1st Olympiad of Metropolises

Chemistry

Theoretical Problems

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

Consider all gases ideal throughout the exam.

Periodic table with relative atomic masses

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

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 -

Country: Name:

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:

$$H_2O(l) + CO_2(g) \rightarrow CH_2O(aq) + O_2(g)$$

where CH_2O denote all carbohydrates formed.

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

Function	$\Delta_r H°$	$\Delta_r G°$
Sign (+, –, 0)		

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

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

Calculations:

$V(CO_2)$ = _______ m^3

$m(CH_2O)$ = ______ kg

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:

The car run = ______ km

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 –

Reaction equation:

b) Substance –

Reaction equation:

c) Substance –

Reaction equation:

d) Substance –

Reaction equation:

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:

Substances and their molar fractions:

Lewis structures:

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

Calculations:

X = **Y** =

Reaction equations:

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

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

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.

Calculations:

Z =

Anion structure:

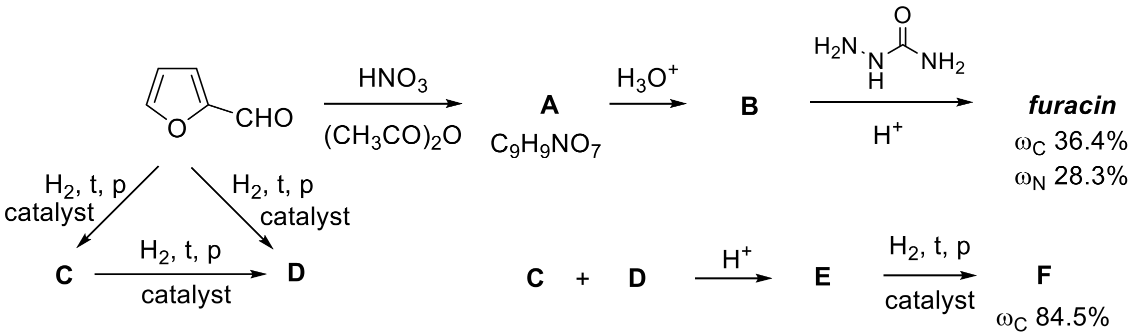
6. What is the use of the initial gas in metropolises?

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.

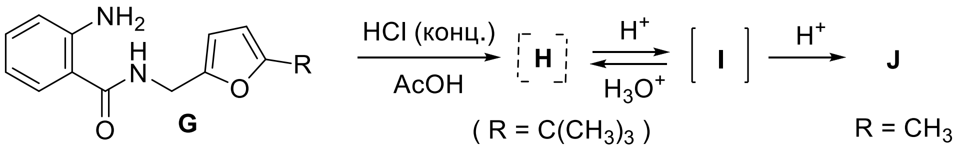


1. Write down the structural formulas of ***furacin*** and compounds **A–F**.

A	**B**	***furacin***

C	**D**	**E**	**F**

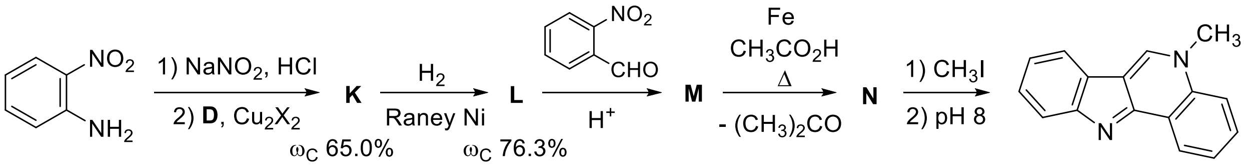
Furan derivatives can be efficiently converted into other heterocycles. Thus, in 1930th professor of Moscow State University Yu. K. Yuriev developed industrial transformation of furans into pyrroles under heating of furan with ammonia (amines) above 400 °C in the presence of alumina. In a laboratory, 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)anthranylamide **G** (R = 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.

H	**I**	**J**

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*.



isocryptolepine

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

K	**L**
M	**N**

Country:	Name:

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

$$2Cl_2O \rightarrow 2Cl_2 + O_2$$

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

(1) $Cl_2O + M \rightarrow Cl\cdot + ClO\cdot + M$ k_1
(2) $Cl\cdot + Cl_2O \rightarrow Cl_2 + ClO\cdot$ k_2
(3) $2ClO\cdot \rightarrow Cl_2 + O_2$ k_3
($k_1 – k_3$ 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.

