2nd Olympiad of Metropolises

Chemistry

Theoretical Problems
with solutions

6 September 2017

Moscow, Russia

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 carbon 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 ^{o}C 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_1 is an oxide, hence X_2 is a chloride of metal X. Denote chloride as XCl_n, then

$$\omega(\mathrm{X}) = \frac{M(\mathrm{X})}{M(\mathrm{X}) + 35.45n} = 0.2524$$

M(X) = 11.87n.

At n = 4, we get M(X) = 47.87 g/mol, X – titanium. X_1 – titanium dioxide, TiO_2.

Reaction between titanium chloride and ammonia gives titanium nitride – the substance with a non-stoichiometric composition. Let us determine the range of its compositions:

$$\mathrm{TiN}_x\text{:}\ \omega(\mathrm{Ti}) = \frac{47.87}{47.87 + 14.01x} = 0.7737\text{, } x = 1.$$

$$\mathrm{TiN}_y\text{:}\ \omega(\mathrm{Ti}) = \frac{47.87}{47.87 + 14.01y} = 0.8507\text{, } y = 0.6.$$

X – titanium, Ti	1 points
X_1 – TiO_2	1.5 points
X_2 – $TiCl_4$	1.5 points
X_3 – $TiN_{0.6}$ – $TiN_{1.0}$	3 points

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

Reaction 1: $Ti + O_2 = TiO_2$	1 point
Reaction 2: $TiO_2 + 2C + 2Cl_2 = TiCl_4 + 2CO$	2 points
Reaction 3: $2TiCl_4 + 2NH_3 = 2TiN + 6HCl + Cl_2$	2 points
Reaction 4: $2Ti + N_2 = 2TiN$	2 points
Reaction 5: $2TiO_2 + 4C + N_2 = 2TiN + 4CO$	2 points

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 – sodium chloride, NaCl (39.3% of Na)	2 points

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

Coordination polyhedron of:	
cation – octahedron	1 point
anion – octahedron	1 point

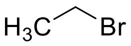
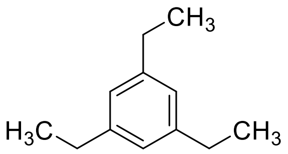
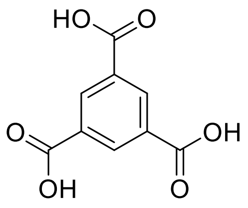
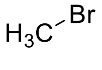
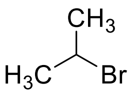
Problem 2. Big adventure of a small alkyl **(10 marks)**

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

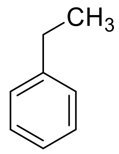
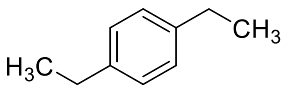
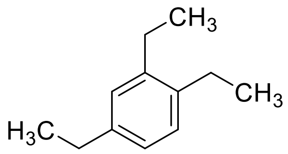
The prolonged heating of benzene (1.56 g) with alkyl bromide $C_mH_{2m+1}Br$ (**A**, 6.54 g) in the presence of $AlBr_3$ (0.001 mol) affords a mixture of alkylbenzenes with the compound **B** as the major component. The stepwise character of the process was proved by periodic sampling and analysis of 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**
 1 point	 1 point	 1 point
Other alkyl bromides which allow for the synthesizing **F** as a single oxidation product   (2 compounds, 1 point for each)		
Calculations proving that only **A** satisfies the problem conditions See the detailed solution (2 × 0.5 points)		

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

C	**D**	**E**
 1 point	 1 point	 1 point

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. According to the problem conditions, the final mixture contains alkylbenzenes only as organic compounds. Therefore, 1.56:78 = 0.02 mol of benzene reacted with 0.06 mol of ethyl bromide producing 0.02 mol of **B** and 0.06 mol of HBr. Moreover, 0.001 mol of $AlBr_3$ is present in the reaction mixture.

