3rd Olympiad of Metropolises

Chemistry

Theoretical Problems

Answers, solutions, and grading scheme

September 5, 2018
Moscow, Russia

Instructions

- Begin only when the START command is given. You have 4 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.

Recommendations

* Read the text carefully. Try to understand properly: a) what is given to you, b) what is required from you.

* All the problems contain questions of various complexity including very simple ones. Try to answer as many questions as you can. Try to leave as few empty spaces in the answer sheets as you can.

* In the calculations, use the atomic masses from the Periodic table given to you.

Good luck!

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.

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 -

Problem 1. Inorganic puzzle (12 marks)

Question	1	2	3	4	5	6	7	**Total**
Points	20	10	10	5	5	5	10	**65**
Result								

Mineral $\mathbf{X_1}$ is a binary compound formed by two elements **X** and **Y** with mass ratio **X** / **Y** ≈ 2 / 1. Upon heating on air $\mathbf{X_1}$ turns into a black powder $\mathbf{X_2}$ and a colorless gas $\mathbf{Y_2}$, which is able to decolor a solution of potassium permanganate. The crystal structure of $\mathbf{X_1}$ contains two different anions in equal amounts and two cations with different coordination numbers.

1. Write the chemical formula of $\mathbf{X_1}$, explain its ionic composition by writing the formulas of all ions, and write down the balance equations of the reactions described.

$\mathbf{X_1}$ – CuS 5 pts

Ionic composition of $\mathbf{X_1}$ – $(Cu^{+})_2Cu^{2+}S^{2-}(S_2)^{2-}$ 5 pts

Reactions: $2CuS + 3O_2 = 2CuO + 2SO_2$ 5 pts
$5SO_2 + 2KMnO_4 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$ 5 pts
($\mathbf{X_2}$ – CuO, $\mathbf{Y_2}$ – SO_2)

In the lab, the compound $\mathbf{X_1}$ can be prepared by passing the gas $\mathbf{Y_3}$ through the solution of the salt $\mathbf{X_3}$ formed by the element **X**. This salt gives a white precipitate with an acidified solution of barium chloride.

2. Write a balanced equation and specify the oxidizer and the reducing agent.

Reaction: $CuSO_4 + H_2S = CuS + Na_2SO_4$ ($\mathbf{Y_3}$ – H_2S, $\mathbf{X_3}$ – $CuSO_4$) 5 pts

Oxidizer: Cu^{2+} $(Cu^{2} + e \rightarrow Cu^{+})$ 2.5 pts

Reducing agent: S^{2-} $(2S^{2-} - 2e \rightarrow S_2^{2-})$ 2.5 pts

3. The simultaneous passing of gases $\mathbf{Y_2}$ and $\mathbf{Y_3}$ through the sodium hydroxide solution gives only one main product $\mathbf{Y_4}$, containing element **Y**. Write a balanced equation of this reaction.

Reaction: $6NaOH + 4SO_2 + 2H_2S = 3Na_2S_2O_3 + 5H_2O$ 5 pts

($\mathbf{Y_4}$ – $Na_2S_2O_3$)

4. Under cooling of the solution of $\mathbf{Y_4}$ the precipitate $\mathbf{Y_5}$ (25.8 wt.% of element **Y**) is formed. Determine the formula of $\mathbf{Y_5}$.

Calculation. $\mathbf{Y_5}$ – $Na_2S_2O_3\cdot nH_2O$.

$$\omega(S) = \frac{2\cdot 32.06}{2\cdot 22.99 + 2\cdot 32.06 + 3\cdot 16 + n\cdot 18.02} = 0.258$$

$n = 5$

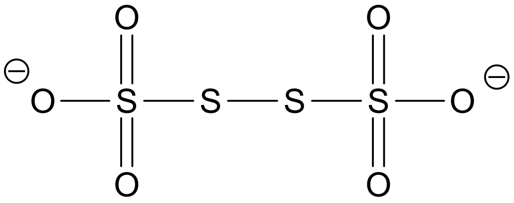
$\mathbf{Y_5}$ – $Na_2S_2O_3\cdot 5H_2O$ 5 pts

(0 pts if the answer is given without any calculations)

The simultaneous passing of gases $\mathbf{Y_2}$ and $\mathbf{Y_3}$ through water leads to a colloidal solution of element **Y**. In addition to **Y**, this solution contains various types of anions.

5. Draw the structure of one of the anions, $\mathbf{Y_6}$, from this solution taking in account that $\mathbf{Y_6}$ can be produced by the reaction between a solution of $\mathbf{Y_4}$ and elemental iodine.

Structure of anion $\mathbf{Y_6}$



5 pts

6. The addition of a large amount of aqueous solution of $\mathbf{Y_4}$ to an aqueous solution of $\mathbf{X_3}$ results in the gradual discoloration of a solution and precipitation of $\mathbf{X_1}$. Write the balanced equation of this reaction.

Reaction: $CuSO_4 + Na_2S_2O_3 + H_2O = CuS\downarrow + Na_2SO_4 + H_2SO_4$ 5 pts

7. From the solution prepared after dissolving of $\mathbf{X_1}$ in 10 M nitric acid the blue crystals of $\mathbf{X_7}$ (25.5 wt.% of element **X**) are formed. Determine the formula of $\mathbf{X_7}$ and write the reaction equation.

Calculation. $M(\mathbf{X_7}) = 63.55 / 0.255 = 249.2$ g/mol

$\mathbf{X_7}$ – $CuSO_4\cdot 5H_2O$ 5 pts

Reaction: $CuS + 8HNO_3 = CuSO_4 + 8NO_2 + 4H_2O$ 5 pts

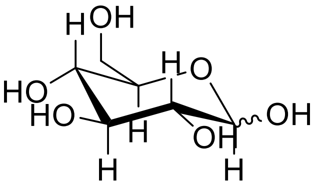
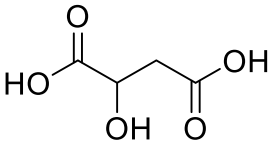
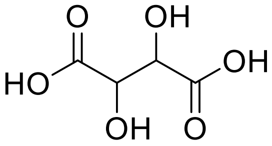
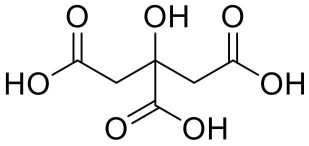
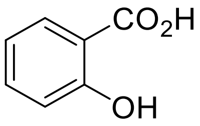
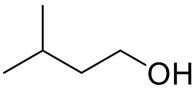
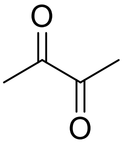
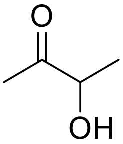
Problem 2. Raspberry chemistry (12 marks)

