



1st Olympiad of Metropolises

Chemistry

Theoretical Problems with solutions

7 September 2016

Moscow, Russia

Instructions

- Begin only when the START command is given. You have 4.5 hours to work on the problems.
- Use only the pen and calculator provided.
- All results must be written in the appropriate boxes within the text. Anything written elsewhere will not be graded. Use the reverse of the problem pages if you need scratch paper.
- Write relevant calculations in the appropriate boxes when necessary. If you provide only correct end results for complicated questions, you will receive no score.
- Raise your hand if you have any questions concerning the text of the problems.
- Raise your hand if you need a restroom break.
- The official English version of this examination is available on request only for clarification.

Constants

Avogadro constant:	$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$
Gas constant:	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Zero of the Celsius scale:	273.15 K

Consider all gases ideal throughout the exam.

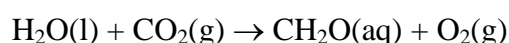
Periodic table with relative atomic masses

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**Problem 1. Circulation of carbon dioxide****(12 marks)**

Question	1	2	3	4	Total
Points	2	6	4	8	20

Moscow is one of the greenest metropolises of the world. Green area in Moscow occupies 340 km^2 , that is about $1/3$ of the total area (without the new territories). Under the action of light green plants absorb carbon dioxide and evolve oxygen in a photosynthesis process, which is described by the simplified equation:



where CH_2O denote all carbohydrates formed.

1. Determine the signs of enthalpy and Gibbs energy for the above reaction.

Function	$\Delta_r H^\circ$	$\Delta_r G^\circ$
Sign (+, -, 0)	+	+

1 pt for each correct answer, total – 2 pts.

2. Calculate the volume of CO_2 consumed (in m^3 , at 25°C and 1 atm) and the mass of carbohydrates formed (in kg) during a sunny summer day (8 h) in Moscow. The necessary information:

- solar energy absorbed by Moscow region in summer time – $150 \text{ W}\cdot\text{m}^{-2}$;
- the Gibbs energy of photosynthesis is 480 kJ/mol of CO_2 ;
- green plants absorb $\sim 10\%$ of the available solar energy;
- 25% of the absorbed energy is used for the photosynthesis process.

Calculations:

Energy absorbed by the plants:

$$150 \frac{\text{J}}{\text{s}\cdot\text{m}^2} \cdot 8 \cdot 3600 \text{ s} \cdot 340 \cdot 10^6 \text{ m}^2 \cdot \frac{10\%}{100\%} = 1.47 \cdot 10^{14} \text{ J} \quad \text{2 pts}$$

The quantity of CO_2 and CH_2O :

$$n(\text{CO}_2) = n(\text{CH}_2\text{O}) = \frac{1.47 \cdot 10^{14} \text{ J} \cdot \frac{25\%}{100\%}}{480 \cdot 10^3 \text{ J/mol}} = 7.65 \cdot 10^7 \text{ mol} \quad \text{2 pts}$$

$$\text{The molar volume of a gas at } 25^\circ\text{C} \text{ and 1 atm: } V_m = \frac{RT}{P} = \frac{8.314 \cdot 298}{1.013 \cdot 10^5} = 0.0245 \text{ m}^3 / \text{mol}$$

$$V(\text{CO}_2) = 7.65 \cdot 10^7 \cdot 0.0245 = \mathbf{1.87 \cdot 10^6 \text{ m}^3}. \quad \text{1 pt}$$

$$m(\text{CH}_2\text{O}) = 7.65 \cdot 10^7 \cdot 0.030 = \mathbf{2.30 \cdot 10^6 \text{ kg}}. \quad \text{1 pt}$$

Total – 6 pts



At the same time there are 4 million of cars in Moscow that strongly pollute the air of the city.

3. How many kilometers (in average) can a typical Moscow car run during one day so that all carbon dioxide from the car exhaust be completely absorbed by green plants within the city? Assume that the formula of car fuel is C_8H_{18} , the fuel density is 0.7 kg/L, the fuel consumption by an average car in the city is 10 L / 100 km.

Calculations:



$$n(C_8H_{18}) = n(CO_2) / 8 = 9.56 \cdot 10^6 \text{ mol} \quad \text{1 pt}$$

$$m(C_8H_{18}) = 9.56 \cdot 10^6 \text{ mol} \cdot 0.114 \text{ kg/mol} = 1.09 \cdot 10^6 \text{ kg}$$

$$V(C_8H_{18}) = 1.09 \cdot 10^6 \text{ kg} / 0.7 \text{ kg/L} = 1.56 \cdot 10^6 \text{ L} \quad \text{1 pt}$$

The average run for one car is:

$$\frac{1.56 \cdot 10^6 \text{ L}}{4 \cdot 10^6} \cdot \frac{100 \text{ km}}{10 \text{ L}} = 3.9 \text{ km} \quad \text{1 pt}$$

The car run = 3.9 km

Total – 4 pts

In addition to natural photosynthesis, CO_2 can be also utilized by artificial chemical processes designed by chemical engineers. In these processes, CO_2 is converted to various useful organic and inorganic substances such as fuels, fertilizers, polymer and construction materials.

4. Write one reaction equation for each process which converts CO_2 to a useful substance with a mass content of carbon:

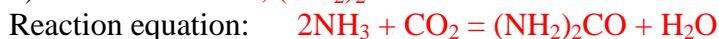
- a) 12%;
- b) 20%;
- c) 37.5%;
- d) 75%.

Hint. In all products, the molecule (the formula unit) contains one carbon atom.

a) Substance – $CaCO_3$



b) Substance – urea, $(NH_2)_2CO$



c) Substance – CH_3OH



d) Substance – CH_4



Each substance – 1 pt

Each balanced equation – 1 pt (0.5 pts – if not balanced, but with correct substances)

Total – 8 pts

Problem 2. Inorganic transformations and structures
(12 marks)

Question	1	2	3	4	5	6	Total
Points	6	6	2	3	6	1	24

A gas with density 1.50 g/L (at 273 K and 1 atm) was passed through a colorless solution containing 1.00 g of inorganic salt **X** that gives a violet flame test. After passage the density of the gas was reduced to 1.43 g/L (at 273 K and 1 atm) but the volume remained unchanged. Evaporation of the obtained solution gave 1.289 g of a white powder **Y** that can also be obtained by oxidation of **X**. If the initial gas is passed through a solution of **X** in the presence of starch, a violet coloration appears.