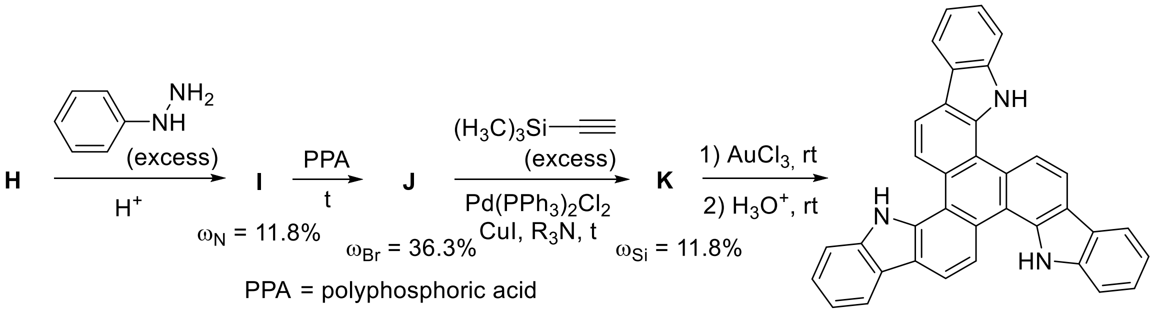
$$HBr + NaHCO_3 = NaBr + CO_2\uparrow + H_2O$$
$$AlBr_3 + 3NaHCO_3 = 3NaBr + 3CO_2\uparrow + Al(OH)_3\downarrow$$

To achieve pH 7.00 it is required to add 0.06 + 3*0.001 = 0.063 mol of $NaHCO_3$. This corresponds to 5.29 g.

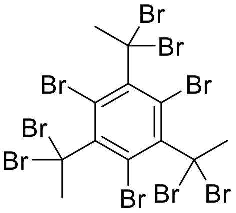
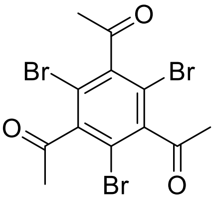
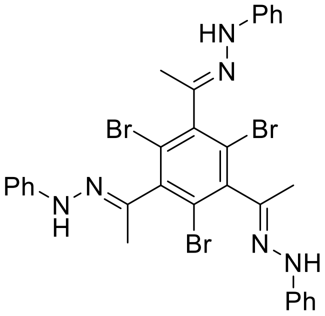
$m(NaHCO_3)$ = 5.29 g 2 points

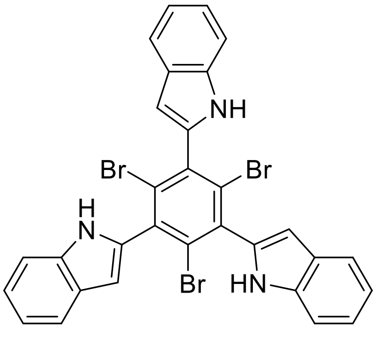
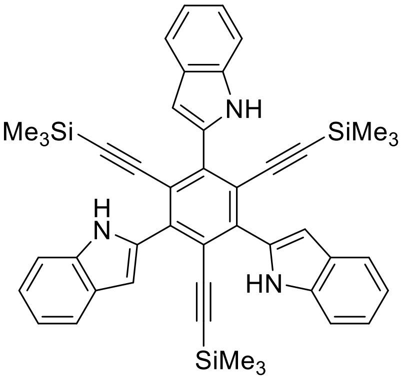
(1 point if $AlBr_3$ is not taken into account)

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**
 1 point	 1 point	 1 point

J	**K**
 1 point	 1 point

Detailed solution.