Question	1	2	3	4	**Total**
Points	8	18	3	1	**30**
Result					

> "Put cream and sugar on a fly and it
> tastes very much like a raspberry"
> (English proverb)

Raspberry (*Rubus idaeus*) is widespread in the central part of Russia, including the Moscow region, a deciduous half-shrub with sweet and healthy fruits used for treatment of colds and flu as antipyretic and diaphoretic remedies in fresh or frozen form, as well as in jam, marmalade, jelly, etc. Raspberry fruits contain up to 11% of sugars as well as organic acids, alcohols, ketones, vitamins A, B, C, anthocyanins (providing red color of "berries") and catechins possessing antioxidant properties.

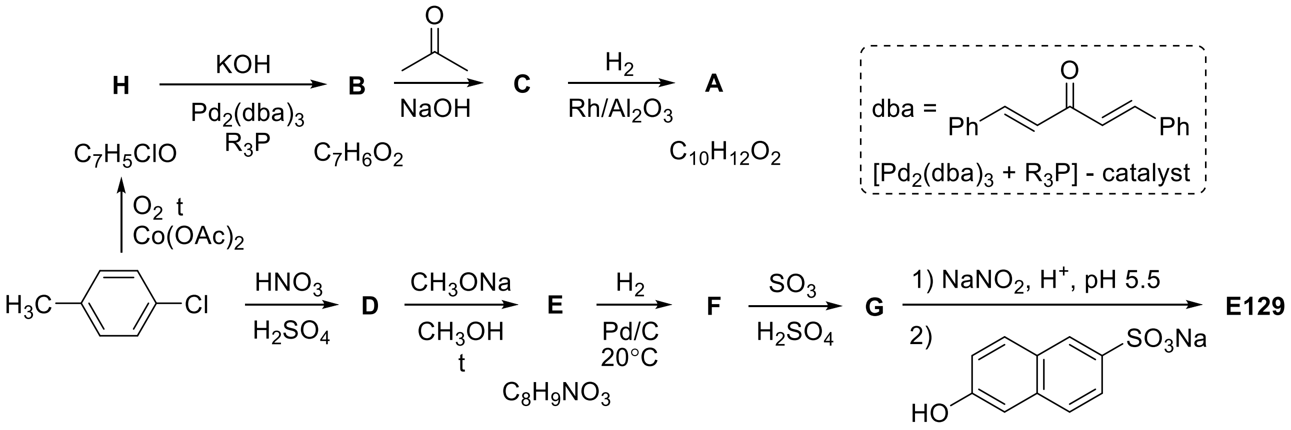
1. Write down the structural formulas (without stereochemical information) of the following compounds that were found in raspberry fruits: glucose ($C_6H_{12}O_6$), malic ($C_4H_6O_5$), tartaric ($C_4H_6O_6$), citric ($C_6H_8O_7$), salicylic ($C_7H_6O_3$) acids, isoamyl alcohol ($C_5H_{12}O$), diacetyl ($C_4H_6O_2$), acetoin ($C_4H_8O_2$).

Glucose	Malic acid	Tartaric acid	Citric acid
			
Salicylic acid	Isoamyl alcohol	Diacetyl	Acetoin
			

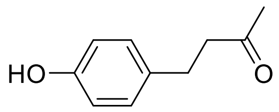
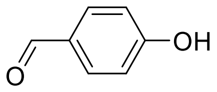
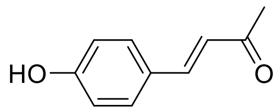
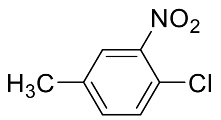
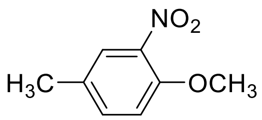
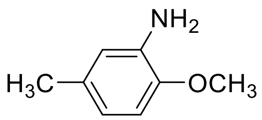
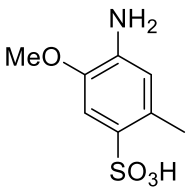
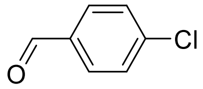
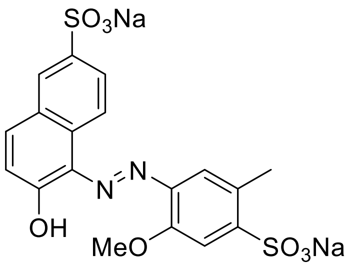
1 pt for each correct structure

It is noteworthy that all of the above substances are used in the food industry as preservatives, food coloring or flavoring agents (isoamyl alcohol in the form of esters). On the other hand, many perfumes, cosmetics, foods, drinks and beverages with the taste and smell of raspberries have nothing to do with the fruits of *Rubus idaeus*; their taste and smell are due to the presence of a number of products of the chemical industry. The most famous of them is a "raspberry ketone" (**A**). This compound, that is actually present in raspberry fruits (1-5 mg per kg), is used in the food, perfume and cosmetic industry to give the products with the required taste and aroma. Natural raspberry ketone is very expensive (about 20,000 US $ per kg), so it is obtained in two stages from compound **B** according to the scheme below. This product costs from 10 to 100 $ per kg.

The color of food and cosmetic "raspberry" products is usually provided using Allura Red AC (E129) which is synthesized from 4-chlorotoluene. From the latter, compound **B** can also be obtained. At the same time, in the stage of its formation from **H**, it is important to use the catalytic version of the reaction, since in the absence of a catalyst the reaction of **H** with strong alkali under harsh conditions proceeds in a different direction affording products **I** and **J**, the oxygen content in **I** being larger than in **H**, and the oxygen content in **J** slightly lower than in **H**.