1. Identify the initial gas – write the formulas of its components, determine their molar fractions and draw their Lewis structures.

Calculations:

Molar mass of the initial gas: $M = \rho V_m = 1.50 \cdot 22.4 = 33.6$ g/mol. There is no individual gas with such molar mass, so we suppose it to be a gas mixture.

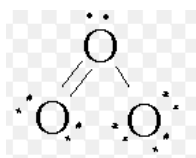
Molar mass of the gas after passage through the solution: $M = \rho V_m = 1.43 \cdot 22.4 = 32$ g/mol, this is pure dioxygen, O_2 . The initial mixture consists of ozone O_3 and dioxygen O_2 .

Let x be the molar fraction of O_2 , then

$$32x + 48(1-x) = 33.6, x = 0.9.$$

Substances and their molar fractions: O_2 – 90%, O_3 – 10%

Lewis structures:



Each formula – 1 pt,

molar fractions – 2 pts

each Lewis structure – 1 pt

Total – 6 pts

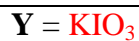
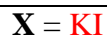
2. Determine the formulas of **X** and **Y**, write down the reaction equations.

Calculations:

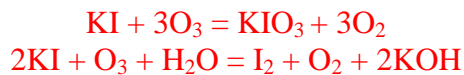
The violet flame coloration is typical for potassium salts, a violet coloration of starch indicates that the salt contains iodine. It can be potassium iodide (**X**). The quantity of this salt should be equal to that of another oxidation product, containing iodine.

$$\text{So, } n(\text{KI}) = 1.00 / 166 = 0.006024 = n(\text{Y}).$$

$$M(\text{Y}) = 1.289 / 0.006024 = 214 \text{ g/mol, it corresponds to potassium iodate } \text{KIO}_3.$$



Reaction equations:



X and Y – 2 pts each (ZERO without calculations)

Reaction equations – 1 pt each (0.5 pts if not balanced)

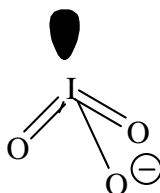
Total – 6 pts

3. What happens if the water solutions of **X** and **Y** are mixed in an acidic medium? Give the ionic equation.



2 pts

4. Draw the geometric structure of **Y**.



2 pts

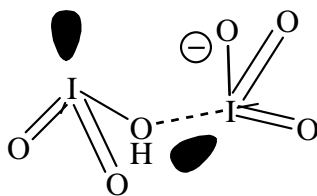
5. In an acidic medium from the water solution of **Y** the white crystals of a salt **Z** containing 24.6 mass.% of oxygen crystallize. Give a formula of **Z** and draw the geometric structure of its anion.

Calculation:

The molar mass corresponding to 3 oxygen atoms: $3 \cdot 16 / 0.246 = 195$ g/mol. After subtracting molar mass of IO_3 we get: $195 - 127 - 3 \cdot 16 = 20$ g/mol. This value is an average between K and H, so **Z** is an acid iodate $\text{KIO}_3 \cdot \text{HIO}_3$, or KHI_2O_6



Anion structure:



Formula of **Z** – 2 pts (ZERO without calculations)

Anion structure – 2 pts

Total – 4 pts

6. What is the use of the initial gas in metropolises?

Ozone in mixture with dioxygen is used for water treatment.

1 pt

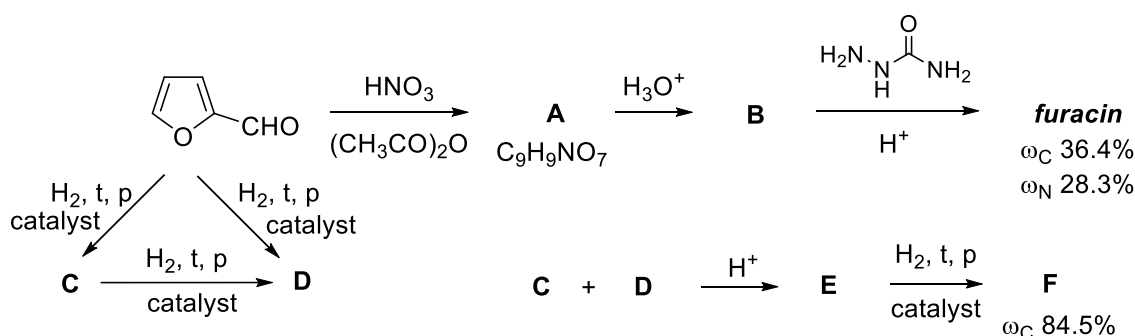
Problem 3. A Silk Purse out of a Sow's Ear, or Drugs from Biomass

(12 marks)

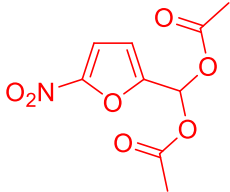
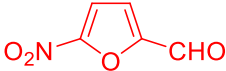
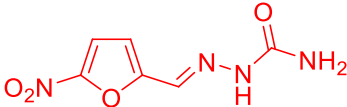
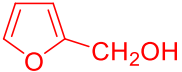
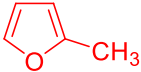
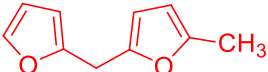

Dedicated to the blessed memory of Professor A.V. Butin

Question	1	2	3	Total
Points	14	6	10	30

A significant attention is now paid to the use of biomass as a source of organic chemicals. One of the most important products of biomass processing is furfural (furan-2-carbaldehyde). It can be easily transformed into other furan derivatives, including medicines, or linear alkanes which can be used as diesel fuel. One of the methods for furfural transformation into biofuel as well as preparation of bactericidal agent **furacin** from furfural are given in the scheme below.

