2nd Olympiad of Metropolises

Chemistry

Theoretical Problems

6 September 2017

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
Faraday constant	$F = 96485$ C mol^{-1}

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 -

Problem 1. Golden domes **(10 marks)**

Question	1	2	3	4	**Total**
Points	7	9	2	2	**20**
Result					

The white substance X_1 can be obtained by burning of powdered metal X in oxygen (*reaction 1*). The treatment of a mixture of X_1 and carbone with chlorine gives a colorless liquid X_2 containing 25.24 wt.% of element X (*reaction 2*). The vapor of X_2 reacts with ammonia at 1000 ^oC giving a brown powder of X_3, containing from 77.37 to 85.07 wt.% of X (*reaction 3*). The compound X_3 is responsible for golden color of domes of several Moscow churches and cathedrals.

The compound X_3 can be synthesized directly from X or X_1 (*reactions 4 and 5*).

1. Name the element X and determine the formulas of $X_1 – X_3$. For X_3 give the range of compositions. In calculations, use the exact values of molecular masses from the Periodic table.

Calculations

X –

X_1 –

X_2 –

X_3 –

2. Write the balanced equations of reactions 1-5.

Reaction 1:
Reaction 2:
Reaction 3:
Reaction 4:
Reaction 5:

3. The crystal structure of ideal X_3 has the same type as that of a binary compound containing 39.3 wt.% of some other metal. Determine this type.

Structural type –

4. Name the coordination polyhedra of cation and anion in the structure of X_3.

Coordination polyhedron of:
cation –
anion –

Problem 2. Big adventure of a small alkyl **(10 marks)**

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

The prolonged heating of benzene (1.56 g) with alkyl bromide $C_mH_{2m+1}Br$ (**A**, 6.54 g) in the presence of $AlBr_3$ (0.001 mol) affords a mixture of alkylbenzenes with the compound **B** as the major component. The stepwise character of the process was proved by periodic sampling and analysis of the reaction mixture content. The major components in the samples were found as follows: benzene, **A**, and the compound **C** in the first sample, the compound **D** in the second sample, and the compound **E** in the third sample.

Once the reaction completed (qualitative and quantitative composition did not change with time), the reaction mixture was neutralized with aqueous $NaHCO_3$. From this mixture, the compound **B** was isolated with a 90% yield (with respect to benzene consumed); other alkylbenzenes were obtained as side products and were not isolated. Heating of **B** with an excess of $KMnO_4$ in the presence of H_2SO_4 produced the acid **F** as a single organic product. It was found that the neutralization of 0.63 g of **F** required 6.84 mL of 5.00% NaOH solution (d = 1.054 g mL^{-1}).

1. Draw the structural formula of the compound **F** accounting for the fact that the molecule of **F** contains 3 types of carbon atoms. Draw the structures of the compounds **A** and **B**. Write down all other alkyl bromides which allow synthesizing the acid **F** as a single organic product of **B** oxidation. Prove by calculations that other alkyl bromides do not satisfy the problem conditions.

A	**B**	**F**
Other alkyl bromides which allow for the synthesizing **F** as a single oxidation product		
Calculations proving that only **A** satisfies the problem conditions		

2. Draw the structures of the compounds **C**, **D** and **E** if these are not isomers.

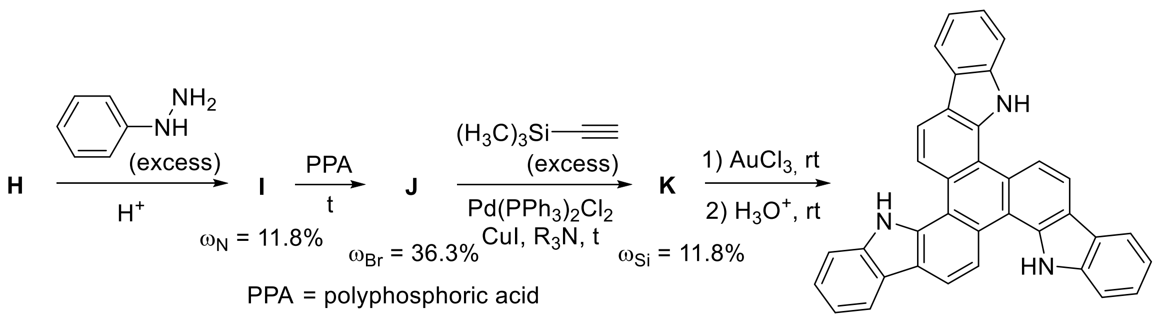
C	**D**	**E**

3. When the reaction mixture obtained after alkylation was poured into water, an acidic solution was formed. How many grams of $NaHCO_3$ should be added to this solution to achieve pH 7.00? Neglect the solubility of carbon dioxide in water.