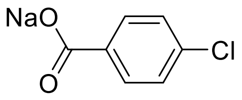
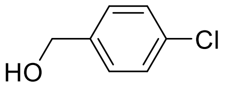


2. Decipher the scheme and write down the structural formulas of compounds **A–H** and **E129**.

A	**B**	**C**
		
D	**E**	**F**
		
G	**H**	**E129**
		

2 pts for each correct structure

3. Write down the structural formulas of the compounds that are formed from **H** during the competitive reaction which is a named reaction. Write down the name of the chemist who discovered this reaction.

I	**J**	Name of the chemist
		Cannizzaro

1 pt for each correct structure, 1 pt for the name

4. Compound **D** is the major product of 4-chlorotoluene nitration. Point out, which effect (inductive or mesomeric) of the substituent in the aromatic ring determines the process regioselectivity.

Inductive	
Mesomeric	√

1 pt

Comments from the author

1. Some of these compounds are well known. It is not difficult to determine the structure of others from the given molecular formulae. Thus, according to the formula $C_4H_6O_5$, it is easy to conclude that malic acid is a diacid, two carboxyl groups being connected by two carbon atoms, one of which is linked to a hydroxy group. There are two variants of the structure under this limitation: $HO_2CCH_2CH(OH)CO_2H$ and $HO_2CC(CH_3)(OH)CO_2H$. The first seems more likely. This is a true structure, which is estimated by a full score (1 mark). The second option is an incorrect structure, but it satisfies the condition, therefore it is estimated as 0.5 marks. Similarly, we can consider the remaining structures. In all cases, the correct structure is estimated at 1 mark, wrong, but chemically possible and satisfying the condition structure as 0.5 or 0.25 marks, depending on the degree of difference from the correct structure. Total – 8 marks.

2. According to the formula of compound **H**, it is possible to establish that this is the product of oxidation of the methyl group to the aldehyde. A comparison of the formulae of the compounds **H** and **B** shows that the chlorine atom is replaced by an OH group at this stage. So, **B** is 4-hydroxybenzaldehyde. The formula of the raspberry ketone (10 carbon atoms) shows that it is formed via the reaction of 1 eq. of **B** with 1 eq. of acetone. Further analysis allows to conclude that **C** is the product of aldol condensation, and the reduction of the C=C bond in **C** gives a saturated ketone **A** (by name it is clear that the keto group did not reduced). The nitration of 4-chlorotoluene yields two isomeric products: 3-nitro-4-chlorotoluene and 2-nitro-4-chlorotoluene. However, only in the first case the aromatic nucleophilic substitution of chlorine for methoxy group can occur under the treatment with a solution of sodium methoxide in methanol under heating, since this reaction is facilitated by an *ortho*-nitro group, but not by a *meta*-nitro group. Therefore, **D** is 3-nitro-4-chlorotoluene, and **E** is 4-methyl-2-nitroanisole. Further, the reduction of the nitro group to the amine takes place (the reduction of the benzene ring does not proceed at room temperature) and the sulfonation of the resulting aniline. Here, in principle, the reaction can take place both in the *para*-

and *ortho*-position with respect to amino group (which is a stronger donor than methoxy group). However, in the latter case, there are considerably larger steric requirements for the approach of the bulk electrophile to an atom surrounded on both sides by substituents, so 4-amino-2-methyl-5-methoxybenzenesulfonic acid **G** is formed (it exists mainly as an internal salt). This compound, under the action of sodium nitrite in the presence of an acid, is converted into a diazonium salt, which attacks the β-naphthol derivative on the C1 atom to form an azo dye **E129**.

3. It is known that heating of non-enolizable aldehydes with strong alkali induces their disproportionation to the corresponding alcohols and acids (their salts). This process is referred to as a Cannizzaro reaction.

4. Chlorine has negative inductive effect but positive mesomeric effect. The latter should be more important than the combination of inductive effects of chlorine atom and methyl group for the formation of 3-nitro-4-chlorotoluene as the major product.

Problem 3. Oil refining within the city (12 marks)

Question	1	2	3	4	5	6a	6b	7a	7b	**Total**
Points	2	2	1	1	1	3	2	3	3	**18**
Result										

Moscow is a pretty clean city, because in recent decades many industrial enterprises have been taken out of its borders. However, there is one large enterprise that operates within the city and is able to strongly pollute the surrounding water and atmosphere. This is the Moscow Refinery, which is the largest supplier of fuel and other petroleum products to the capital of Russia.

The plant processes about 10 million tons of crude oil per year. The main products are motor gasoline (2 million tons) and diesel fuel (1.7 million tons). Both types of fuel meet the emission standard "Euro-5". One of the requirements of the standard is a very low sulfur content, not more than 0.001 wt.%.

1. In the "Euro-4" standard, the permissible sulfur content is 5 times higher than that in "Euro-5". If the plant produced fuel according to the previous standard, how many tons of sulfur dioxide would additionally be released into the atmosphere during the combustion of this fuel?

Calculations

m(fuel) = $3.7 \cdot 10^6$ t,
m(S,Euro-4) = $3.7 \cdot 10^6 \cdot 0.005\% / 100\% = 185$ t
m(S,Euro-5) = $3.7 \cdot 10^6 \cdot 0.001\% / 100\% = 37$ t
Δm(S) = $185 - 37 = 148$ t 1 pt

$S + O_2 = SO_2$

$\Delta m(SO_2) = 148 / 32 \cdot 64 = 296$ t 1 pt

To remove sulfur, oil products are subjected to hydrodesulfurization – they are treated by an access of hydrogen at temperature of about 300 °C and pressure of tens of atmospheres. Under such conditions, all organic substances are converted into alkanes and inorganic non-metal hydrides.

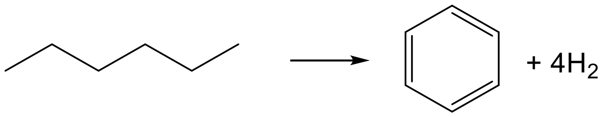
2. Write down the reactions of pyridine C_5H_5N and thiophene C_4H_4S with hydrogen during hydrotreatment. Use only molecular formulas, structures are not necessary.

Reaction of pyridine: $C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$ 1 pt
(0.5 pts, if cycloalkane is written)

Reaction of thiophene: $C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S$ 1 pt
(0.5 pts, if cycloalkane is written)

3. Hydrogen required for hydrotreatment is not produced separately, because it is formed during one of the chemical stages of oil refining. Write down the equation of any reaction which gives hydrogen in the oil refinery (use the structural formulas for organic substances).