1. It is clear that compound **B** belongs to the class of alkylbenzenes which has the general formula of $C_6H_n(C_mH_{2m+1})_{6-n}$. Heating of alkylbenzenes with $KMnO_4$ in the presence of acid leads to the oxidation of side alkyl chain to the corresponding carboxylic acid. So, the product of the oxidation of **F** can be described as $C_6H_n(COOH)_{6-n}$. The neutralization of 0.63 g **F** requires 6.84×1.054 = 7.2 g of 5% aq. NaOH solution. This corresponds to 9 mmol of NaOH. If **F** is monoacid (n = 5), its molecular weight should be equals to 0.63:0.009 = 70. This is impossible. Only tricarboxylic acid (n = 3; $M_{\mathbf{F}}$ = 210) satisfies the problem conditions. As compound **F** has three types of carbon atoms, this can be only benzene-1,3,5-tricarboxylic acid. Therefore, **B** is 1,3,5-trialkylbenzene. The formation of **F** as a single organic product of the oxidation of **B** is possible for 1,3,5-trimethylbenzene, 1,3,5-triethylbenzene, 1,3,5-triisopropylbenzene. So, possible alkyl bromides are ethyl bromide (**A**), methyl bromide (**A'**) and isopropyl bromide (**A''**).

1.56:78 = 0.02 mol of benzene were introduced into the reaction. Weight of alkyl bromide (6.54 g) corresponds to 0.0688 mol of CH_3Br, 0.06 mol of C_2H_5Br and 0.053 mol of isopropyl bromide. If methyl bromide was a started alkylation agent, 0.06 mol of CH_3Br is consumed for the formation of 0.02 mol of trialkylbenzene; after that 0.0088 mol of CH_3Br should further react with trialkylbenzenes producing the mixture of 0.0112 mol of trimethylbenzenes and 0.0088 mol of tetramethylbenzenes (in the reaction mixture some quantities of di- and pentamethylbenzenes can also be present but this does not affect the general conclusion). Evidently, it is impossible to isolate 1,3,5-trimethylbenzene in 90% yield from this mixture. In the case of isopropyl bromide, 0.04 mol of alkyl halide is consumed for the formation of dialkylbenzenes; after that 0.013 mol of isopropyl bromide should react with dialkylbenzenes producing trialkylbenzenes. In other words, after the reaction will finished it should contain approximately 65% (0.013×100%/0.02) of trialkylbenzene and 35% of trialkylbenzene. Again, this is impossible to isolate 1,3,5-triisopropylbenzene in 90% yield from this mixture. On the contrary, ethyl bromide is the ideal substrate from this point of view as in this case the theoretical yield of triethylbenzene is 100%. Evidently, in this case it is possible to isolate 1,3,5-triethylbenzene in 90% yield. Therefore, **B** is 1,3,5-triethylbenzene, **A** is ethyl bromide.

2. Compounds **C**, **D** and **E** are not isomers. Therefore, they are products of the sequential alkylation of benzene with ethyl bromide Therefore, **C** is ethylbenzene. Compound **D** is diethylbenzene. Ethyl group is electron-donating substituent and directs electrophilic attack to *ortho*- and *para*-positions. Steric demands prevent *ortho*-attack. Therefore, the major product in the second probe should be 1,4-diethylbenzene (compound **D**). Minor product is 1,2-diethylbenzene (**D'**). Compound **E** is the product of **D** alkylation. This is 1,2,4-triethylbenzene (the same compound is formed from **D'**). Under the prolonged keeping in the presence of Lewis acid and HBr evolved during the previous alkylation steps, **E** undergoes isomerization to the more stable isomer (1,3,5-triethylbenzene).

