) = _____	EC (anion) = _____
KP (cation) _____	KP (anion) _____

When ammonia is passed over **X** at 280°C, dark green crystals of the binary substance **Y** are formed, which crystallizes in the structural type of *anti-ReO<sub>3</sub>*. The structure of *ReO<sub>3</sub>* can be considered as a derivative of the perovskite structure - *CaTiO<sub>3</sub>* - by complete removal of ions from calcium positions.

3. Picture the unit cell of  $\text{ReO}_3$  and determine the number of formula units in it.

Number of formula units  $Z =$  \_\_\_\_\_

Unit cell parameter  $\mathbf{Y}$   $a = 3.72 \text{ \AA}$ , density  $d = 6.60 \text{ g/cm}^3$ .

4. Calculate the molar mass of  $\mathbf{Y}$  and determine its composition.

Molar mass of  $\mathbf{Y} =$  \_\_\_\_\_ g/mol.      Composition  $\mathbf{Y}$  \_\_\_\_\_

5. What type of centering does the unit cell  $\mathbf{Y}$  have?

A) face-centered
B) volume-centered
B) base-centered
D) no centering

6. Determine which Miller indices  $hkl$  the first three reflexes in the diffractogram  $\mathbf{Y}$  have, and calculate their corresponding interplanar distances and  $2\theta$  values. The wavelength of X-ray radiation is  $\lambda = 1.5406 \text{ \AA}$ .

1 reflex $hkl$ = _____ $d_{hkl}$ = _____ Å $2\theta$ = _____ °
2 reflex $hkl$ = _____ $d_{hkl}$ = _____ Å $2\theta$ = _____ °
3 reflex $hkl$ = _____ $d_{hkl}$ = _____ Å $2\theta$ = _____ °

Treatment of **Y** with an excess of concentrated hydrochloric acid leads to the formation of a colorless solution of **P1**. When **P1** is poured into cold water, a white precipitate **O** falls out. In air, solution **P1** quickly acquires a yellow-green color (solution **P2**), and when diluted with water, the color of solution **P2** changes to blue (solution **P3**). It is *known that the complex particle in P3 solution has no spatial isomers*.

7. Write down the equations of these chemical reactions and identify the unknown substances.

<b>X</b> - _____
Education <b>Y</b> :
Interaction of <b>Y</b> with hydrochloric acid:
Dilution of <b>P1</b> with cold water:
<b>O</b> - _____
Formation of a <b>P2</b> solution:
Formation of a <b>P3</b> solution:

8. Why does the **P1** solution have no coloration?

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9. Depict the splitting of the *d-orbitals of the* central atom (without taking into account the Jahn-Teller distortion) in the particles responsible for the coloring in **P2** and **P3** solutions. Indicate the distribution of electrons on the split *d-orbitals*. Sign the group orbitals.

Solution <b>P2</b>	Solution <b>P3</b>

10. Calculate the value of the splitting energy in the complex particle in **P3** solution if the maximum in its absorption spectrum is observed at 610 nm.

$\Delta_{\text{splitting}} = \text{_____ kJ/mol}$

11. How will the wavelength of the maximum in the absorption spectrum change when adding to the solution **P3** potassium oxalate?

A) decrease	B) increase	C) will not change
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When **X** is alloyed with manganese(+3) oxide, a complex oxide belonging to the spinel family is formed ( $\omega(\text{O}) \approx 27\%$ ).

12. Establish the composition of the spinel.

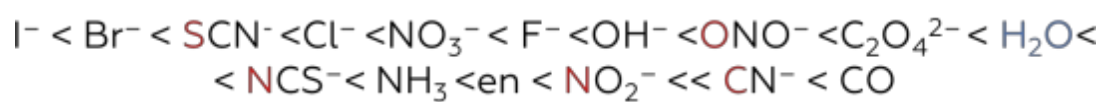
Composition of spinel: \_\_\_\_\_

13. Using crystal field theory, determine the type of spinel. Calculate the EPO for each cation.

Spinel type: A) direct B ) reversed B ) cannot be precisely defined

**Reference data:**

Spectrochemical series of ligands



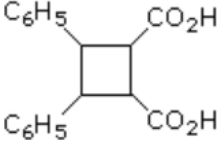
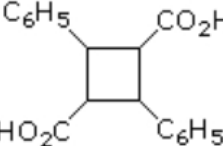
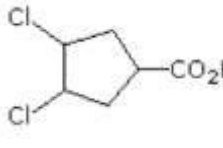
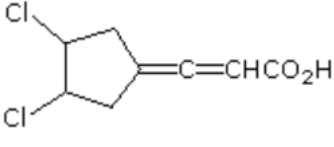
Planck's constant  $h = 6.626 \cdot 10^{-34} \text{ J}\cdot\text{s}$  speed of light