Reaction:



1 pt

(any reasonable reaction is accepted)

4. During hydrotreatment, sulfur is converted to hydrogen sulfide, the maximum permissible content of which in the urban atmosphere is 0.008 mg/m^3. How many H_2S molecules are found in a billion molecules of air at this concentration (25 °C, 1 atm)? Round the result to the integer value.

Calculation:

$n(H_2S) / n(\text{air}) = (0.008\cdot10^{-3}/34) / (1000\cdot101.3/(8.314\cdot298)) \approx 6\cdot10^{-9}$

$N(H_2S) = 6$ 1 pt

(0 pts if the answer is given without any calculations)

5. For separation of hydrogen sulfide from the gas mixture after hydrotreatment, the gases are passed through a solution of monoethanolamine (2-aminoethanol), in which hydrocarbons are insoluble. What happens to hydrogen sulfide in this solution? Write down the reaction.

Reaction: $HOCH_2CH_2NH_2 + H_2S \rightarrow HOCH_2CH_2NH_3^+HS^-$ 1 pt

To prevent the release of hydrogen sulfide into the atmosphere, it is converted into elemental sulfur using the so called Claus process involving two stages. First, one third of hydrogen sulfide is burned in a stream of air at a high temperature (1000 °C), and then the gases formed are mixed with the remaining hydrogen sulfide in the presence of a catalyst at 250° C. As a result, more than 99% of hydrogen sulfide are consumed and the emissions to the atmosphere do not exceed the permissible content.

6. a) Write the equations of both reactions and the total oxidation equation for hydrogen sulphide. In the equations, specify the aggregate states of the substances.
   b) Calculate the enthalpy of the total reaction, assuming that it does not depend on temperature.

a) Reactions:

$H_2S_{(g)} + 3/2\ O_{2(g)} \rightarrow SO_{2(g)} + 2H_2O_{(g)}$ 1 pt

$SO_{2(g)} + 2H_2S_{(g)} \rightarrow 3S_{(l)} + 2H_2O_{(g)}$ 1 pt

The total reaction:

$H_2S_{(g)} + 1/2\ O_{2(g)} \rightarrow S_{(l)} + H_2O_{(g)}$ 1 pt

b) Calculation

$\Delta H = 2 + (-242) - (-21) = -219$ kJ/mol 2 pts

(1 pt if solid sulfur is used in the calculation)

7. a) The second stage of the Claus process is reversible. Calculate its equilibrium constant K_p at 250 °C.
   b) Assuming that the initial mixture is stoichiometric, determine at what initial pressure of the hydrogen sulfide its degree of conversion at this stage will reach 99%. Assume that entropy and enthalpy of this reaction do not depend on temperature and the reaction takes place at a constant volume and temperature of 250 °C.

a) Calculation

$SO_{2(g)} + 2H_2S_{(g)} \rightarrow 3S_{(l)} + 2H_2O_{(g)}$

$\Delta H^\circ = 3\cdot 2 + 2\cdot(-242) - (-297) - 2\cdot(-21) = -139$ kJ/mol 0.5 pts

(0 pts if solid sulfur is used)

$\Delta S^\circ = 3\cdot 37 + 2\cdot 189 - 248 - 2\cdot 206 = -171$ J/(mol·K) 0.5 pts

$\Delta G^\circ_{523} = \Delta H^\circ - T\Delta S^\circ = -139 - 523\cdot(-171\cdot 10^{-3}) = -49.57$ kJ/mol 1 pt

$K_p = \exp(-\Delta G^\circ/(RT)) = \exp(49570/(8.314\cdot 523)) = 8.93\cdot 10^4$ 1 pt

b) Calculation

Denote $p_0(H_2S) = p$, then $p_0(SO_2) = p/2$.

Equilibrium pressures: $p(H_2S) = 0.01p$, $p(SO_2) = 0.005p$, $p(H_2O) = 0.99p$

$K_p = p(H_2O)^2 / (p(SO_2)\cdot p(H_2S)^2) = (0.99p)^2 / (0.005p\cdot(0.01p)^2) = 8.93\cdot 10^4$

$p_0(H_2S) = 22.0$ bar 3 pts

Reference data.

Sulfur: melting point 113 °C, boiling point 445 °C.

Substance	$H_2S_{(g)}$	$S_{(l)}$	$SO_{2(g)}$	$H_2O_{(g)}$
$\Delta_f H^\circ_{298}$, kJ/mol	–21	2	–297	–242
S°_{298}, J/(mol·K)	206	37	248	189

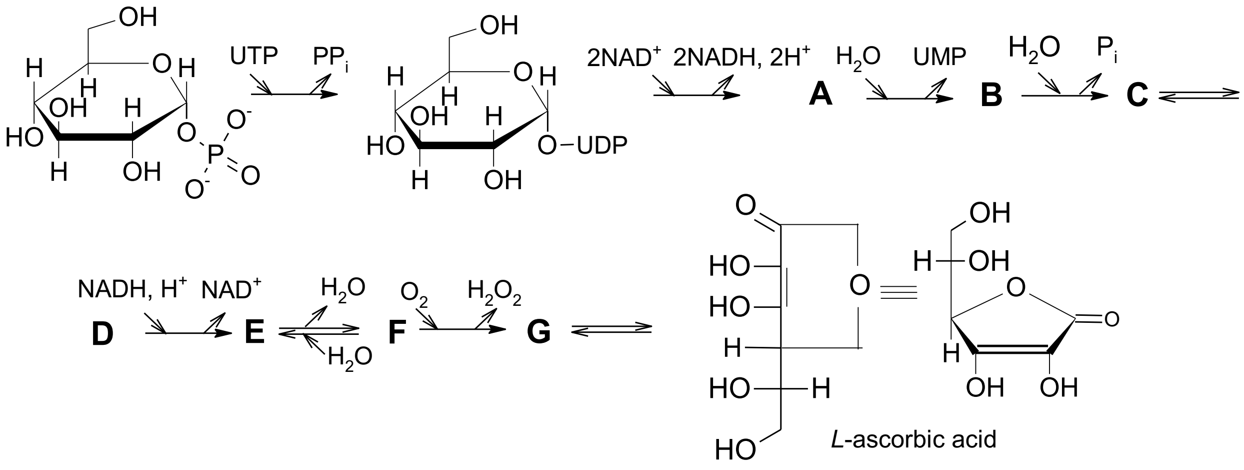
Problem 4. Synthesis of vitamin C (12 marks)