Calculations

$m(NaHCO_3)$ =

Treatment of **B** with an excess of bromine in the presence of $FeBr_3$ followed by UV-irradiation of the reaction mixture yielded the mixture of products with the compound **G** as the major component. Slow hydrolysis of **G** with diluted aq. NaOH solution led to the compound **H**; ^{1}H NMR spectra of both **G** and **H** contain one signal only (i.e. in both compounds all hydrogen atoms are identical). Further transformations of **H** into a compound used in organic electronics is shown in the scheme below.



4. Draw the structures of the compounds **G-K**.

G	**H**	**I**

J	**K**

Problem 3. Clean water for the big city **(10 marks)**

Question	1	2	3a	3b	4a	4b	5	6	**Total**
Points	3	2	3	2	2	2	4	2	**20**
Result									

Purification of water is one of the most important problems of a big city. In Moscow, water is quite clean; one can drink cold tap water without any additional filtrations or other procedures. Such purity is achieved by the integrated use of mechanical, physico-chemical and chemical methods in the urban water purification system.

1. Chlorination is the most common method of water purification. Indicate what other methods are suitable for use in urban water treatment systems.

1) UV irradiation
2) Ozonation
3) Binding of heavy metal ions by concentrated ammonia solutions
4) Oxidation by silver and gold ions
5) Adsorption on carbon filters
6) Precipitation of heavy metal ions by hydrogen sulfide

Numbers of the correct answers:

For many years in Moscow, pure chlorine was used for chlorination of water. Chlorine was stored as a liquid at elevated pressure. However, since 2012 urban services use another reagent – sodium hypochlorite, which is safe for humans, but effectively kills most of microorganisms. Being dissolved in water, both chlorinating reagents form (reversibly) the same substance.

2. Give the structural formula of this substance.

3. According to the Russian sanitary standards, pH of drinking water must be kept in the range from 6.0 to 9.0.

a) How many milligrams of pure sodium hypochlorite can be dissolved in 1 liter of water so that the pH value still does not exceed the limits? The acidity of hypochlorous acid: pK_a = 7.54.

Calculation

m(NaOCl) = ______ mg

b) The optimal technological scheme of water purification involves preparation of sodium hypochlorite solutions in which the concentrations of the ionic and protonated forms are the same. What is the pH of such solutions?

Calculation

pH =

4. Chlorine-containing oxidants used for water purification or bleaching are characterized by the content of "active chlorine" defined as the ratio of the mass of chlorine obtained by the interaction of the oxidant with hydrochloric acid to the mass of the oxidant (in %).

a) Can the «active chlorine content» exceed 100%? If yes, give an example. If not, explain why it is impossible.

Answer (yes, no):

Reaction equation or arguments:

b) Solid sodium hypochlorite is not stable. For this reason, it is produced as a 15 wt.% solution. What is the percentage of «active chlorine» in such solution?

Calculation

% of “active chlorine” =

5. The high-quality sodium hypochlorite needed for purification is obtained by electrolysis directly at the water treatment plant. What substance is used as the reagent? Write the equations of the cathode and anode processes, as well as the overall equation of electrolysis.

Reagent:

Cathode process:

Anode process:

Overall equation:

6. In general, Moscow citizens spend water very moderately (partly due to the installation of water consumption meters): on average, each of the 14.2 million residents of the capital uses 141 liters of water per day. Assuming that 0.3 mg / L of "active chlorine" in water is needed for the effective purification, calculate how many tons of 15% sodium hypochlorite solution is consumed by the city every day?

Calculation:

m(solution) = _____ t

Problem 4. How do organisms obtain energy? **(10 marks)**

Question	1	2	3	4	5	6	**Total**
Points	2	7	3	2	10	6	**30**
Result							

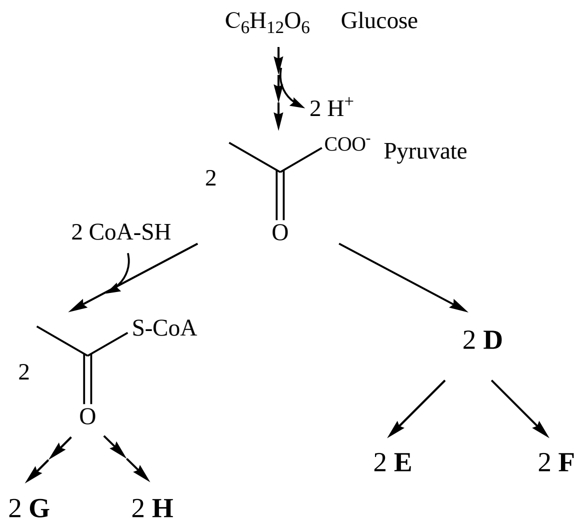
Many living things obtain energy by oxidizing organic molecules with reduced and/or partially oxidized carbon atoms. A substance in a more reduced state provides for greater energy that can be potentially obtained from it. Some carbon containing compounds are given hereunder in an arbitrary sequence: CO, CH_4, C_2H_5OH, $HCOOH$, CO_2, CH_3OH, $C_6H_{12}O_6$, C, $HCHO$, CH_3CHO.

1. Arrange the compounds in the increasing order (from the most reduced to the most oxidized) of the averaged oxidation degree (oxidation number) of its carbon atoms. If two or more compounds are equal in this parameter, write down the corresponding molecules one below the other.

Increasing of the averaged oxidation degree (oxidation number) of carbon atoms

Being the initial stage of digestion of monosaccharides, glycolysis occurs under both aerobic (with oxygen) and anaerobic (without oxygen) conditions leading to one and the same product (pyruvate, the pyruvic acid anion) in both cases. Further direction of pyruvate transformation depends on particular organism and conditions. Metabolic pathways of pyruvate are extremely diverse in anaerobic bacteria. These processes referred to as fermentations allow accumulating energy in the form of ATP as a result of oxygen free oxidation of organic substrates. Apart from widely known lactic acid and alcoholic fermentations, there are other fermentation types leading to organic products with 1 to 4 carbon atoms as well as to mixtures of these products. Some fermentation pathways will be considered below.

A process typical of *Escherichia* and *Salmonella* genera is shown on the hereunder scheme. It starts with the lyase (the enzyme facilitating a C–C bond cleavage) catalyzed transformation of pyruvate into acetyl-coenzyme A and the compound **D**. In some bacterial species, **D** turns out to be the final fermentation product; whereas other species degrade it to a mixture of equimolar amounts of two gases **E** and **F** (**E** is more than 15 times lighter than **F**). Acetyl-coenzyme A affords two asymmetric compounds **G** and **H** containing two carbon atoms each. Only one carbon atom in each of **G** and **H** is linked with oxygen atom(s). The averaged oxidation degree of carbon atoms in **G** is higher than that in **H**. Under definite conditions, **G** and **H** interact at 1:1 molar ratio leading to the compound **I** with a specific strong odor. **I** is free of asymmetric carbon atoms.



2. Draw the compounds **D-I**.

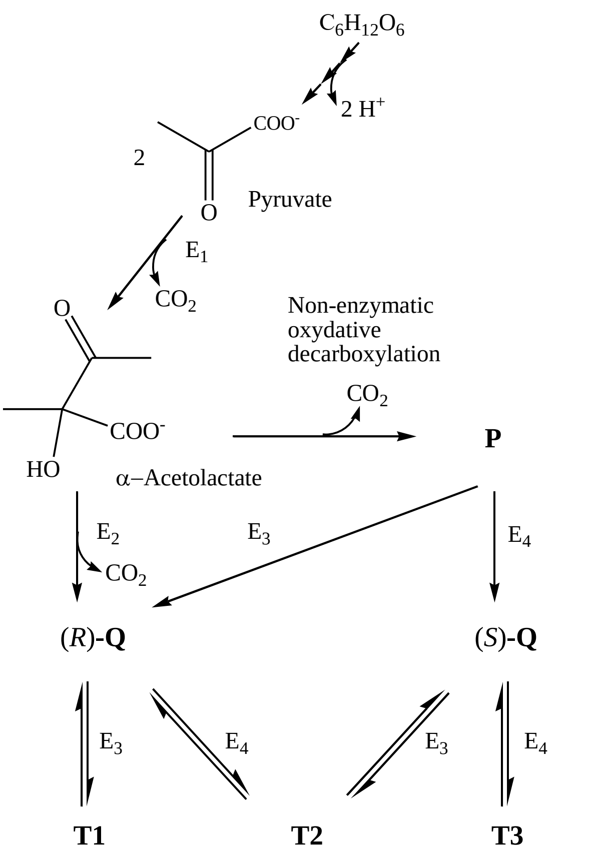
D	**E**	**F**
G	**H**	**I**

Another type of fermentation is met in *Clostridium* genus. In this case one molecule of glucose affords a mixture of the same gases **E** and **F** (in the same ratio as in i. 2), as well as an unbranched anion **J** composed of 3 elements. The corresponding acid **J1** contains 54.52 % by mass of C.