$2Cl_2O \rightarrow 2Cl_2 + O_2$

$\Delta_r H^o =$

$Cl_2O + M \rightarrow Cl\cdot + ClO\cdot + M$

$\Delta_r H^o =$

$Cl\cdot + Cl_2O \rightarrow Cl_2 + ClO\cdot$

$\Delta_r H^o =$

$2ClO \rightarrow Cl_2 + O_2$
$\Delta_r H^o =$

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

(1) ☐ (2) ☐ (3) ☐

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

Calculations:

$$-\frac{d[Cl_2O]}{dt} =$$

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

$$2FO\cdot \rightarrow F_2 + O_2$$

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:

(1) $OF_2 + M \rightarrow F\cdot + FO\cdot + M$ k_1
(2) $F\cdot + OF_2 \rightarrow F_2 + FO\cdot$ k_2
(3) $2FO\cdot \rightarrow 2F\cdot + O_2$ k_3
(4) $2F\cdot + M \rightarrow F_2 + M$ k_4

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

Note that this is a chain reaction: F· radical produces FO·, then FO· radical produces F· and the process repeats itself. The radicals F· and FO· are the carriers of the chain process.

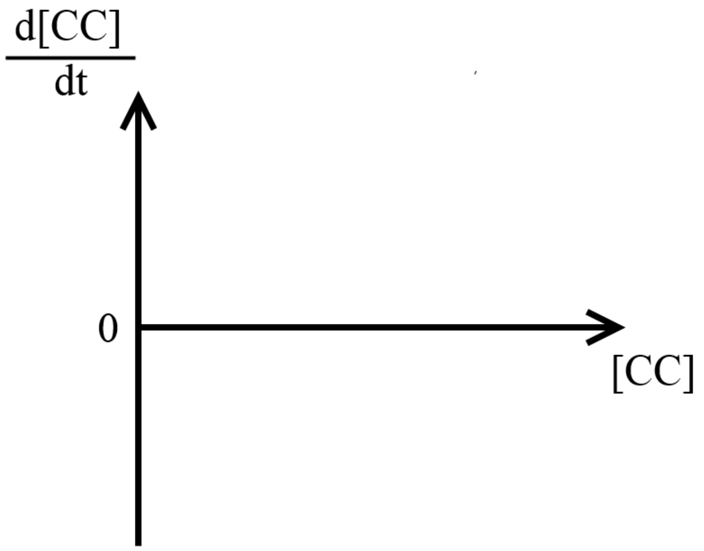
Under the certain conditions exothermic chain reactions can proceed with increasing rates. There are two possible reasons for this: a) self-heating of the reaction mixture as the reaction proceeds causes the increase of the rate constants which makes the reaction go faster and b) over a cycle of chain 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, [CC], in the reaction of OF_2 decomposition. Do not express [M] in terms of concentrations of certain substances. Note that concentrations of radical species are negligible regardless of the reaction mode.

Calculations:

$$\frac{d[\mathrm{CC}]}{dt} = \frac{d\left([\mathrm{F}]+[\mathrm{FO}]\right)}{dt} =$$

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



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

thermal ☐ chain-branching ☐

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

Calculations:

$$-\frac{d[OF_2]}{dt} =$$

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

Species	·O·	Cl·	ClO·	Cl_2O	ClO_2	F·	FO·	OF_2
$\Delta_f H^o$, kJ/mol	249	121	101	88	105	79	109	25

Country: Name:

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.

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):

$$D\text{-glucose} \xrightarrow[-\ Ph\text{-}NH_2,\ -\ NH_3]{3\ Ph\text{-}NHNH_2} \mathbf{E} \xrightarrow[-2PhCH{=}NNH_2\text{-}Ph]{2\ Ph\text{-}CHO} \mathbf{C} \xrightarrow{Na\ amalgam} \mathbf{F}$$

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	☐ Yes ☐ No	☐ Yes ☐ No	☐ Yes ☐ No	☐ Yes ☐ No
Structural formula				