Question	1	2	3	4	5	6	**Total**
Points	14	4	2	16	8	6	**50**
Result							

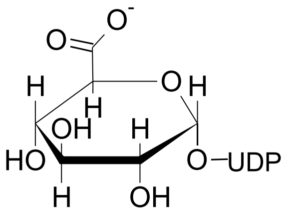
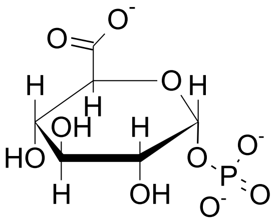
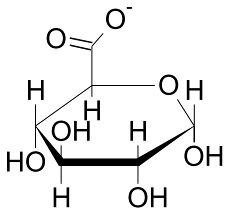
The problem of healthy eating is extremely important in modern metropolises, since many inhabitants of big cities regularly eat deeply processed food and semi-finished products lacking essential nutrients. Vitamin C, or *L*-ascorbic acid (see the formula at the end of the first reaction scheme), is one of these. Man cannot synthesize this substance and must get it with food. In this task, we will consider different pathways of *L*-ascorbic acid synthesis.

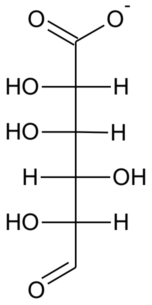
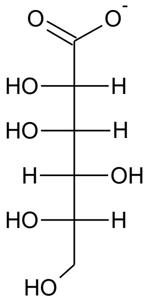
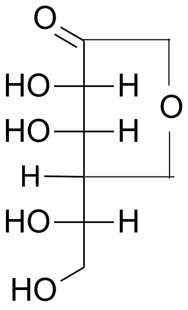
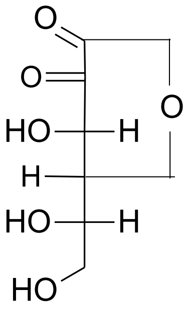
Biosynthesis of vitamin C typically starts with *D*-glucose or its mono-phosphorylated derivatives. Transition from *D*- to *L*- sugar family achieved in different ways is one of the key steps towards the target product.

An important pathway affording vitamin C typical of most animals and plants is shown in the hereunder scheme (UMP, UDP and UTP are uridinemono-, di-, and triphosphate, P_i and PP_i are inorganic phosphate and pyrophosphate, NAD^+ and NADH are oxidized and reduced forms of co-enzyme nicotinamide adenine dinucleotide, respectively):



1. Draw the Fischer projections of **A**–**C** and the Haworth projections of **D**–**G**. Note that all steps at the scheme are reaction equations; **C** and **D** have the same molecular formula; **F**, **G**, and vitamin C contain the same number of oxygen atoms; all the stages but the last (which is tautomerization) are enzymatically catalyzed.

A	B	C
		

D	E	F	G
			

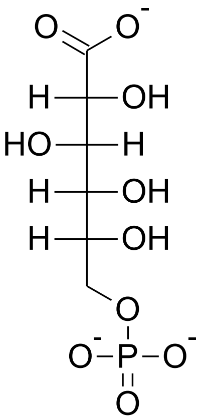
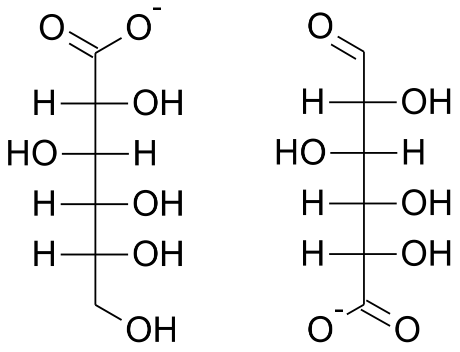
2 pts for each structure

Notes about Fischer projections.

A. By definition, the most oxidized group is written atop a projection.

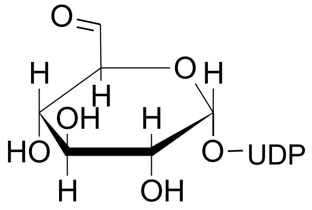
B. If a chemical reaction results in a product with the most oxidized group on the bottom, whereas the rest oxygen-containing groups are hydroxyl ones, the projection must be rotated by 180° in the projective plane.

2. Suppose *D*-glucose-6-phosphate (A) or *D*-glucose (B) is used as the starting substance instead of *D*-glucose-1-phosphate. Draw the product(s) expected as a result of reaction(s) of each starting substance with NAD^+ in systems containing all enzymes needed for corresponding redox reaction(s).

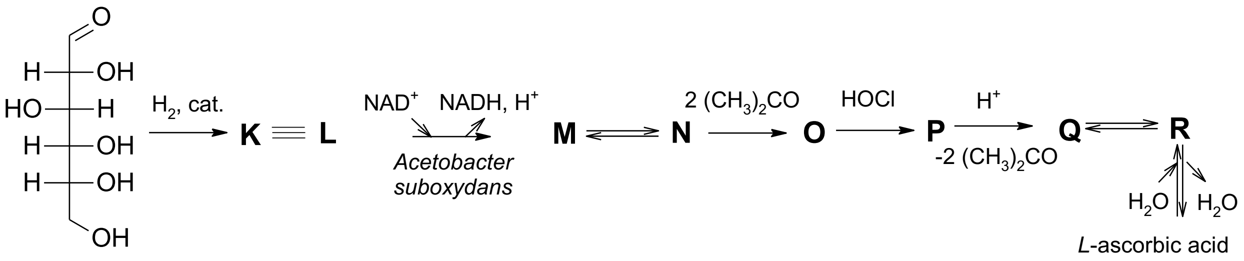
A)	B)
	