3. Write down the equation of glucose fermentation into **E**, **F**, and **J1**, occurred in *Clostridium* bacteria.

Calculations and work
Equation

P, **Q**, and **T** composed of 4 carbon atoms each are formed as a result of glucose fermentation by bacteria belonging to *Enterobacter* genus (see the rightwards scheme).
Information about the enzymes on the scheme:
E_1 is α-acetolactate synthase,
E_2 is α-acetolactate decarboxylase,
E_3 and E_4 belong to same class of enzymes.
There is one peak in the ^{1}H NMR spectrum of **P**, and four peaks of different intensity in that of **Q**. **Q** contains one asymmetric center. **T1-T3** are stereoisomers. Transformation of **P** into **Q** occurs in both directions in some bacteria.

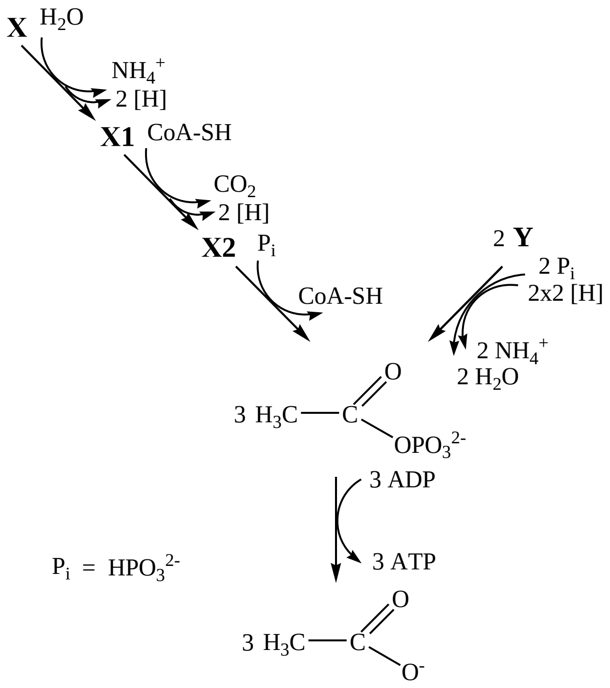


4. What class of enzymes do E_3 and E_4 belong to? Tick the appropriate box.

☐ Decarboxylase
☐ Carboxylase
☐ Oxidoreductase
☐ Lipase
☐ Synthase

5. Draw the structural formulae of **P**, **Q**, and **T**. Indicate the absolute configuration (writing *R* or *S*) of each stereocenter in **T1-T3**.

P	(*R*)-**Q**	(*S*)-**Q**
T1	**T2**	**T3**



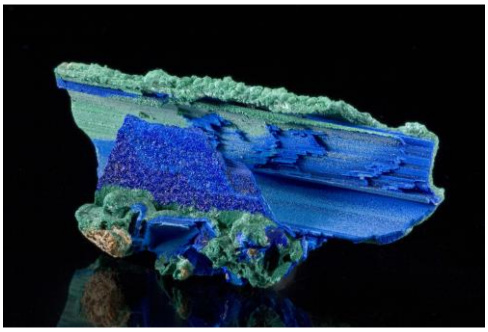
Compounds other than products of carbohydrate digestion can be involved in fermentation. A redox reaction between a pair of amino acids referred to as Stickland fermentation is found in bacteria *Pseudomonas*. The leftwards scheme illustrates the Stickland reaction between two canonical α-amino acids **X** and **Y**.

6. Draw the structural formulae of **X-X2** and **Y**.

Designations used in the text:
CoA-SH is co-enzyme A,
ADP and ATP are adenosine diphosphate and adenosine triphosphate, respectively,
P_i is inorganic phosphate.

X	**X1**	**X2**	**Y**

Problem 5. Equilibrium between the copper minerals **(10 marks)**



Question	1	2	3	4	5	**Total**
Points	8	10	16	20	34	**88**
Result						

The Ural mountains, dividing Europe and Asia, have long been a source of a large number of minerals. The glory of the Urals was brought by deposits of "gems" – precious, semiprecious and ornamental stones. Among them, malachite stands out – a beautiful patterned dark green mineral. It was used for a long time not only as an ornamental stone, but also as a copper ore, which led to the almost complete exhaustion of the Ural deposits.