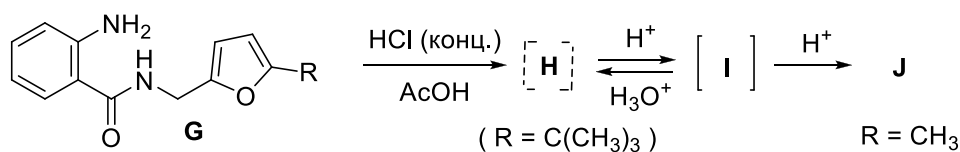


1. Write down the structural formulas of **furacin** and compounds **A–F**.

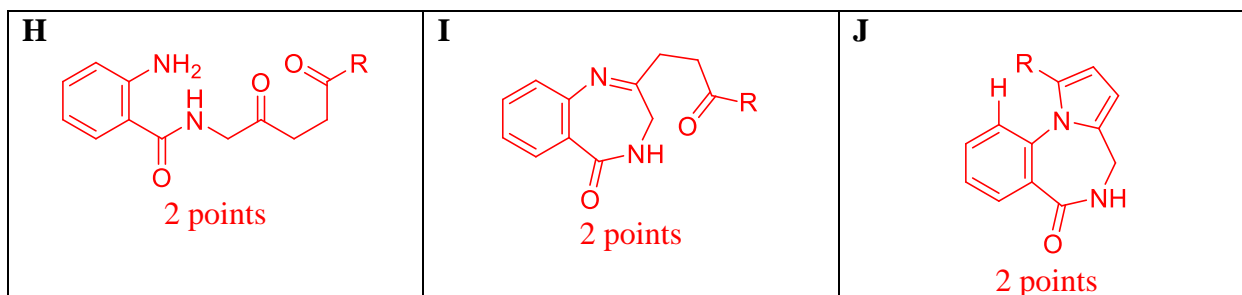
A  2 points	B  2 points	<i>furacin</i>  2 points	
C  2 points	D  2 points	E  2 points	F  2 points

Furan derivatives can be efficiently converted into other heterocycles. Thus, in 1930th professor of Moscow State University Yu. K. Yuriev developed industrial transformation of furans into pyrroles under heating of furan with ammonia (amines) above 400 °C in the presence of alumina. In a laboratory, the sequence of furan hydrolysis followed by Paal-Knorr reaction with ammonia (amine) is used for this transformation. This sequence can be realized as a two-step procedure or as a domino reaction. For example, *N*-(furfuryl)anthranilamide **G** ($\text{R} = \text{CH}_3$) under treatment with conc. HCl in acetic acid afforded the new heterocyclic compound **J** via intermediates **H** and **I**. Nevertheless,

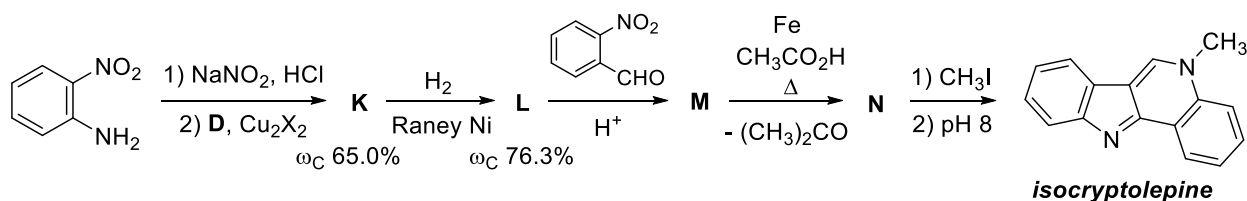
compound **G** with $R = C(CH_3)_3$ under the same conditions produced the corresponding product **H** only.



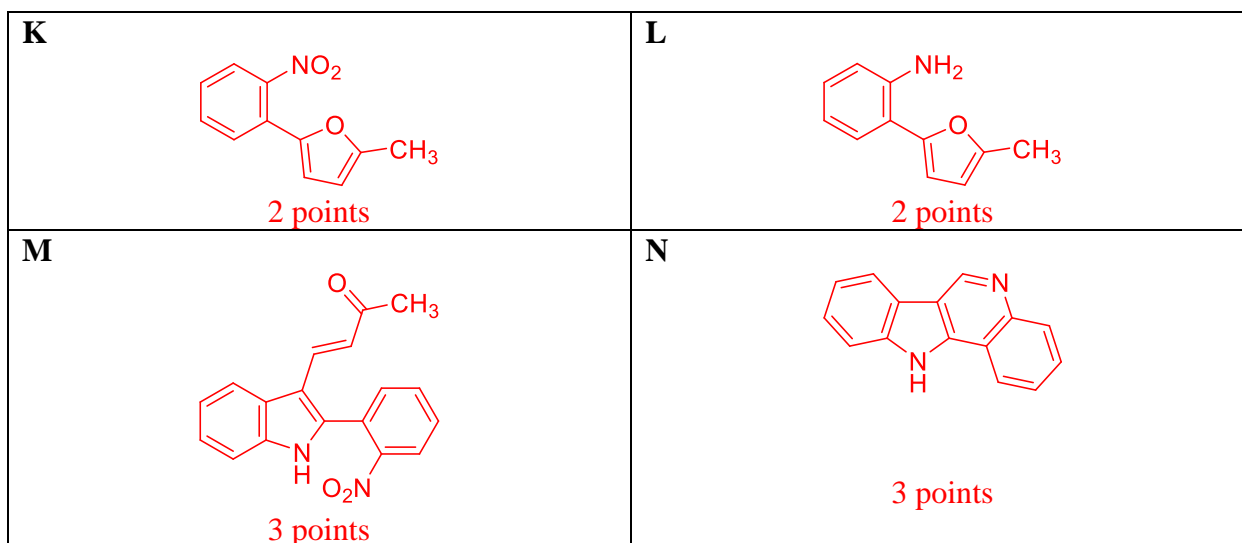
2. Write down the structural formulas of compounds **H–J** in general form (pointing out the substituent in the furan ring as R) taking into account that **I** is a bicyclic species.