$c = 2.998 \cdot 10^8 \text{ m/s}$

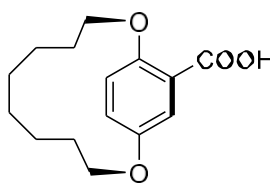
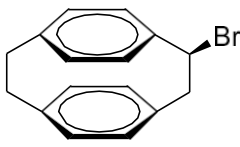
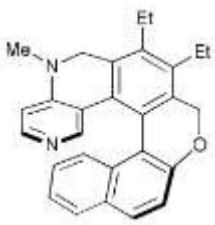
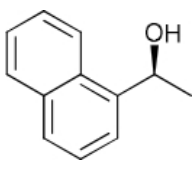
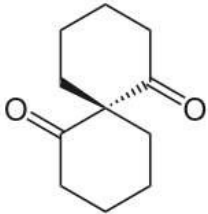
### Task 3: Chirality and Stereoselective Synthesis (10 points)

Question	1	2	3.1	3.2	4.1	4.2	5.1	5.2	Amount
Glasses	6	10	4	2	10	4	12	2	<b>50</b>

1. The following molecules may exist as two or more stereoisomers. These stereoisomers can be classified into enantiomeric pairs and meso-forms. For each of the structures below, determine the total number of stereoisomers, the number of enantiomeric pairs, and the number of meso-forms. Write the values obtained in the table.

Molecule	Total number stereoisomers	Enantiomer pairs	Meso-form
			
			
			
			

2. It is important to be able to distinguish chiral molecules from each other. Different stereochemical descriptors are used to specify the configuration of a chiral molecule. For the following chiral molecules, determine the absolute configuration and indicate it under the structure with the appropriate descriptor (R/S, R<sub>a</sub>/S<sub>a</sub>, R<sub>p</sub>/S<sub>p</sub>, M/P):

3. The choice of Lewis acid can dramatically affect the stereochemistry of the carbonyl group attachment. The interaction of the following aldehyde with silyl-enol ether may lead to the formation of isomeric products **C1** and **C2**, with  $\text{BF}_3$  as the Lewis acid (LA) leading to the formation of **C1** and  $\text{MeAlCl}_2$  leading to the formation of **C2**.



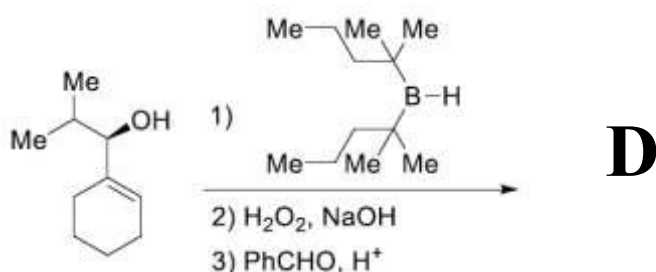
3.1. Depict the structures of compounds **C1** and **C2** with stereochemistry indicated.

Structure <b>C1</b> :	Structure of <b>C2</b>

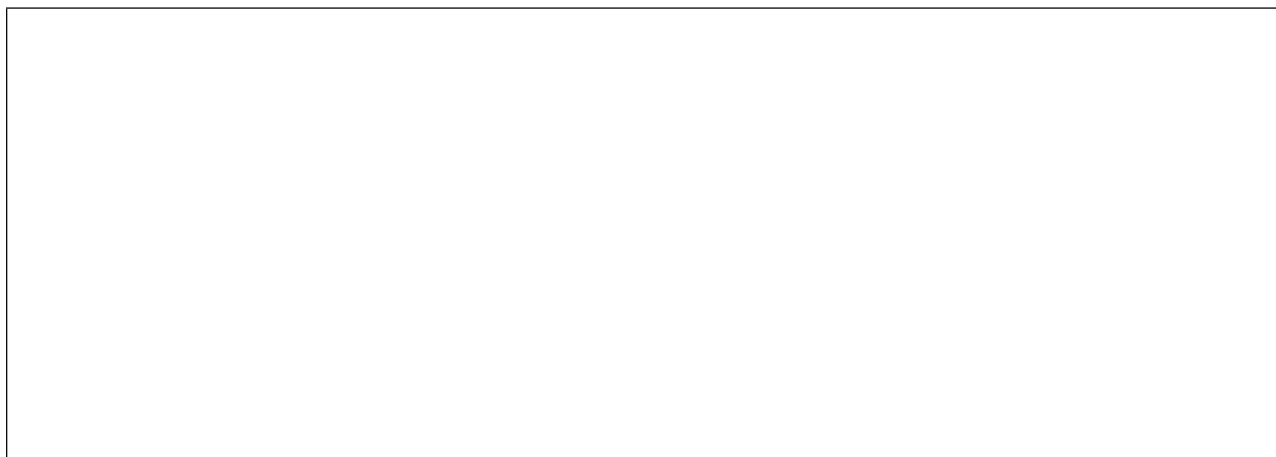
3.2. What are **C1** and **C2** in relation to each other? (Choose one or more correct answers):