1. 2.21 g of malachite (hereinafter **M**) was heated at 500 ° C to constant weight, yielding 1.59 g of black powder. The evolved gases were successively passed through the tubes with phosphorus (V) oxide and calcium oxide, the mass of the first tube being increased by 0.18 g and the second by 0.44 g. With stronger heating, above 1100 ° C in the nitrogen flow, the black powder loses up to 10.06% of its weight. Determine the composition of **M**, write down the equations of all these reactions.

Calculations   Formula of **M**:
Reaction equations:

2. Azurite (hereinafter **A**) is a mineral of blue color with the same qualitative composition as **M**, but other quantitative. Upon heating to 500 ° C, **A** loses 30.77% of its mass. Determine the formula of **A**.

Calculations

Formula of **A**:

3. In copper ores, **A** is often found together with **M**. One of them is able to replace the other while maintaining the shape of the original mineral, forming pseudomorphs, as in the image above. Estimate the carbon dioxide pressure at which both minerals can coexist at room temperature.

Calculations

$P(CO_2)$ = ________

4. At a low carbon dioxide pressure, both minerals can be converted to tenorite (hereinafter **T**), a mineral identical in composition to the black powder formed by the thermal decomposition of **M**. Atmospheric air contains 400 ppm (parts per million) of carbon dioxide. Which of the copper minerals – **M**, **A** or **T** – is the most stable under the given conditions (temperature 25 ^oC)? Confirm your answer by calculations and estimates.

Thermodynamic data:

Substance	Malachite	Azurite	Tenorite	$H_2O(l)$	$CO_2(g)$
$\Delta_f G^o$(298 K), kJ/mol	–883	–1389	–130	–237	–394

Calculations and estimates

The most stable mineral –

5. **M** can be precipitated from the solutions under mild conditions using baking soda as a source of carbonate ions.

a) Determine whether a precipitate will be formed when 1 drop of 1.00 M copper sulfate solution is added to 20.0 ml of 0.100 M sodium hydrogen carbonate solution. 1 ml contains about 20 drops.

b) Is it possible to assert with confidence that the precipitate contains an individual mineral? If so, which one? If not, why?

Solubility products K_{sp}: $8.8 \cdot 10^{-44}$ for azurite and $1.0 \cdot 10^{-32}$ for malachite.
Acidity constants for carbonic acid: $K_1 = 4.5 \cdot 10^{-7}$, $K_2 = 5.0 \cdot 10^{-11}$.

Calculations

a) The precipitate is formed is not formed

b) Answer (yes (formula), no):

Problem 6. Reserve battery **(10 marks)**

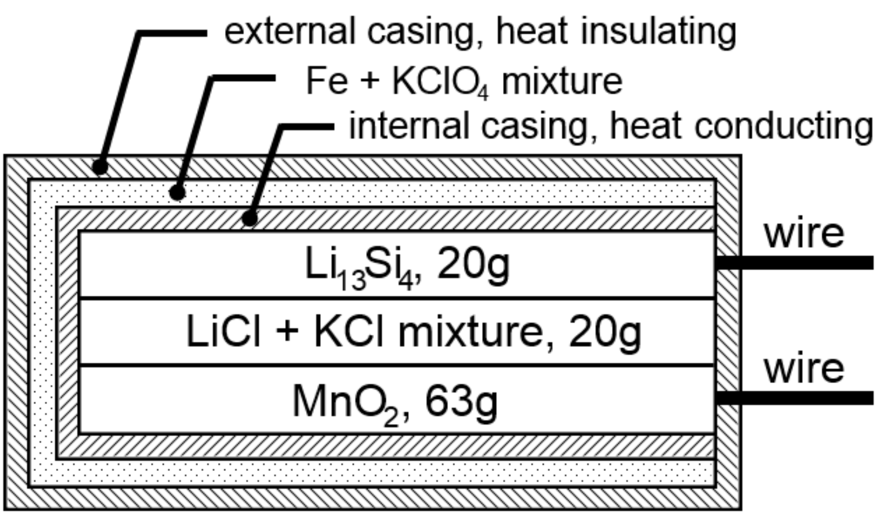
Question	1a	1b	1c	2	3	4	5	**Total**
Points	2	2	2	2	4	4	4	**20**
Result								

Reserve batteries are electrochemical cells which can be stored for decades without discharge but can be promptly activated when needed. This is achieved by isolating the cell components (cathode, anode and electrolyte) from one another prior to activation. One example of such a cell is the magnesium-silver chloride battery which is used in seaborne devices. During storage, the space between electrodes is empty but once the device is in water, chemical reaction starts.