4. Compound **B** has three types of hydrogen atoms (aromatic CH, methylene protons and methyl groups protons) while in compound **G** all protons are identical. This shows that during bromination only protons of methyl groups left intact. On the contrary, other protons were substituted by bromine atoms (aromatic protons *via* aromatic electrophilic substitution catalyzed by $FeBr_3$; methylene protons *via* radical bromination which demonstrate high selectivity in regard to benzylic C-H bonds. Therefore, **G** is 1,3,5-tribromo-2,4,6-(1,1-dibromoethyl)benzene. Diluted alkali solution hydrolyzed selectively Ar–C–Br but not Ar-Br bonds. As a result, every CBr_2 moiety is transformed into C=O group. The reaction of **H** with phenylhydrazine is the formation of hydrazone. All three carbonyl groups are transformed in hydrazones, this is supported by nitrogen content in **I**. Under heating in polyphosphoric acid, phenylhydrazones are transformed into indoles (Fischer reaction). This is supported by both bromine content in **J** and (this is more important and conclusive) structure of the final product which has three indole fragments. The comparison of **J** with the final product shows that **J** has bromine atoms in the central benzene ring and hydrogen atoms at the C(3) position of indole moieties but in the target product these atoms are substituted by CH=CH fragments. Despite school students do not know reactions used for these transformations (Sonogashira coupling and Au-catalyzed alkyne cyclization), it is possible to understand that the source of two carbon atoms is alkyne used at the **J**-to-**K** step. So, during this step it is needed to substituted bromines with Me_3SiCC fragments (Si content supports this conclusion), the last two steps are Au-induced cyclization and hydrolysis for removal of silyl groups.

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: 1, 2, 5

1 point for each correct answer,

–1 point for each wrong answer

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.

H–O–Cl 2 points

(1 point without structure)

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

$OCl^- + H_2O = HOCl + OH^-$ 1 point

$$K = \frac{[HOCl][OH^-]}{[OCl^-]} = \frac{[OH^-]^2}{C - [OH^-]} = \frac{K_w}{K_a} = 10^{-6.46}$$ 1 point

At pH = 9, $[OH^-] = 10^{-5}$ M.

$C(OCl^-) = [OH^-]^2/K + [OH^-] = 2.98\cdot10^{-4}$ M 0.5 points

$m(NaOCl) = 2.98\cdot10^{-4}\cdot74.5\cdot10^3 = 22$ mg 0.5 points

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

$HOCl = H^+ + OCl^-$

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]}$$ 1 point

If $[OCl^-] = [HOCl]$, then $[H^+] = K_a$, pH = pK_a

pH = 7.54 1 point

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): Yes

Reaction equation or arguments:

$NaClO_2 + 4HCl = NaCl + 2Cl_2 + 2H_2O$,

$m(Cl_2) / m(NaClO_2) > 1$

2 points

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

$NaOCl + 2HCl = Cl_2 + NaCl + H_2O$ 1 point

Take 100 g of the solution. $m(NaOCl) = 15$ g, $n(NaOCl) = 15/74.5 = 0.20$ mol $= n(Cl_2)$.

$m(Cl_2) = 0.2\cdot71 = 14.2$ g. $m(Cl_2) / m(\text{solution}) = 14.2\%$ 1 point

% of "active chlorine" = 14.2%

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: NaCl 1 point

Cathode process: $2H_2O + 2e \rightarrow H_2\uparrow + 2OH^-$ 1 point

Anode process: $Cl^- + 2OH^- - 2e \rightarrow OCl^- + H_2O$ 1 point

Overall equation: $Cl^- + H_2O \rightarrow OCl^- + H_2\uparrow$
or $NaCl + H_2O \rightarrow NaOCl + H_2\uparrow$ 1 point

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:

Total volume of water: $141 \cdot 14.2 \cdot 10^6 = 2.0 \cdot 10^9$ L 0.5 points
Total mass of active chlorine: $2.0 \cdot 10^9$ L $\cdot$ $0.3 \cdot 10^{-3}$ g/L = $6.0 \cdot 10^5$ g = 600 kg 0.5 points
m(solution) = 600 / 0.142 = 4200 kg = 4.2 t 1 point

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.