- ☒ enantiomers
- ☒ diastereomers
- ☒ epimers
- ☒ structural isomers
- ☒ spatial isomers
- ☒ tautomers

4. Conformation effects have a decisive influence on the stereoselectivity of the process. Determine the structure of the bicyclic product **D**. Note that thermodynamic control is realized in the third step.



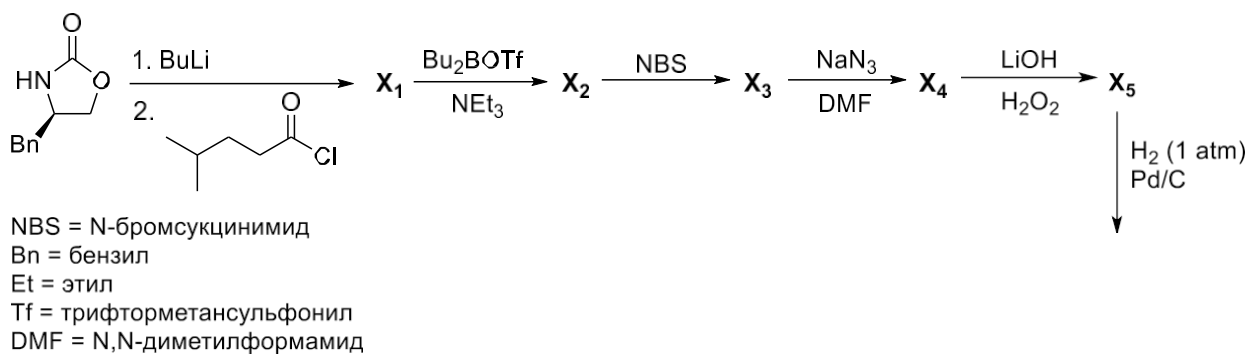
4.1. Depict the structure of compound **D**, clearly labeling the stereochemistry of all asymmetric centers using wedge bonds.



4.2. Draw a stereochemical model of the interaction of reagents at the first stage. Denote the substituents on the boron atom as R.

A stereochemical model:

5. Evans' oxazolidinones are widely used in the asymmetric synthesis of natural compounds and their derivatives. The simplest example of such synthesis is given below:



Y

5.1. Sketch the structure of the intermediates **x1-x5** and the target compound **Y**, indicating the stereochemistry by means of wedge bonds.

<b>x1</b>	<b>x2</b>
<b>x3</b>	<b>x4</b>
<b>x5</b>	<b>Y</b>

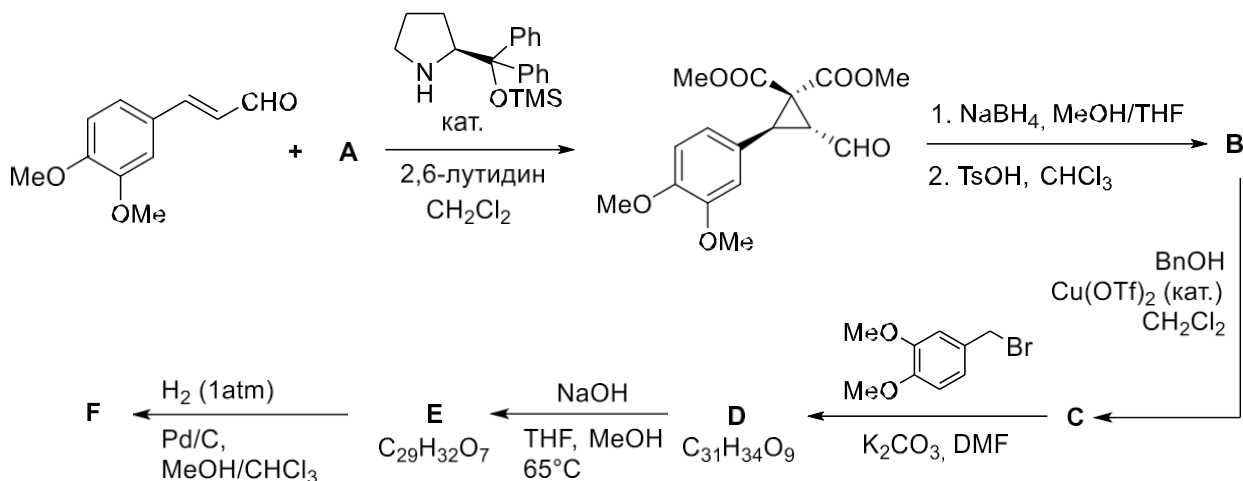
5.2. Which group of natural compounds does substance **Y** belong to? What is the name of the substance **Y**?