Another type of reserve batteries is a so-called thermal battery. In this type of batteries an electrolyte is a solid ionic compound which melts upon activation due to ignition of a pyrolant (heat-producing mixture). When melted, electrolyte conducts electricity. In this problem, we consider a specific thermal battery with the following composition:

$$Li_{13}Si_4 \mid LiCl + KCl \mid MnO_2$$

The products of the discharge reaction in the cell are lithium silicide Li_7Si_3 and lithium-manganese spinel $LiMn_2O_4$. Li^+–conducting electrolyte is a relatively low-melting (melting point 352 ^oC) eutectic[1] mixture of LiCl and KCl with molar fractions of the salts 56 and 44%, respectively. Pyrolant which heats the battery during activation is a mixture of iron and potassium perchlorate with mass ratio 86 : 14. The scheme of the battery and the masses of the electrodes and the electrolyte are provided in the picture below. Ignition device for iron-perchlorate mixture is not shown. The working temperature of the battery is 380 ^oC. It can be maintained for a sufficient time due to heat insulation.



[1] Eutectic mixture has the lowest melting point among all mixtures with the same qualitative composition

1a. Write the balanced equation for the discharge reaction of this battery. Note that silicon does not leave anode at all times.

1b. Write the balanced equation for the burn reaction of the $Fe/KClO_4$ mixture. Note that iron is in large excess thus the oxide of iron in the lowest oxidation state is formed.

1c. Large excess of iron in the pyrolant is used for two reasons: a) with this particular composition the linear burn rate is the largest and b) excess of iron prevents another reaction in which a gas is produced which can mechanically destroy the battery. Write the reaction equation.

Use the data and formulae below for the questions that follow:

Substance	$Li_{13}Si_4$	Li_7Si_3	MnO_2	$LiMn_2O_4$	Fe	FeO	KCl	$KClO_4$
$\Delta_f H^o_{298}$ kJ/mol	–517	–294	–520	–1404	0	–272	–436	–430
S^o_{298} J/(mol·K)	370	225	53	165	27	61	83	151

Substance	$Li_{13}Si_4$	MnO_2	Fe	FeO	KCl	$KClO_4$
C_p J/(mol·K)	372	54	25	68	74	111

Properties of the LiCl+KCl mixture:

Heat of fusion	230 J/g
Heat capacity (solid)	0.90 J/(g·K)
Heat capacity (liquid)	1.27 J/(g·K)

Relation between electric charge Q, current I, and time t $\quad Q = I \cdot t$

Assume that all heat capacities are constant, the pressure is constant (1 bar), ΔH and ΔS for all reactions do not depend on temperature.

2. Calculate the capacity of this battery in mA·h. Note that SI units for charge, current, and time are coulomb, ampere and second, respectively.

Calculations

Capacity = _______ mA·h

3. Calculate the electromotive force of this battery at 380°C.

Calculations

emf = _____

4. What mass of the iron-perchlorate mixture is required to heat the battery from the temperature 25 °C to the working temperature 380 °C? Neglect the heat capacity of the battery casing.

Calculations

Mass of the mixture = ______

The maximum current density (electric current per surface area of the electrode) is the parameter of a battery which is no less important than its capacity or electromotive force. In electrochemical cells, the current density is usually limited by kinetic parameters such as rate of diffusion of ions in the electrolyte or the rate of their discharge on the electrodes. In this particular battery, another factor is also important. You'll have to deduce it from the description of a certain phenomenon that takes place in the battery and answer the question.

As long as the current density does not exceed the certain threshold, the battery functions as intended until the cathode or anode material runs out. Gradual increase of the current density leads to formation of a white precipitate near cathode. A larger increase in the current density leads to formation of a white precipitate near anode also. The larger the current density, the more crystals are formed. At some point the amount of crystals becomes so large that they block the surface of one of the electrodes and the reaction stops. This phenomenon is reversible – disconnecting the battery from the electric load causes gradual dissolution of the precipitates (if the battery has not cooled down in the meantime) and the cell becomes functional again.

5. Write down the formulas of the crystals that precipitate near cathode and anode. Note that the reactions in the battery do not depend on the current density.

Cathode	
Anode	