An interesting transformation of simple furan, which is a product of biomass processing, to antimalarial and anticancer alkaloid isocryptolepine was recently reported by A.V. Butin *et al.*

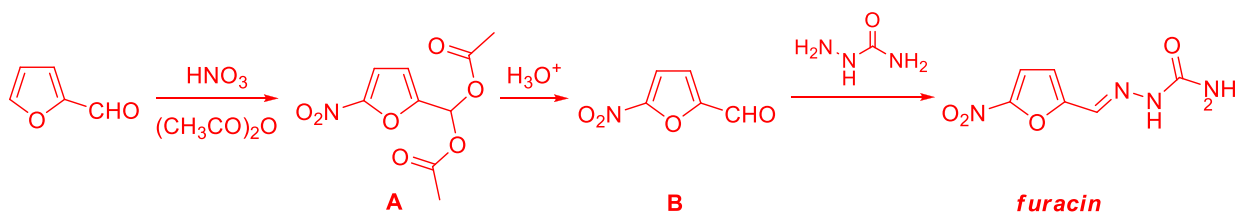


3. Write down the structural formulas of **K–N** accounting for that **M** contains the indole ring.



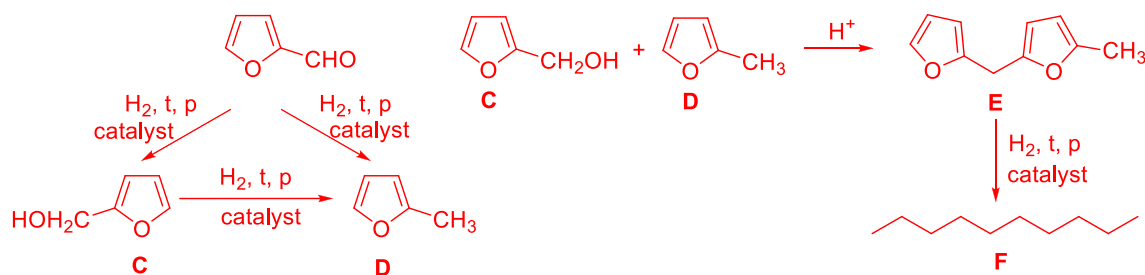
Detailed solution

1. The comparison of molecular formulas of furfural and compound **A** allows to conclude that at this step furan ring nitration is accompanied by addition of acetic anhydride. The last step in the synthesis of furacin is the reaction with semicarbazide, *i.e.* furacin has 4 nitrogen atoms (three from semicarbazide and 1 from nitro group). From the mass content of nitrogen and carbon we can determine the molecular formula of furacin as $C_6H_6N_4O_4$. Therefore, formula of **B** is $C_5H_3NO_4$, and the transformation of **A** to **B** is hydrolysis of diacetyl ketal moiety producing aldehyde function.



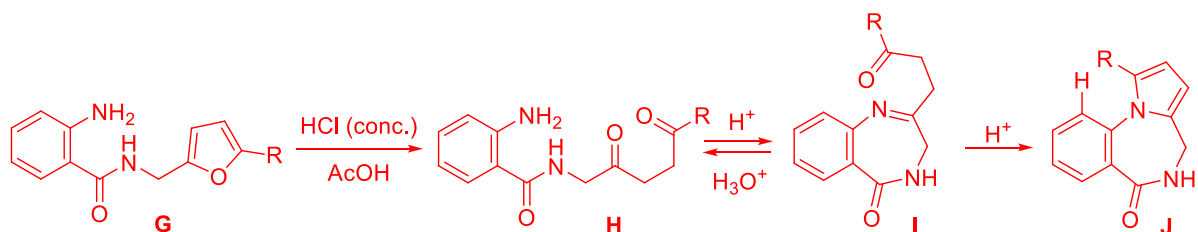
According to the text of the problem, compound **F** is a linear alkane. The content of carbon in **F** allows to conclude that this is *n*-decane ($C_{10}H_{22}$), *i.e.*, in the formation of **F** one molecule of **C** reacts with one molecule of **D**. This reaction proceeds under acid catalysis. It is possible to suppose that this is Friedel-Crafts alkylation of the furan ring by furan-containing alcohol which is obtained from furfural by catalytic hydrogenation. Evidently, hydrogenation of side chain should proceed faster than hydrogenation of the furan ring itself. So, **C** is furfuryl alcohol. Hydrogenolysis of **C** produces then 2-methylfuran (**D**) which is alkylated by **C** under Friedel-Crafts conditions affording 5-methyldifurylmethane **E**. Its hydrogenation is accompanied by C–O bonds hydrogenolysis furnishing linear alkane **F**.

(7 structures, 2 points for each, 14 points in total).

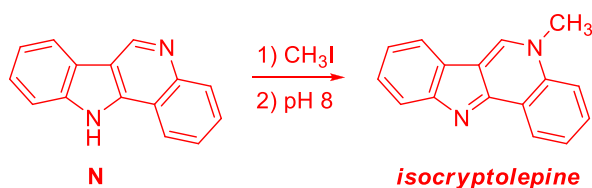


2. It is clear from the text of the problem, that the first step is hydrolysis of the furan ring. The product then enters the Paal-Knorr synthesis, producing pyrrole ring in **J**. This ring formation is a stepwise process: initially, nucleophilic amino group attacks the closest carbonyl function affording 7-membered ring in **I** (bicyclic compound). Then tautomerization of imine to enamine and attack of amino group on the second carbonyl function accomplished the pyrrole ring formation furnishing tricyclic product, pyrrolo[1,2-*a*]benzo[1,4]diazepine. The bulky *tert*-butyl group prevents cyclization of **I** to **J** due to steric repulsions. As a result, the intermediate imine **I** undergoes hydrolysis to diketone **H** instead of cyclization.