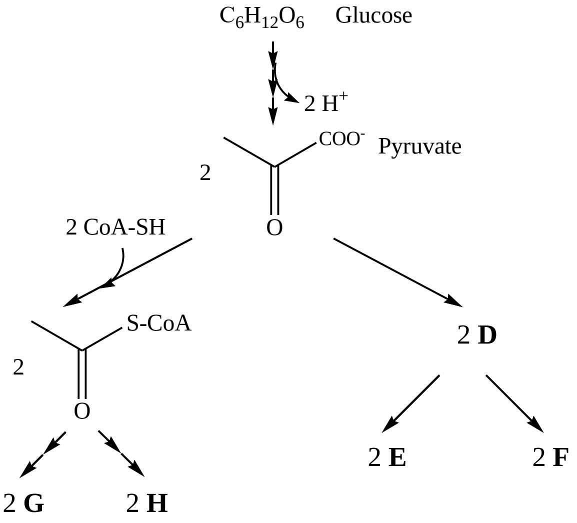
CH_4 (–4), C_2H_5OH (–2), CH_3OH (–2), CH_3CHO (–1), $C_6H_{12}O_6$ (0), C (0), HCHO (0), CO (+2), HCOOH (+2), CO_2 (+4)

$\xrightarrow{\hspace{10cm}}$

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**
HCOOH	H–H	O=C=O
G	**H**	**I**
CH_3COOH	CH_3CH_2OH	$CH_3COOCH_2CH_3$

Comment.
*Pyruvate and acetyl contain 3 and 2 carbon atoms, respectively, which strongly suggests that **D** is a single carbon compound. It originates from the carboxylate group of pyruvate, and cannot be carbon dioxide, since the latter cannot give two gases meeting the task conditions. Thus, **D** (the product of lyaze reaction) is formate (or formic acid HCOOH), **E** is* H_2*, **F** is* CO_2 *(other gases like* CH_4*, CO,* O_2 *are not suitable for chemical reasons and do not meet the task conditions).*

*Asymmetry of **G** and **H** structures allows excluding ethylene glycol, glyoxal and oxalic acid (oxalate) from the list. Oxygen linkage to only one carbon atom in **G** and **H** makes glycol aldehyde, glycolic acid (glycolate) and glyoxylic acid (glyoxylate) impossible. Thus, ethanol, acetaldehyde and acetic acid (acetate) are left under consideration. Since **G** and **H** are different substances, **I** can be neither diethyl ester, nor acetic anhydride, now a product of acetaldehyde homocondensation. Acetaldehyde interaction with ethanol would lead to hemiacetal (contains an asymmetric carbon atom) or acetal (the reagents ratio of 1:2). Acetaldehyde does not interact with acetate. With due regard to the averaged oxidation degree of carbon atoms in the molecules, **G** is acetate (acetic acid), **H** is ethanol, and **I** is ethyl acetate.*

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.

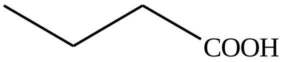
Calculations and work

J (and **J1**), like glucose and pyruvate is composed of C, H, and O atoms. Calculation of the mass fraction left for H and O leads to the following variants depending on the number of C atoms:

- No O atoms possible in the case of 1 C atom;
- C_2H_4O could have been acetaldehyde and ethylene oxide, still none of these is an acid;
- $C_3H_{14}O$ is impossible because the limit of alkyl moiety saturation exceeded;
- $C_4H_{24}O$ is impossible because the limit of alkyl moiety saturation exceeded; $C_4H_8O_2$ is butyric acid (with butyrate **J** as its anion) with due regard to its unbranched character;
- $C_5H_{34}O$ and $C_5H_{14}O_2$ are impossible because the limit of alkyl moiety saturation exceeded; $C_5H_2O_3$ is too unsaturated;
- **J** with 6 C atoms is impossible, since at least one C atom of glucose is found in CO_2;

A number of C atoms exceeding 6 is impossible due to **J** formation from one glucose molecule.