2 pts for each structure

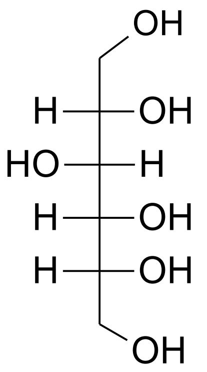
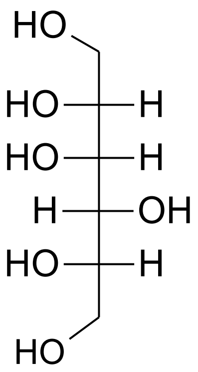
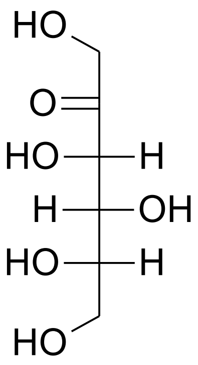
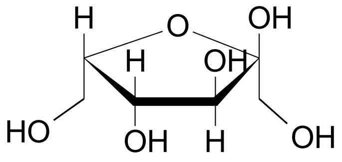
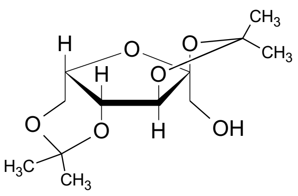
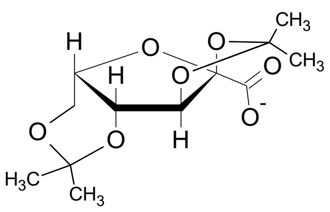
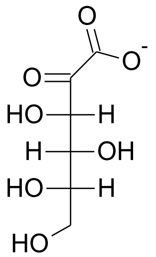
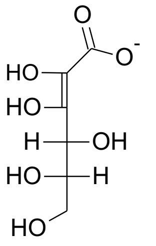
3. What would be the product of UDP-*D*-glucose transformation, if one (instead of two) NAD^+ equivalent enters into the reaction?



Vitamin C is industrially produced via Reichstein-Grussner process (see the hereunder scheme) with *D*- to *L*-sugar family transition occurring at one of the initial stages. The starting *D*-glucose is first catalytically reduced to the hexabasic alcohol *D*-glucitol (**K**), which can be also considered as *L*-sorbitol (**L**) due to specific features of its structure. The next step catalyzed by bacteria *Acetobacter suboxydans* results in *L*-sorbitol oxidation to *L*-sorbose (**M**), which turns out to be a ketose. A chain of subsequent chemical transformations affords *L*-ascorbic acid.



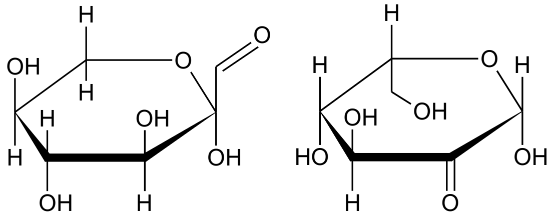
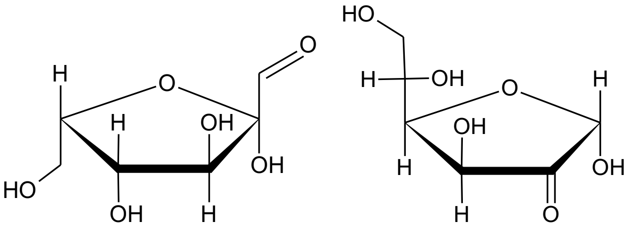
4. Draw the Fischer projections of **K**–**M**, **Q**, **R** and the Haworth projections of **N**, **O**, **P**.

K	**L**	**M**	**N**
			
O	**P**	**Q**	**R**
			

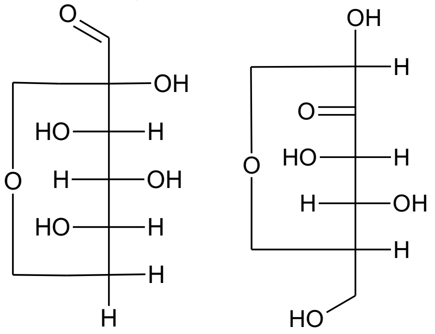
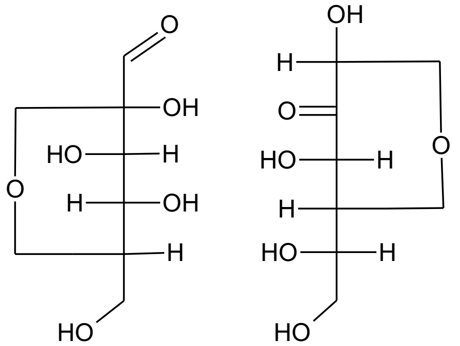
2 pts for each structure

The described above synthesis is not cost-effective, thus researches do not give up trying to develop a more efficient biotechnological process of *L*-ascorbic acid production. It was found that *L*-sorbosone, an *L*-sorbose derivative containing two carbonyl groups (at the 1st and 2nd positions), is the key intermediate in the pathway leading to vitamin C if bacteria *Ketogulonicigenium vulgare* is used.

5. Draw all possible pyranose and furanose forms of *L*-sorbosone. *Hint*: the Haworth projections of pyranose and furanose forms of *D*-glucose are given at the end of the task.

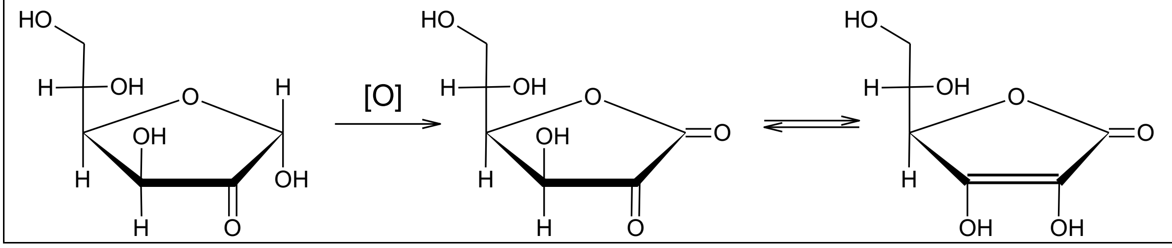
Pyranose forms	Furanose forms
	

The same forms in the Fischer projections

Pyranose forms	Furanose forms
	

2 pts for each correct form in any projection

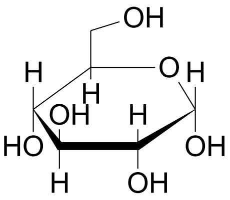
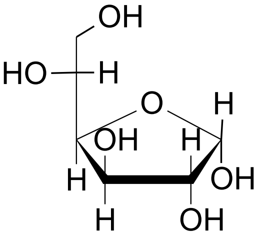
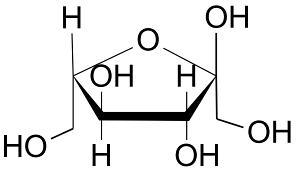
6. Suggest a synthetic scheme leading from *L*-sorbosone to *L*-ascorbic acid if it is known that one of the forms from question 5 is the pathway intermediate. Note that the latter is transformed into the target product in two steps, the enzymatic one being followed by the spontaneous one.