<p>Compound Group: _____</p>    <p>Name of substance Y: _____</p>
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#### Task 4: Complete asymmetric synthesis of natural compounds (10 points)

Question	1	2	Total:
Glasses	12	24	36

Donor-acceptor cyclopropanes (DACs) are used in the synthesis of complex natural molecules. The chiral DAC obtained with compound **A** was used in the synthesis of lignan **F** isolated from the plant *Tupistra chinensis*.



1. Determine the structure of compounds **A-F**. Give their structural formulas with stereochemistry where necessary. All stages proceed stereoselectively, and the stereoselectivity of all reactions is determined solely by the steric factor.

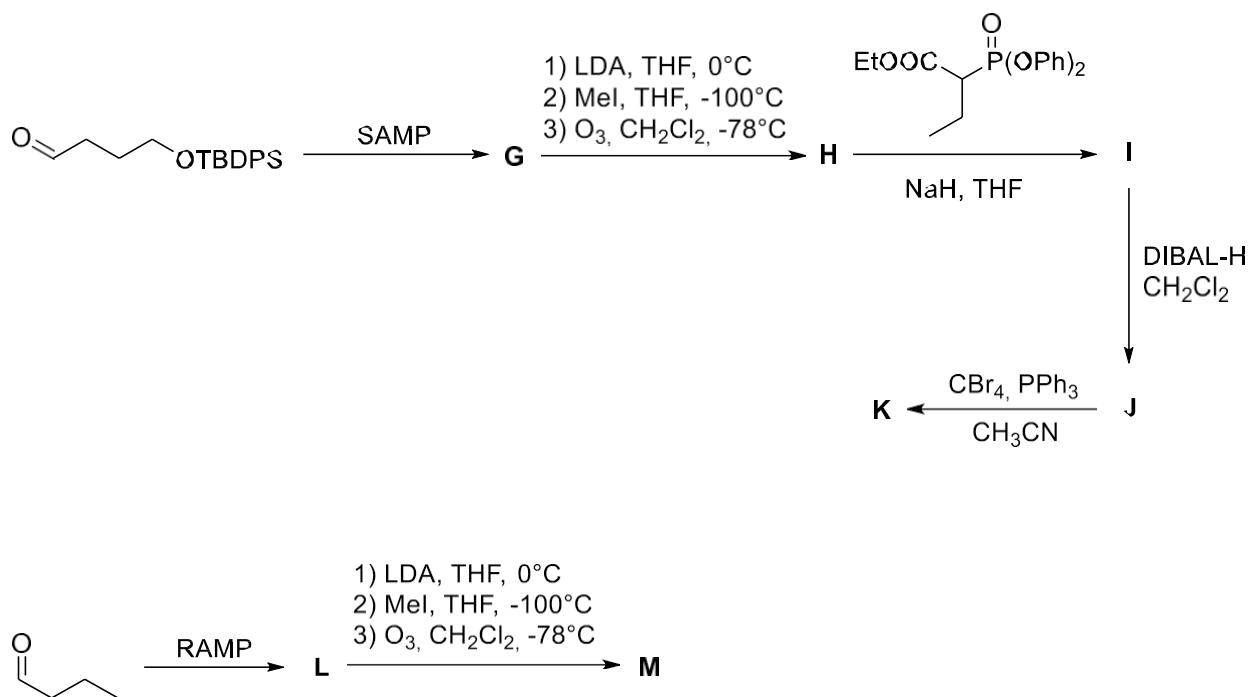
<b>A</b>	<b>B</b>
<b>C</b>	<b>D</b>

<b>E</b>	<b>F</b>

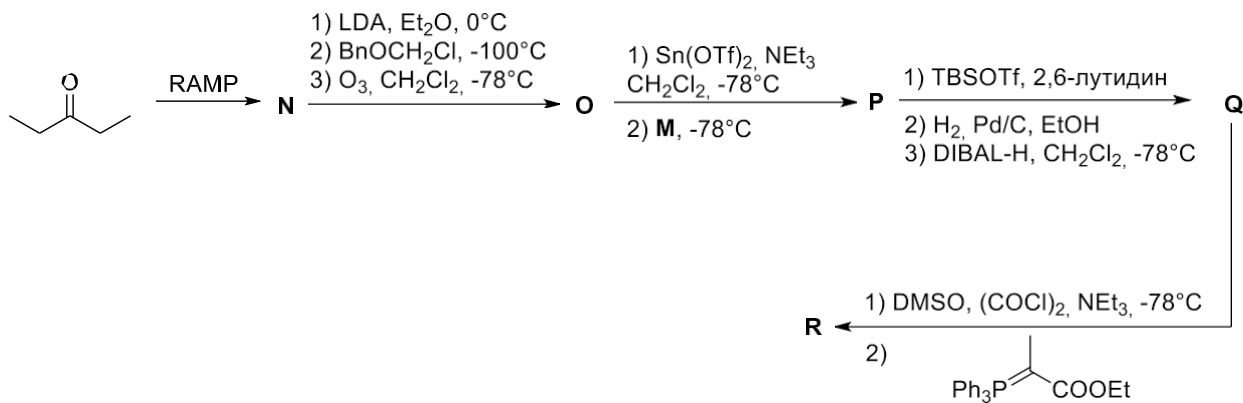
Enders' reagents, the chiral hydrazines SAMP and RAMP, are widely used for asymmetric alkylation of carbonyl compounds.



Enders used SAMP/RAMP alkylation three times in his work on the complete synthesis of some polyketide. The synthesis fragments using SAMP/RAMP are given below:







*Designations:*

TBDPS, *tert*-butyldiphenylsilyl; LDA, lithium diisopropylamide;  
 DIBAL-H, diisobutylaluminum hydride; Bn, benzyl; Tf, trifluoromethanesulfonyl; TBS, *tert*-butyldimethylsilyl

Additionally, it is known that:

- in the  $^1\text{H}$  NMR spectrum of compound **K** a doublet at 5.34 m.d. is present;
- mild enolization with tin triflate gives *Z*-enolate