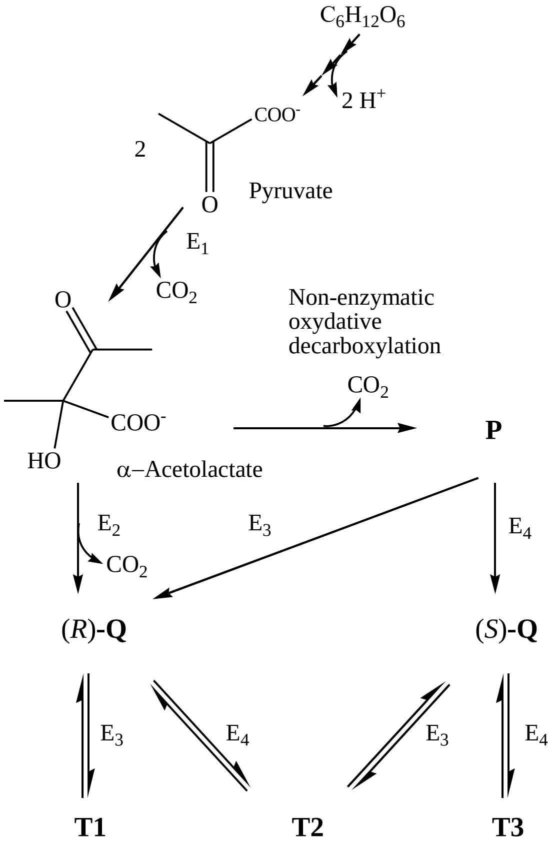
Equation

$C_6H_{12}O_6 \longrightarrow$  $+ \quad 2\,H_2 \quad + \quad 2\,CO_2$

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 stereo-isomers. Transformation of **P** into **Q** occurs in both directions in some bacteria.

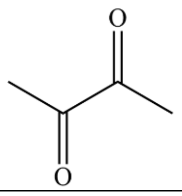
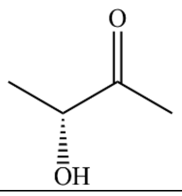
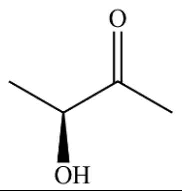
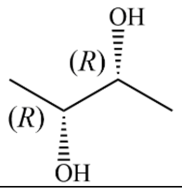
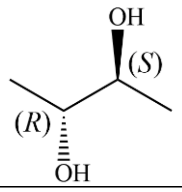
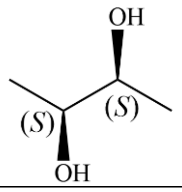


4. What class of enzymes do E_3 and E_4 belong to? Tick the appropriate box.

☐ Decarboxylase
☐ Carboxylase
☑ Oxidoreductase
☐ Lipase
☐ Synthase

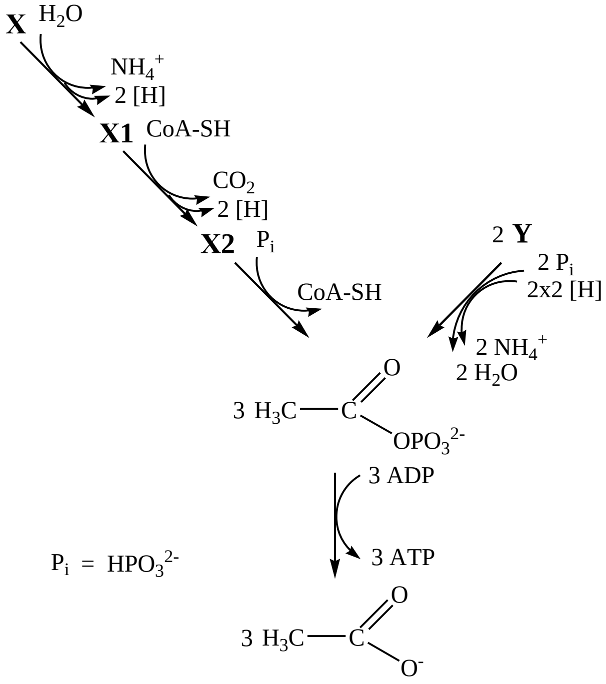
Comment.
*Since **P**, **Q**, and **T** have equal number of carbon atoms (4), the enzyme can be neither decarboxylase nor carboxylase (both leading to a change in the number of C atoms). Lipase is impossible because carbohydrate catabolism is being considered in this part of the task. Synthetase is an invalid option, since there are no high-energy phosphorylated compounds (e.g. ATP) involved. Finally, oxidoreductase is the only suitable option.*