6 pts for the correct scheme

Note. If you failed to deduce the *L*-sorbose formula in question 4, use the *L*-fructose one (given hereunder) to answer the questions 5 and 6.

Reference information. Haworth projections of cyclic forms of α-*D*-glucose and α-*L*-fructose.

α-*D*-Glucose		α-*L*-Fructose
Pyranose form	Furanose form	
		

Comments from the author

1. UDP-*D*-glucose is subjected to a 4-electron oxidation without C-C bond cleavage (there 6 carbon atoms in vitamin C). Oxidation of the 6th hydroxyl group to the carboxylic one resulting in the formation of UDP-derivative of *D*-glucuronic acid turns out to be the only possibility. This is followed by elimination of the UMP and phosphate residues as well as the cycle opening and selective reduction of the carbonyl group to hydroxyl one, which results in the transition to *L*-family (*L*-gulonic acid). The reaction sequence is completed by lactonization, oxidation of one of the hydroxyl groups and tautomerization.

2. The carbonyl group is the only one in *D*-glucose-6-phosphate that can be oxidized affording 6-phospho-*D*-gluconate. The carbonyl group will also be the main target in the case on non-phosphorylated D-glucose. Still, definite fraction of the monosaccharide molecules will be converted into *D*-glucuronic acid due to the presence of enzymes with different specificity and existence of *D*-glucose mostly in pyranose form in an aqueous solution. It should be mentioned that oxidating power of NAD^+ is insufficient for oxidation of two groups (in the 1st and 6th positions) affording D-glucaric acid.

3. 2-Electron oxidation of the hydroxyl group to carbonyl one will be observed if one NAD^+ equivalent enters into the reaction. Due to the reasons similar to those considered in question1, the 6th group is the only oxidation target.

4. *D*-Glucose reduction leads to the hexabasic alcohol. It is impossible to find the most oxidized group in this substance, thus it can presented in two projections, one belonging to *D*-, and the other to *L*-family. Selective oxidation of *L*-sorbitol leads to the ketose *L*-sorbose. Treatment of the letter with two equivalents of acetone allows protection of four hydroxyl groups in the furanose form of the monosaccharide. Further oxidation affords 2-keto-*L*-gulonic acid. Tautomerization and lactonization of the latter finally gives vitamin C.

5. *L*-sorbosone will give pyranose forms if the 1st group interacts with the 5th one, and the 2nd group interacts with the 6th one. Furanose forms can be obtained if the 1st group interacts with the 4th one, and the 2nd group interacts with the 5th one.

6. Only furanose form of *L*-sorbosone formed by interaction of the 1st and 4th groups can by transformed into *L*-ascorbic acid in two steps. First, the semi-acetal bond is transformed into the ester one (the carbonyl group oxidation to carboxylic one), which is followed by tautomerization affording vitamin C.

Problem 5. Methane pyrolysis (12 marks)

Question	1	2	3	**Total**
Points	10	10	10	**30**
Result				

One of the ways to produce hydrogen on an industrial scale is by thermal decomposition of methane according to the reversible reaction

$$CH_{4(g)} = C_{(s)} + 2H_{2(g)}$$

The raw material for the process is relatively cheap (it is natural gas) but the reaction is highly endothermic and requires high temperatures to proceed at a substantial rate. Luckily, methane can be also used as a fuel. When combusted in oxygen according to the equation

$$CH_{4(g)} + 2O_{2(g)} = CO_{2(g)} + 2H_2O_{(g)},$$

it produces a lot of heat: the enthalpy of this reaction is $\Delta_r H^\circ_{298} = -798$ kJ/mol. This heat can be used to convert methane into hydrogen and coke.

Note: throughout the problem assume that enthalpies and entropies of all reactions and heat capacities of all compounds do not depend on temperature.

Question 1: The equilibrium and the yield of methane pyrolysis

1. Under isobaric conditions (p_{total} = 2 bar), 47% of methane is converted into hydrogen and carbon at 1000 °C and 61% – at 1100 °C. What is the yield of the reaction at 1300 °C under the same constant pressure?

Calculation

Denote the yield as Y. For each mole of reactant, the resulting quantities of substances at equilibrium are:

$CH_4 = C + 2H_2$

$(1-Y)\quad Y\quad 2Y$ 1 pt

The total quantity of gases is $(1+Y)$.

If the total pressure is 2 bar, then the partial pressures of the gases are:

$p(CH_4) = 2*(1-Y)/(1+Y)$

$p(H_2) = 2*2Y/(1+Y)$ 2 pts

Expression for the equilibrium constant :

$K = p(H_2)^2/p(CH_4)$ 1 pt

$K = (2*2Y/(1+Y))^2 / (2*(1-Y)/(1+Y)) = 8Y^2/(1-Y^2)$

At 1273 K, $K = 2.27$, $\Delta G° = –8.63$ kJ/mol 1 pt
At 1373 K, $K = 4.74$, $\Delta G° = –17.76$ kJ/mol 1 pt

$\Delta S°$ = (17760–8630)/100 = 91.3 J/mol/K 1 pt
$\Delta H°$ = –8630 + 1273*91.3 = 107.6 kJ/mol 1 pt

