3rd Olympiad of Metropolises

Chemistry

Theoretical Problems

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 balanced equations of the reactions described.

$\mathbf{X_1}$ –

Ionic composition of $\mathbf{X_1}$ –

Reactions:

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:

Oxidizer:

Reducing agent:

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:

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

$\mathbf{Y_5}$ –

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 $\mathbf{Y_6}$

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:

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

$\mathbf{X_7}$ –

Reaction:

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)

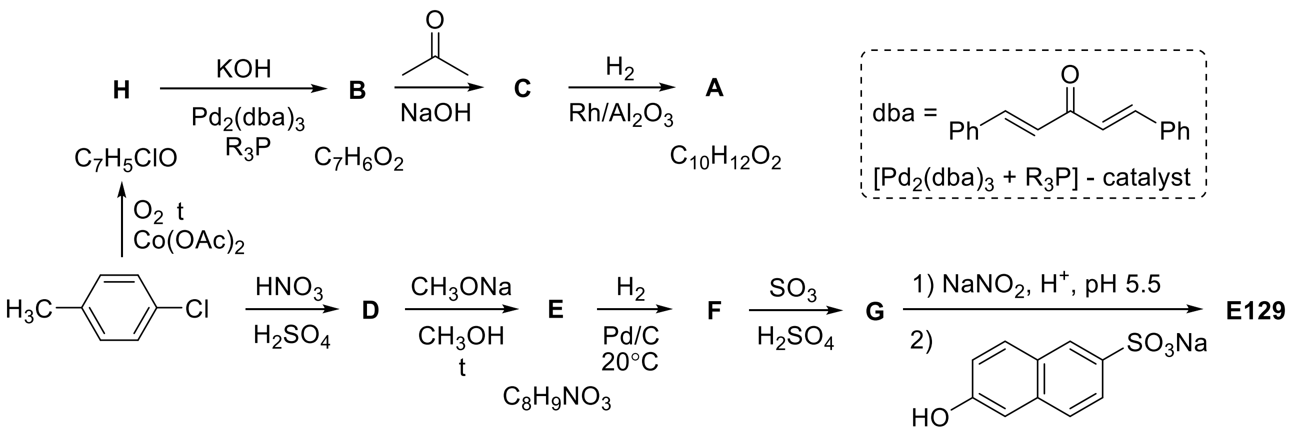
Raspberry (*Rubus idaeus*) is widespread in the central part of Russia, including the Moscow region, a deciduous half-shrub with sweet and healthy fruits used for treatment of colds and flu as antipyretic and diaphoretic remedies in fresh or frozen form, as well as in jam, marmalade, jelly, etc. Raspberry 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**

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

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

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	

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

$m(SO_2)$ =

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:

Reaction of thiophene:

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:

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:

$N(H_2S)$ =

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:

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:

The total reaction:

b) Calculation

ΔH = ________ kJ/mol

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

K_p = ________

b) Calculation

$p_0(H_2S)$ = ________

Reference data.

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

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

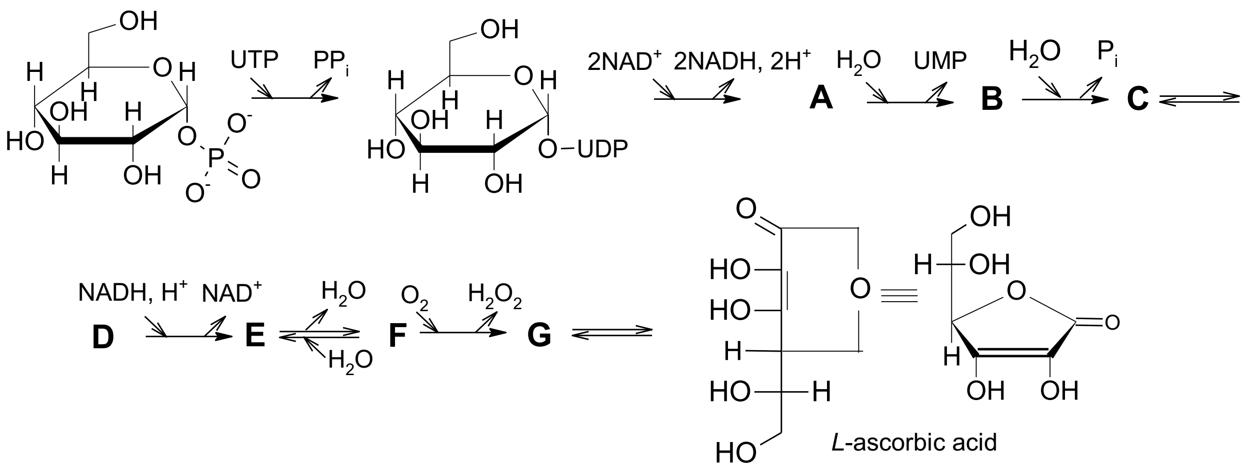
Problem 4. Synthesis of vitamin C **(12 marks)**

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

Notes about Fischer projections.