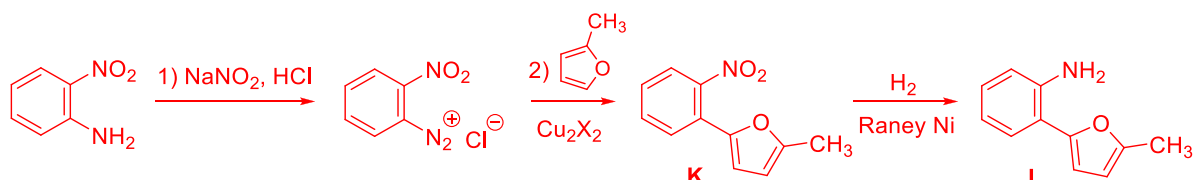
(3 structures, 2 points for each, 6 points in total).



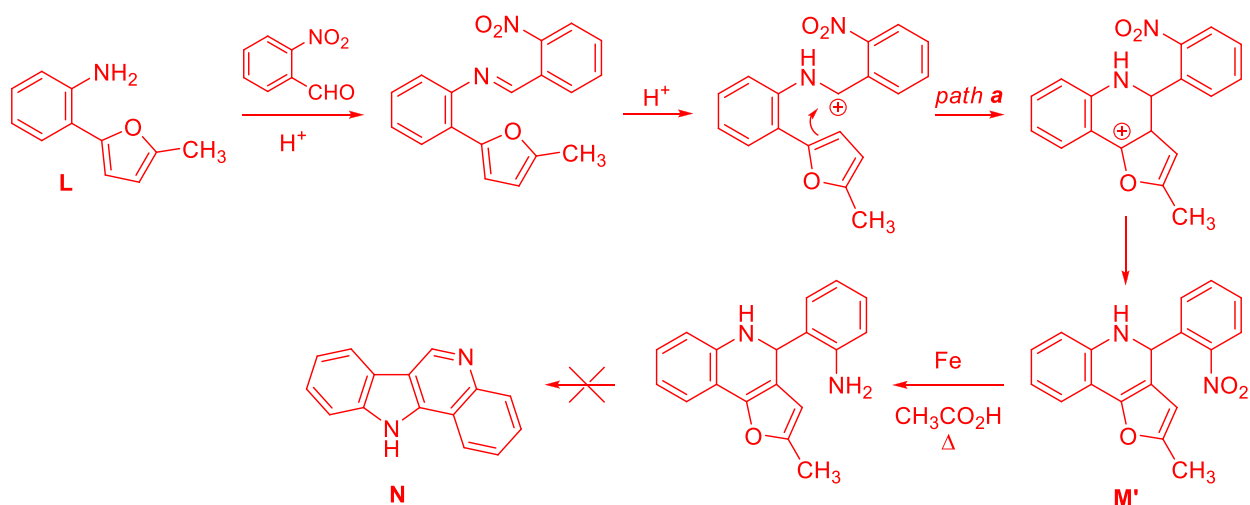
3. Evidently, the last step of isocryptolepine synthesis is methylation of the nitrogen atom. Therefore, **N** is the corresponding desmethyl derivative. The fully aromatic indoloquinoline is the most stable tautomer for compound **N**.



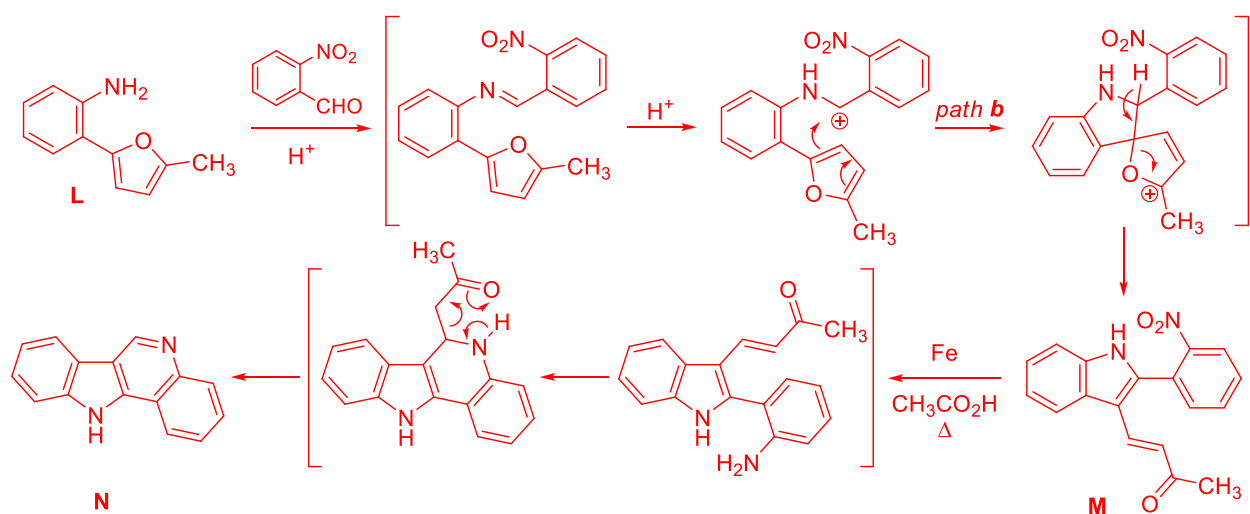
Compound **K** is formed by diazotization of *o*-nitroaniline (6 carbon atoms) followed by the reaction of the formed diazonium salt with 2-methylfuran **D** (5 carbon atoms) in the presence of Cu(I) salt. This is Meerwein arylation furnishing 2-aryl-5-methylfuran. The structure can be also determined from the carbon content. Molecular weight of **K** is $132/0.65 = 203$ a.u. Compound **K** contains nitro group (46 a.u.) and furan oxygen atom (16 a.u.). Therefore, molecule of **K** has no more nitrogen atoms and has 9 hydrogen atoms. Furan is known to have excellent α/β -selectivity in both radical and electrophilic reactions. So, 2-nitrophenyl group substitutes α -hydrogen atom. From the carbon content in compound **L** we can find that its molecular weight is 173, *i.e.* 30 a.u. smaller than that of **K**. So, this is a result of reduction of nitro group leading to the corresponding aniline.