- The stereochemistry of the stage of obtaining substance **P** is described by the Felkin-An model

2. Determine the structure of **G-R** compounds. Give their structural formulas with stereochemistry where necessary.

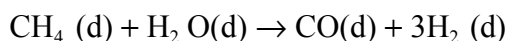
<b>G</b>	<b>H</b>
<b>I</b>	<b>J</b>

<b>K</b>	<b>L</b>
<b>M</b>	<b>N</b>
<b>O</b>	<b>P</b>
<b>Q</b>	<b>R</b>

**Task 5: Methane conversion (10 points)**

Question	1	2	3	4	5	Total
Glasses	8	4	8	4	8	32

Methane conversion reaction



is widely used to produce hydrogen and carbon monoxide, valuable reagents used to produce many chemical products. Most of the hydrogen produced in the world is synthesized by this process. The reaction is usually carried out at temperatures of 800-900° C in the presence of a catalyst, thanks to which equilibrium is established in the reaction mixture in a short time.

Thermodynamic data:

	H <sub>2</sub> (d)	CH <sub>4</sub> (d)	H <sub>2</sub> O(d)	CO(d)
$\Delta_f H^\circ_{298}$ , kJ/mol	-	-74.8	-241.8	-110.5
$S^\circ_{298}$ , J/(mol-K)	130.7	188.7	188.8	197.7
$c_p$ , J/(mol-K)	28.8	34.9	33.5	29.2

Using the above thermodynamic data, calculate  $\Delta_r H^\circ$ ,  $\Delta_r S^\circ$ ,  $\Delta_r G^\circ$  and  $K_p$  for this reaction at 800° C. Remember to consider the temperature dependence of  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  as well:

$$H^\circ (T_2) = H^\circ (T_1) + c_p^\circ (T_2 - T_1)$$

$$S^\circ (T_2) = S^\circ (T_1) + c_p^\circ \ln(T_2/T_1)$$

Response:

$\Delta_r H^\circ =$  \_\_\_\_\_

$\Delta_r S^\circ =$  \_\_\_\_\_

$\Delta_r G^\circ =$  \_\_\_\_\_

$K_p =$  \_\_\_\_\_

2. Determine at what temperatures the reaction is endothermic.

Response: \_\_\_\_\_

3. What would be the yield in this reaction (i.e., methane conversion rate in %) if it were carried out at a constant temperature  $T = 800^\circ \text{C}$ , constant total pressure  $p = 1 \text{ bar}$ , and using a stoichiometric mixture of methane and water vapor as reactants? If you were unable to calculate the equilibrium constant in question 1, use the value  $K_p = 11$  hereafter.

Answer: conversion = \_\_\_\_\_ %

4. How do you need to change the pressure in question 3 to achieve an 80% conversion rate?

The answer is:  $p =$  \_\_\_\_\_

5. How would the answer to question 3 change if you filled a vessel with a stoichiometric mixture of methane and water vapor at  $T = 800^\circ \text{C}$  and a total pressure of  $p = 1 \text{ bar}$ , but then kept the volume, but not the pressure, constant?

Answer: conversion = \_\_\_\_\_%

### Task 6: Electrochemistry of ferrocene derivatives (10 points)

Question	1	2	3	4	5	Total
Glasses	4	4	5	5	2	20

The ferrocenium/ferrocene redox couple ( $\text{Fc}^+/\text{Fc}$ ) is widely used in electrochemical studies. This is primarily due to the fact that this redox process proceeds quantitatively, reversibly, and with the participation of only one electron.

In addition, the standard redox potential, which in the case of ferrocene is  $E^0(\text{Fc}^+/\text{Fc}) = 0.647 \text{ V}$ , can be varied considerably by introducing different substituents.

To study the effect of substituents on the redox potential, the following electrochemical cell was constructed:



where FcX is modified ferrocene. The measurements were carried out at a temperature of 300 K, the cell EMFs for different FcX are given in the table.

$\epsilon$ , mV	-35.92	78.08	215.08	382.08
FcX	FcTMA	FcHM	Fc(t-Bu) <sub>4</sub>	FcMe8

Where TMA denotes trimethylammonium, HM denotes hydroxymethyl, t-Bu denotes tert-butyl and Me denotes methyl.

1. Calculate standard redox potentials for modified ferrocenes.

$$E^0(\text{FcTMA}^+/\text{FcTMA}) \quad \text{B}$$
$$E^0(\text{FcHM}^+/\text{FcHM}) \quad \text{B}$$

$$E^0 (\text{Fc}(\text{t-Bu})_4^+ / \text{Fc}(\text{t-Bu})_4) = \quad \text{B}$$

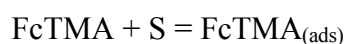
$$E^0 (\text{FcMe}_8^+ / \text{FcMe}_8) = \quad \text{B}$$

Directions. If you were unable to calculate the potential  $E^0 (\text{FcTMA}^+ / \text{FcTMA})$ , assume further that it is 0.680 V.

2. Calculate what the concentration of FcTMA will be once equilibrium is established in the cell.

$$[\text{FcTMA}] = \quad \text{mM}$$

The adsorption of the redox couple  $\text{FcTMA}^+ / \text{FcTMA}$  was studied. It was shown that the oxidized form is practically not adsorbed, while the reduced form can be adsorbed, the adsorption obeying the Langmuir isotherm:



3. Derive the equation relating the concentration of  $[\text{FcTMA}^+]$ , the adsorption constant, the degree of filling  $\theta$ , and the redox potential for particles in solution  $E(\text{FcTMA}^+ / \text{FcTMA})$ .



The table shows the dependence of the amount of adsorbed FcTMA on the electrochemical potential in solution. The experiment was carried out at a temperature of 300 K, the concentration of the oxidized form was kept constant  $[\text{FcTMA}^+] = 1,000 \text{ mM}$ .