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

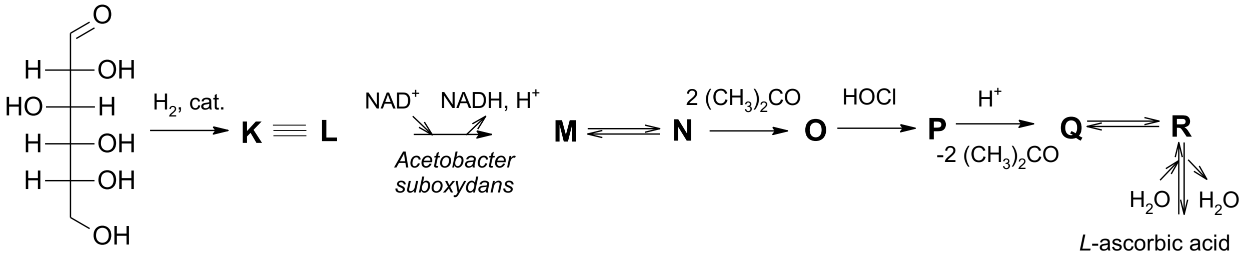
B. If a chemical reaction results in a product with the most oxidized group on the bottom, whereas the rest oxygen-containing groups are hydroxyl ones, the projection must be rotated by 180^{o} in the projective plane.

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)

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**

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.

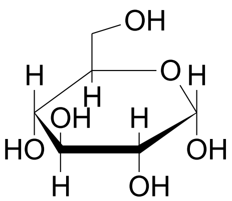
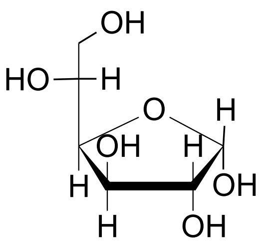
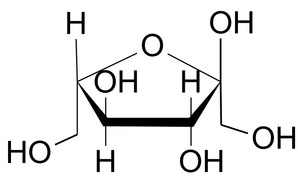
5. Draw all possible pyranose and furanose forms of *L*-sorbosone. *Hint*: the Haworth projections of pyranose and furanose forms of *D*-glucose are given at the end of the task.

Pyranose form(s)	Furanose form(s)

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.

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.

<table>
<tr><th colspan="2">α-D-Glucose</th><th rowspan="2">α-L-Fructose</th></tr>
<tr><th>Pyranose form</th><th>Furanose form</th></tr>
<tr><td>
</td><td>
</td><td>
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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 $\Delta_r H^o_{298} = -798$ 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 ^oC and 61% – at 1100 ^oC. What is the yield of the reaction at 1300 ^oC under the same constant pressure?

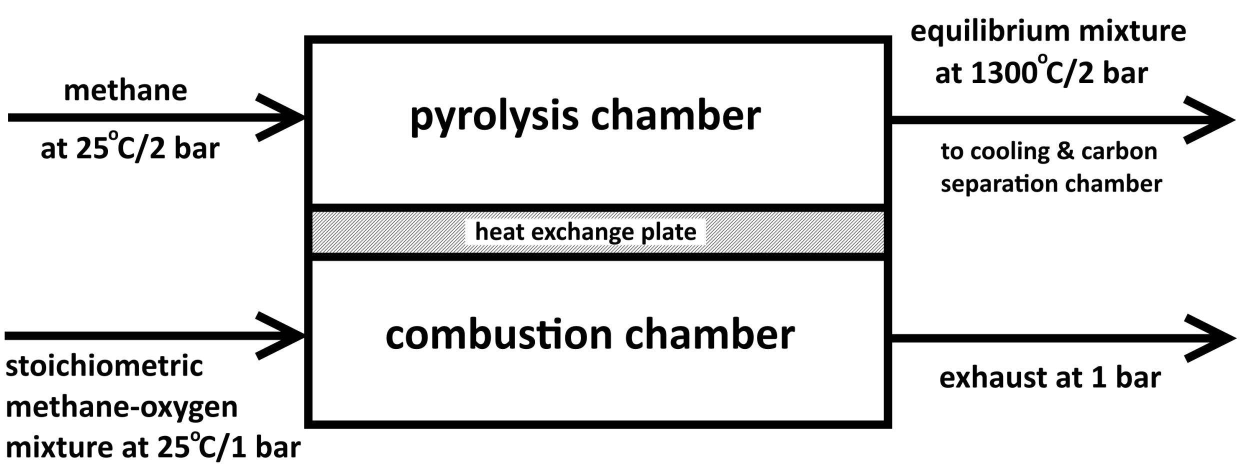
Calculation

Yield = ______________ %

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 $\Delta_f H^o_{298} = -90$ kJ/mol.

Question 2: Heat balance

Assume that methane pyrolysis proceeds at constant pressure (p_{total} = 2 bar) and constant temperature (1300 ^{o}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

$n(CH_4)$ = __________ mol

$n(O_2)$ = ___________ 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

Price(H_2) = ______________ $/kg

b) air is used for combustion

Price(H_2) = _______________ \$/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:

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