The next step is quite unusual. This is started by acid-catalyzed imine formation *via* reaction between the aldehyde and amine moieties. The protonation of the imine nitrogen increases electrophilicity of the imine carbon atom and it attacks the furan ring located in close proximity. For other arenes this attack proceeds onto *ortho*-carbon atom producing six-membered ring. However, if we try to write the corresponding product in this case, we will obtain compound **M'** which cannot produce **N** after reduction with iron and acetic acid.



There is an alternative possibility – electrophilic attack of the protonated imine on the substituted α -carbon atom (*ipso* attack). This attack is provided by the extremely high α/β -selectivity of the furans in the reaction with electrophiles and leads to the spiro-intermediate which undergoes furan ring opening affording 2-(2-nitrophenyl)-3-(3-oxobut-1-en-1-yl)indole **M**. The reduction of nitro group in **M** produces the corresponding amino group which adds to α,β -unsaturated ketone moiety (Michael addition) producing tetracyclic intermediate. It undergoes aromatization *via* elimination of acetone molecule (in its enol form) through the concerted six-membered transition state.



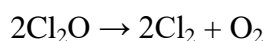
(Structural formulas of **K**, **L**, **N** – 2 points for each. Structural formulae of **M** – 4 points. 10 points in total).

Determination of the structure of **M** is a rather complex task. However, this structure contributes only 4 points of 30. Those students who are able to determine this structure will get much pleasure from the unusual transformations leading to **M** and from **M** to **N** as well as from their personal ability to find the solution.

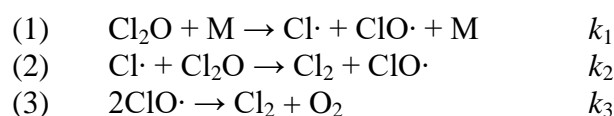
Problem 4. Radical decomposition (12 marks)

Question	1	2	3	4a	4b	4c	5	Total
Points	12	3	10	6	4	4	20	59

Almost all halogen oxides are endothermic compounds, i.e. they are formed from elements with absorption of heat. Chlorine (I) oxide, a brownish-yellow gas, is not an exception. Upon mild heating it decomposes exothermically into chlorine and oxygen according to the equation

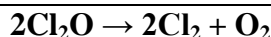


This reaction is not an elementary one. It proceeds through several consecutive elementary steps:



($k_1 - k_3$ are the rate constants, M is any molecule)

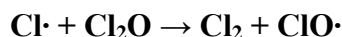
1. Using the Hess' law calculate the reaction enthalpies for all elementary steps and for the overall reaction. For each case note whether the reaction is exothermic (write " $Q>0$ ") or endothermic (" $Q<0$ "). The necessary data are provided at the end of the problem.



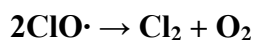
$$\Delta_r H^\circ = 2 \cdot 0 + 0 - 2 \cdot 88 = -176 \text{ kJ/mol, } Q > 0$$



$$\Delta_r H^\circ = 121 + 101 - 88 = 134 \text{ kJ/mol, } Q < 0$$



$$\Delta_r H^\circ = 0 + 101 - 121 - 88 = -108 \text{ kJ/mol, } Q > 0$$



$$\Delta_r H^\circ = 0 + 0 - 2 \cdot 101 = -202 \text{ kJ/mol, } Q > 0$$

2 points for each enthalpy, 1 point for each assignment of Q,

Total – 12 points

2. Which elementary step would you expect to be the slowest one? Tick the appropriate box.

(1) ☒

(2) ☐

(3) ☐

3 points for the correct answer

3. Derive the expression for the rate of Cl_2O depletion using the steady-state approximation. Do not express $[\text{M}]$ in terms of concentrations of specific substances, leave it as it is.

Calculations:

$$0 = d[\text{Cl}]/dt = r_1 - r_2 \quad (2 \text{ points})$$

$$0 = d[\text{ClO}]/dt = r_1 + r_2 - 2r_3 \quad (2 \text{ points})$$

Therefore

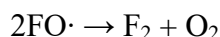
$$r_1 = r_2 = r_3$$

$$-d[\text{Cl}_2\text{O}]/dt = r_1 + r_2 = 2r_1 \quad (2 \text{ points})$$

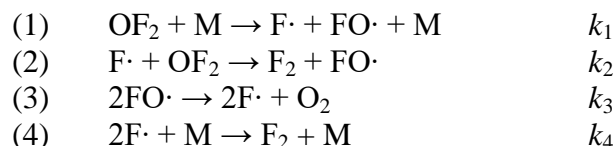
$$-\frac{d[\text{Cl}_2\text{O}]}{dt} = 2k_1[\text{Cl}_2\text{O}][\text{M}] \quad (4 \text{ points})$$

Total – 10 points

Decomposition of oxygen difluoride, OF_2 , to fluorine and oxygen proceeds via a similar mechanism with the notable exception: reaction between two $\text{FO}\cdot$ radicals yields two fluorine atoms rather than a difluorine molecule. This is due to the fact that the reaction



is highly exothermic, and the amount of heat released is enough to break the F–F bond. The fluorine atoms formed then either dimerize or react with OF_2 . So, the overall mechanism is as follows:



($k_1 - k_4$ are the rate constants, M is any molecule)

Note that this is a chain reaction: $\text{F}\cdot$ radical produces $\text{FO}\cdot$, then $\text{FO}\cdot$ radical produces $\text{F}\cdot$ and the process repeats itself. The radicals $\text{F}\cdot$ and $\text{FO}\cdot$ are the carriers of the chain process.

Under the certain conditions exothermic chain reactions can proceed with increasing rates. There are two possible reasons for this: a) self-heating of the reaction mixture as the reaction proceeds causes the increase of the rate constants which makes the reaction go faster and b) over a cycle of chain propagation the number of the chain carriers increases which leads to exponential growth of their concentrations. These two regimes are called *thermal mode* and *chain-branching mode*, respectively.