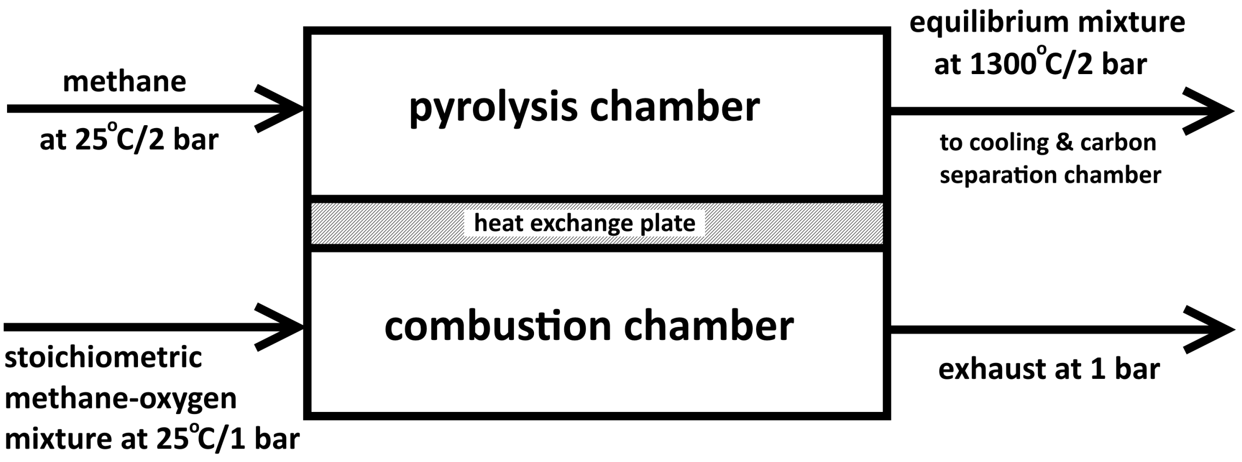
At 1573 K, K = exp((1573*91.3–107600)/(8.314*1573)) = 15.7 1 pt
Therefore, $Y = 0.81$ 1 pt

Yield = 81 %

If you failed to answer this question, use the following values for subsequent calculations: yield of methane is 70%, standard enthalpy of formation of methane is $\Delta_f H°_{298} = –90$ kJ/mol.

Question 2: Heat balance

Assume that methane pyrolysis proceeds at constant pressure (p_{total} = 2 bar) and constant temperature (1300 °C) in the setup schematically shown below.



2. Calculate the total quantities (in moles) of methane and oxygen required to produce one mole of hydrogen using the results from question 1 and assuming that a) thermal equilibrium is established between the combustion chamber and the pyrolysis chamber, b) no heat is dissipated into environment. The isobaric heat capacities of methane and oxygen are 36 and 29 J/(mol·K), respectively.

Calculation

Quantity of methane required to produce 1 mol of H_2:
n = 1/2 / yield = 0.5 / 0.81 = 0.617 mol 1 pt

Heat required to heat methane to 1300 °C:
Q = (1300–25)*0.617*36 = 28.3 kJ 1 pt

Heat required to decompose 0.5 mol of methane at 1300 ^{o}C:
$Q = 0.5\Delta H = 0.5*107.6 = 53.8$ kJ 1 pt

Total $Q = 28.3 + 53.8 = 82.1$ kJ 1 pt

Heat released per mole of methane in a two-step process: heating methane-oxygen mixture to 1300^{o}C, then burning it isothermically:
$Q = 798000 – (1300–25)*(36 + 2*29) = 678.2$ kJ 3 pts
(1 pt for total heat capacity of gas mixture, 1 point for each heat contribution)

Quantity of methane required to get the heat for pyrolysis:
$n = Q / \Delta H = 82.1 / 678.2 = 0.121$ mol 1 pt

Quantity of oxygen
$n = 0.121*2 = 0.242$ mol 1 pt

Total quantity of methane both for pyrolysis and combustion
$n = 0.617 + 0.121=0.738$ mol 1 pt

$n(CH_4) = 0.738$ mol
$n(O_2) = 0.242$ mol

If you failed to answer this question, use the following values for subsequent calculations: $n(CH_4)$ = 1.21 mol, $n(O_2)$ = 1 mol.

Question 3: Bookkeeping

Cost planning is vital for industrial processes. In the question above we assumed that oxygen is used to burn methane but what if we use air? Pure oxygen comes at a cost of 1.50$ per kilogram while air is free. However, air contains only 21 mol.% of oxygen, thus some heat produced by combustion will be spent for heating inert air components.

3. Using the same assumptions as in Question 2, calculate the price of one kilogram of hydrogen in two cases: a) pure oxygen is used for combustion, b) air is used for combustion (CH_4/O_2 ratio is stoichiometric). Assume that mole fraction of nitrogen in air is 79% (neglect argon) and its isobaric heat capacity is 29 J/(mol·K). Methane price is 0.70$ per kilogram.

a) oxygen is used for combustion

Per 1 mol of hydrogen:
$m(CH_4) = nM = 0.738*16 = 11.8$ g 0.5 pts
$m(O_2) = nM = 0.242*32 = 7.74$ g 0.5 pts

Per 1 kg of hydrogen:
$m(CH_4) = 11.8*1000/2 = 5.90$ kg 0.5 pts

$m(O_2) = 7.74*1000/2 = 3.87$ kg 0.5 pts

Price = 5.9*0.70 + 3.87*1.50 = 9.94 \$/kg 1 pt

Price(H_2) = 9.94 \$/kg

b) air is used for combustion

Heat released per mole of methane in a two-step process: heating methane-air mixture to 1300 °C, then burning it isothermally:
$Q = 798000 – (1300–25)*(36 + 2*29/0.21) = 400.0$ kJ 3 pts
(1 pt for total heat capacity of gas mixture, 1 point for each heat contribution)

Quantity of methane needed to burn to get the heat for pyrolysis:
$n = Q/\Delta H = 82.1 / 400.0 = 0.205$ mol 1 pt

Total quantity of methane both for pyrolysis and combustion
$n = 0.617 + 0.205 = 0.822$ mol 1 pt

Per one mole of hydrogen:
$m(CH_4) = nM = 0.822*16 = 13.2$ g 0.5 pts
Per 1 kg of hydrogen:
$m(CH_4) = 13.2*1000/2 = 6.60$ kg 0.5 pts

Price = 6.60*0.70 = 4.62 \$/kg 1 pt

Price(H_2) = 4.62 \$/kg

Hint. Thermodynamic equations

Relation between equilibrium constant and thermodynamic functions:

$$\Delta G^\circ = -RT\ln K_p = \Delta H^\circ - T\Delta S^\circ$$

Enthalpy change during isobaric heating:

$$\Delta H = nC_p\left(T_2 - T_1\right)$$