$\nu(\text{FcTMA}), \mu\text{mol/m}^2$	0.183	0.539	0.893	1.262	1.621
$\varepsilon, \text{V}$	0.743	0.708	0.686	0.644	0.629

4. Determine the adsorption constant  $K$  and the maximum number of moles adsorbed by the surface.

$K = \text{_____} \text{M}^{-1} \nu_{\text{vmax}} = \text{_____} \mu\text{mol/m}^2$

5. Calculate the redox potential for the half-reaction.  $\text{FcTMA}^+ + \text{e}^- + \text{S} =$

$\text{FcTMA}_{(\text{ads})}$

$E^0 (\text{FcTMA}^+ / \text{FcTMA}_{(\text{ads})}) = \text{_____} \text{B}$

**Background Information:**

Nernst equation:

$$E = E^0 + \frac{RT}{nF} \ln \frac{[Ox]}{[Redd]};$$

where  $E^0$  is the standard potential for a given redox couple,  $E$  is the potential at concentrations of the oxidizing and reducing agents equal to  $[Ox]$  and  $[Redd]$  respectively,  $n$  is the number of electrons involved in the reaction,  $F = 96,485.332$  Cl/mol is the Faraday value.

Langmuir adsorption isotherm:

$$K = \frac{\theta}{C(1 - \theta)};$$

where  $K$  is the adsorption constant,  $C$  is the concentration of the adsorbed substance in solution,  $\theta$  is the degree of filling of the surface with this substance.

### Task 7: Titration "without complexes" (10 points)

Question	1	2	3	4	5	6	Total:
Glasses	2	5	2	3	2	6	20

In this problem you have to determine the composition of substance **X**, which is light orange in color. It is known that **X** contains calcium and, among other things, another metal **M**. To analyze 87.8 mg of **X** was dissolved in dilute nitric acid and **Y** gas was observed. The resulting colorless solution was transferred to a 100.0 mL volumetric flask and diluted with distilled water to the mark, yielding *solution 1*.

To determine the content of metals in the obtained solution, a complex-metric titration was carried out. The burette was filled with a standard solution of 0.0100 M Na<sub>2</sub>H<sub>2</sub>EDTA and the initial reading of the burette was set to 0.00 mL. An aliquot of 25.00 mL was taken from *solution 1* and transferred to the titration flask. Then methylthymol blue indicator and solid urotropine were added until pH 6 was reached. The titration was carried out until the color changed from blue to yellow, which occurred at a burette reading of 6.25 mL. To the obtained solution in the titration flask 20 mL of NaOH solution was added until pH 12 was reached, after which the color changed to blue. The titration was continued until a gray color was reached, the final burette reading was 18.75 mL.

H<sub>4</sub>EDTA dissociation constants:  $pK_{a1} = 2.00$ ,  $pK_{a2} = 2.67$ ,  $pK_{a3} = 6.16$ ,  $pK_{a4} = 10.26$ . Stability constants of the complexes:  $\lg\beta_{Ca} = 10.70$  for the [CaEDTA] complex<sup>2-</sup>,  $\lg\beta_M = 18.04$  for EDTA complex<sup>4-</sup> with **M**<sup>n+</sup>.

1. Calculate the concentrations of Ca and **M** ions in *solution 1*.

Calculations:	
$c(\text{Ca}) = \text{_____M}$	$c(\text{M}) = \text{_____M}$

2. Determine the metal **M** and the composition of substances **X** and **Y**. Write the equation of the dissolution reaction  
**X** in dilute nitric acid.

Reaction equation:
--------------------

Calculations:		
<b>M</b> - _____	<b>X</b> - _____	<b>Y</b> - _____

3. Express the conditional stability constant  $\theta'_M = \frac{[MEDTA]}{[M] \cdot s_{EDTA}}$ , где  $from_{EDTA}$  - concentration of all EDTA forms bound to protons and calcium ions (but not **M** ions) through  $\beta_M$ ,  $[H^+]$  and the acidity constants  $H_{4EDTA}$ ,  $[Ca^{2+}]$  and the  $\beta_{Ca}$  constant.

Formula derivation:
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4. For the first equivalence point (before the addition of a l k a l i), calculate the concentrations of free calcium ions and **M**. Assume that the pH value does not change during the titrations.

Calculations:	
$[Ca^{2+}]_{t.eq.1} = \text{_____M}$	$[M^{n+}]_{t.eq.1} = \text{_____M}$

5. Does calcium hydroxide precipitate after adding alkali at pH 12 before the second titration? The product of solubility  $K_{sp}(\text{Ca}(\text{OH})_2) = 3.9 \cdot 10^{-6}$ .