4a. Using the law of mass action derive the expression for the change rate of the total concentration of chain carriers, $[\text{CC}]$, in the reaction of OF_2 decomposition. Do not express $[\text{M}]$ in terms of concentrations of certain substances. Note that concentrations of radical species are negligible regardless of the reaction mode.

Calculations:

$$d[F]/dt = r_1 - r_2 + 2r_3 - 2r_4$$

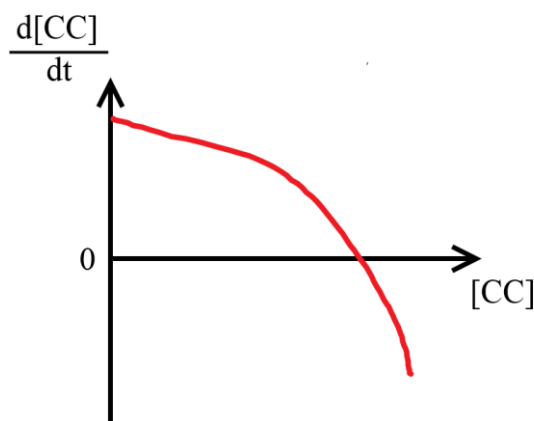
$$d[FO]/dt = r_1 + r_2 - 2r_3$$

$$d[CC]dt = d[F]/dt + d[FO]/dt = 2r_1 - 2r_4 = 2k_1[OF_2][M] - 2k_4[F]^2$$

$$\frac{d[CC]}{dt} = \frac{d([F] + [FO])}{dt} = 2k_1[OF_2][M] - 2k_4[F]^2$$

Total – 6 points

4b. Draw a sketch of dependence of $d[CC]/dt$ on $[CC]$.



4 points if consistent with (4a)

If there is no (4a): there is no branching in the mechanism hence $d[CC]/dt$ should decrease with increasing $[CC]$, 4 points for the qualitatively same sketch

4c. Decide whether OF_2 decomposition is a thermal process or a chain-branching process.

thermal ☒

chain-branching ☐

4 points if consistent with (4a)/(4b)

5. Using the steady-state approximation, derive the expression for the rate of OF_2 depletion. Do not express $[\text{M}]$ in terms of concentrations of specific substances, leave it as it is.

Calculations:

$$0 = d[\text{F}]/dt = r_1 - r_2 + 2r_3 - 2r_4 \quad (3 \text{ points})$$

$$0 = d[\text{FO}]/dt = r_1 + r_2 - 2r_3 \quad (3 \text{ points})$$

Therefore

$$r_1 = r_4$$

Hence

$$k_1[\text{M}][\text{OF}_2] = k_4[\text{F}]^2[\text{M}] \quad \text{and} \quad [\text{F}] = (k_1/k_4)^{1/2}[\text{OF}_2]^{1/2} \quad (6 \text{ points})$$

$$-d[\text{OF}_2]/dt = r_1 + r_2 \quad (2 \text{ points})$$

$$-d[\text{OF}_2]/dt = k_1[\text{OF}_2][\text{M}] + k_2[\text{OF}_2][\text{F}] = k_1[\text{OF}_2][\text{M}] + k_2(k_1/k_4)^{1/2}[\text{OF}_2]^{3/2} \quad (6 \text{ points})$$

$$-\frac{d[\text{OF}_2]}{dt} = k_1[\text{OF}_2][\text{M}] + k_2(k_1/k_4)^{1/2}[\text{OF}_2]^{3/2}$$

Total – 20 points

Standard enthalpies of formation of gaseous compounds and radical species at 298 K

Species	$\cdot\text{O}\cdot$	$\text{Cl}\cdot$	$\text{ClO}\cdot$	Cl_2O	ClO_2	$\text{F}\cdot$	$\text{FO}\cdot$	OF_2
$\Delta_f H^\circ$, kJ/mol	249	121	101	88	105	79	109	25

**Problem 5. Sugars****(12 marks)**

Question	1	2	3	4	5	6	7	8	9	Total
Points	1	2	4	1	3	3	4	2	5	25

Glucose is the most common monosaccharide on Earth. Glucose was among the first sugars with postulated molecular formula ($C_6H_{12}O_6$). This fact was behind the proposition to refer all sugars to as carbohydrates, or «carbon hydrates», with the general formula of $C_n(H_2O)_m$. Many monosaccharides and their derivatives were further found to have different molecular formulae, still very often such compounds are also classified as carbohydrates.

Equimolar mixture of *D*-glucose derivatives **A**, **B**, **C**, and **D**, as well as each of pair-wise equimolar mixtures **A-B** and **C-D** have the content of $C_n(H_2O)_n$ on a per-mole basis. However, none of the individual compounds **A-D** is described by the formula of $C_n(H_2O)_n$. The number of carbon atoms remains unchanged upon *D*-glucose transformation into each of **A-D**.

1. Determine the value of n in the four-compound mixture.

$n =$

A is formed from *D*-glucose as a result of its interaction with the Tollens reagent. The latter is prepared by adding aqueous ammonia to a solution containing silver nitrate and sodium hydroxide. Finally, the medium is acidified once the reaction is completed.

2. Write down the reaction equations of the Tollens reagent formation.

--

3. a) Write down the reaction of the Tollens reagent interaction with *D*-glucose in the molecular form. b) Draw **A** in Fischer projection.

a)	b)

4. Write down the molecular formula of **B**.

--

B completely blocks the vitally important process of glycolysis at the stage of *D*-glucoso-6-phosphate isomerization into *D*-fructose-6-phosphate.

5. Draw **B** in Fischer projection.

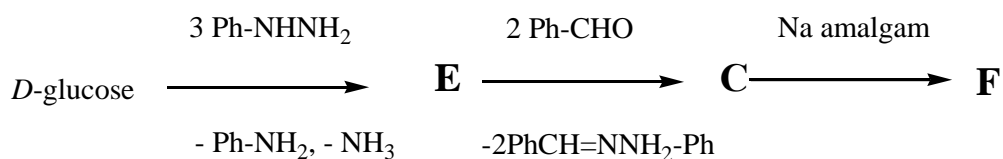
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The absolute configuration of the asymmetric carbon atom used for assigning to the *D*- or *L*-series remains unchanged in both **C** and **D** as compared to that in the starting *D*-glucose.

6. Propose the molecular formulae of **C** and **D**.

C	D

C is formed as a result *D*-glucose interaction with phenylhydrazine according to the following scheme (**F** is a glucose isomer):



7. Draw **E**, **C**, and **F** in Fischer projection.

E	C	F

8. Write down the reaction of **D** formation from *D*-glucose. Draw **D** in Fischer projection.

9. Which of the compounds **A-D** can exist in a cyclic form (tick the correct answers)? Draw the appropriate structural formulae.

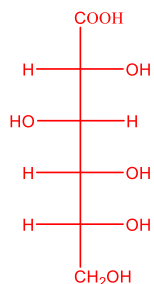
Compound	A	B	C	D
Cyclic form	<input type="checkbox"/> Yes <input type="checkbox"/> No	<input type="checkbox"/> Yes <input type="checkbox"/> No	<input type="checkbox"/> Yes <input type="checkbox"/> No	<input type="checkbox"/> Yes <input type="checkbox"/> No
Structural formula				

Detailed solution and grading scheme

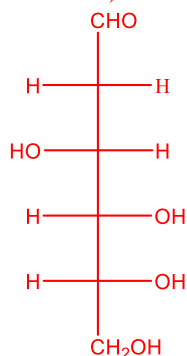
- Since the four-component mixture is composed of compounds **A-D**, which are obtained from *D*-glucose with retention of the number of carbon atoms, $n = 6$.
- 1 point for each of the reactions of the Tollens reagent preparation or 2 points for the generalized reaction (**2 points** in total).



- 2 points for the reaction (1 point if unbalanced), 2 points for **A** (1 point in case of correct formula and mistake(s) in Fischer projection), **4 points** in total.

<p>a)</p> $\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{Ag}[(\text{NH}_3)_2]\text{OH} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{Ag}\downarrow + 4\text{NH}_3 + \text{H}_2\text{O}$	<p>b)</p> 
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- The molecular formula of **A** is $\text{C}_6\text{H}_{12}\text{O}_7$. Thus, that of **B** is $\text{C}_6\text{H}_{12}\text{O}_5$ (**1 point**).
- B** contains by 1 oxygen atom less than *D*-glucose, thus being deoxy-*D*-glucose. *D*-glucose can be prevented from isomerization into *D*-fructose only if it lacks the OH-group in the second position. Thus, **B** is 2'-deoxy-*D*-glucose (**3 points** in total, 2 points in case of no OH-group in the second position and mistake(s) in Fischer projection, 1 point in case of no OH-group in the second position and mistakes in the *D*-glucose formula).



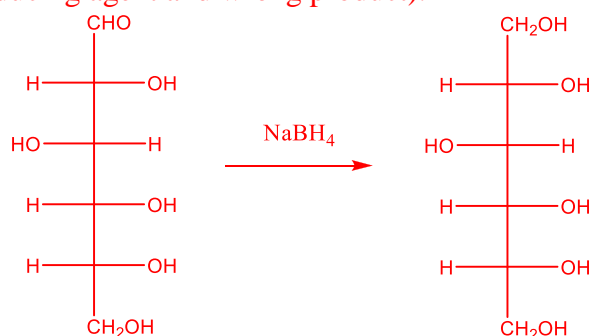
- One can suppose even higher number of oxygen atoms in either **C** or **D**, let us say, eight. Taking into account chemical properties of monosaccharides, this would correspond to a dicarboxylic *D*-glucaric acid (with carboxyl groups at the 1st and 6th positions). Still, the absolute configuration of the 5th carbon atom in *D*-glucaric acid is different from that in *D*-glucose. Thus, **C** and **D** differ from *D*-glucose by the number of hydrogen atoms. Two-electron redox reactions are most typical

of this class of compounds. Then one can suppose that the molecular formulae of **C** and **D** (without precise assigning) are written as $C_6H_{14}O_6$ and $C_6H_{10}O_6$. This supposition needs to be further checked when answering the subsequent questions (1.5 point for each formula, **3 points** in total).

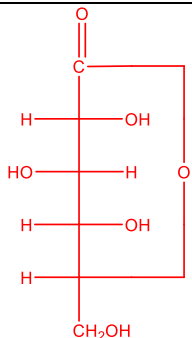
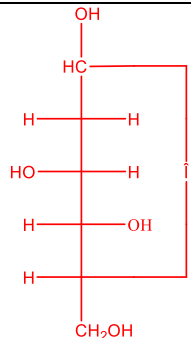
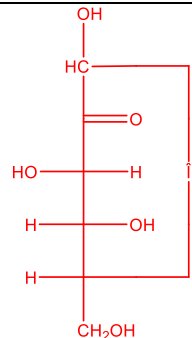
7. **E** is *D*-glucozazone, **C** is *D*-glucozone, and **F** is *D*-fructose (1.5 point for each of **E** and **C**, 2 points for **F**, **4 points** in total)

E	C	F
$ \begin{array}{c} \text{HC}=\text{NNHC}_6\text{H}_5 \\ \\ =\text{NNHC}_6\text{H}_5 \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	$ \begin{array}{c} \text{HC}=\text{O} \\ \\ =\text{O} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	$ \begin{array}{c} \text{CH}_2\text{OH} \\ \\ =\text{O} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $

8. Other suitable reducing agents accepted (**2 points** in total, 1.5 point for the correct product and invalid reducing agent, 1 point for the correct reaction and mistake(s) in the Fischer projection, 1 point for the correct reducing agent and wrong product).



9. 0.5 point for each correct choice, 1 point for the formula of each of **A**, **B**, and **C** (**5 points** in total).

Compound	A	B	C	D
Cyclic form	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No
Structural formula				-