Calculations:

6. Calculate the volume of 0.0100 M  $\text{Na}_2\text{H}_2\text{EDTA}$  that would theoretically be used for the first titration if the initial solution did not contain calcium ions. Consider that the color transition of the indicator is determined by the same concentration of  $[\text{M}^{n+}]_{t.eq.1}$  calculated in step 4. What is the error ( $\Delta$ , %) of this titration? If you did not obtain the  $[\text{M}^{n+}]_{t.eq.1}$  value in step 4, use the value  $6.05 \cdot 10^{-7}$  M.

Calculations:

$V(\text{Na}_2\text{H}_2\text{EDTA}) = \underline{\hspace{2cm}} \text{ ml}$

$\Delta = \underline{\hspace{2cm}} \%$

### Task 8: Oligopeptides (10 points)

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

Nanopeptide **X** (M.M. 1006 g/mol when the molecular masses of amino acid residues are rounded to integers) contains a cycle of 6 amino acid residues. **X** was found to contain an N-terminal  $\alpha$ -amino group. Reduction of **X** by glutathione ( $\gamma$ -~~XXXXXXXXXXXX~~) leads to the opening of the cycle to form a linear derivative of **X1**. Complete hydrolysis of **X1** through all peptide and amide bonds (no other changes in the amino acid structure occurred) leads to a mixture of 8 amino acids (in alphabetical order): Asp, Cys, Glu, Gly, Ile, Leu, Pro, Tyr.

Note 1: Use molecular weights of amino acids rounded to whole numbers. Note 2: When answering questions 1-6, use three-letter symbols for amino acids. When answering questions 1-6, use three-letter symbols for amino acids.

1. Identify the repeating amino acid in **X**.

The repeating amino acid in **X** - \_\_\_\_\_

2. Identify the amino acids from which **X** is constructed.

Calculation:

Response: \_\_\_\_\_

The N-terminal amino acid in **X1** was found to be Cys. Treatment of **X** with the enzyme chymotrypsin (catalyzes the hydrolysis of peptide bonds from the C-terminus of Tyr and Trp residues) yielded a single product - branched oligopeptide **X2**. When **X2** was reduced, dipeptide **X3** (containing the N-terminal Cys) and heptapeptide **X4** were formed.

3. Picture **X3**.

**X3** - \_\_\_\_\_

Treatment of **X1** with a protease from *Staphylococcus aureus* (hydrolyzes peptide bonds formed by carboxyl groups of Asp and Glu) gave the N-terminal tetrapeptide **X5**, which differs from **X3** by 242 g/mol, Asp, and tetrapeptide **X6**. The amino acid residue at position 7 contains a cycle, and the amino acid residue at position 8 has no asymmetric C atoms in the side substituent consisting of atoms of two elements.

4. Picture **X5**.

**X5** - \_\_\_\_\_

5. Determine the final sequence of amino acids in **X**. Visualize **X**.

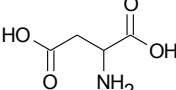
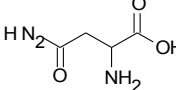
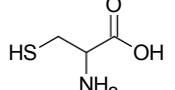
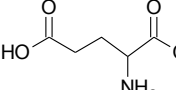
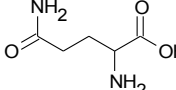
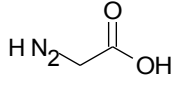
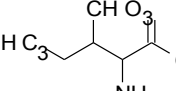
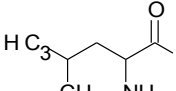
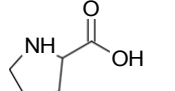
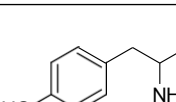
6. Write down the reduction reaction of **X** by glutathione.

**X1** can undergo autosplitting with intermediate formation of thioester **X7**, which undergoes intramolecular rearrangement to form cyclic thioester **X8** and acyclic product **X9**. After that, **X8** undergoes acyl migration to form the product **X10**.

7. Depict **X1**, **X7-X10** by writing the structures of the residues involved in the reactions; use three-letter symbols for unchanged residues.

<b>X1</b>		<b>X7</b>	
<b>X8</b>		<b>X9</b>	<b>X10</b>

**Formulas, symbols and molecular weights (g/mol) of amino acids**

 <p>Asp, 133</p>	 <p>Asn, 132</p>	 <p>Cys, 121.</p>
 <p>Glu, 147</p>	 <p>Gln, 146</p>	 <p>Gly, 75.</p>
 <p>Ile, 131.</p>	 <p>Leu, 131</p>	 <p>Pro, 115.</p>
 <p>Tyr, 181</p>		