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**
		

Comment.
*The presence of only one peak in the ^{1}H NMR spectrum of **P** suggests that the molecule possesses high symmetry. Two carbonyl carbons are left in **P** after oxidative decarboxylation of α-acetolactate. Thus,*

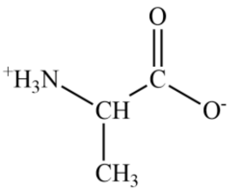
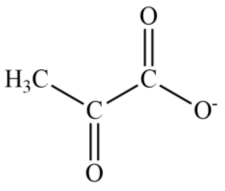
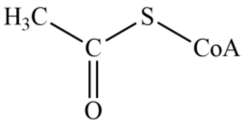
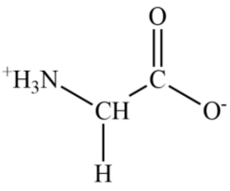
***P** is diacetyl. Since its enzymatic oxidation with retention of the number of carbon atoms in **Q** is impossible, one of the carbonyl groups of **P** is reduced to hydroxyl group in **Q** (acetoin). Then, stereoisomers of **T** (2,3-butanediol) contain two hydroxyl groups each, attribution of stereoisomers (2R,3R)-, (2S,3S)- and meso form being unambiguous if stereochemistry of asymmetric centers in **Q** stereoisomers as well as E_3 and E_4 specificity are taken into account.*



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
			

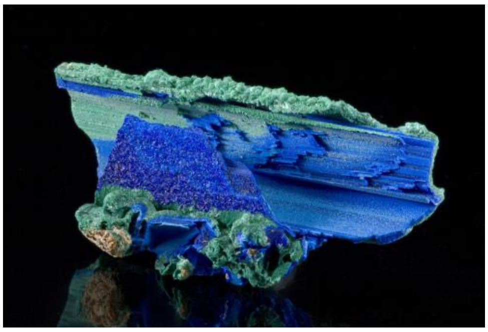
Comment.

*Mowing backwards from the products to **X**, one concludes that **X2** is acetyl coenzyme A. Then, **X1** is pyruvate, since it undergoes oxidative decarboxylation, and **X** is alanine, which, being subjected to deamination, affords pyruvate.*

*There is no change in the number of carbon atoms on the way from **Y** to acetyl phosphate. Thus, **Y** is the only canonical two-carbon α-amino acid – glycine.*

It is worth mentioning that alanine is oxidized in this pair of amino acids due to glycine reduction.

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

$n(CuO) = 0.02$ mol, $n(CO_2) = 0.01$ mol, $n(H_2O) = 0.01$ mol
each substance – 0.5 points, each quantity – 0.5 point

Formula of **M**: $Cu_2(OH)_2CO_3$ 2 points

Reaction equations:

$Cu_2(OH)_2CO_3 \rightarrow 2CuO + H_2O + CO_2$ 1 point
$P_2O_5 + H_2O \rightarrow 2HPO_3$ 0.5 points
$CaO + CO_2 \rightarrow CaCO_3$ 0.5 points
$4CuO \rightarrow 2Cu_2O + O_2$ 1 point

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

Suppose, azurite is a basic copper carbonate $Cu_x(OH)_y(CO_3)_z$ 2 points
mass balance:
$(63.5+16)x / (63.5x+17y+60z) = 0.6923$
charge balance:
$2x = y + 2z$ 4 points
The simplest solution in natural numbers is: $x = 3, y = 2, z = 2$

Formula of **A**: $Cu_3(OH)_2(CO_3)_2$ 4 points

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

$3Cu_2(OH)_2CO_3 + CO_2 \rightarrow 2Cu_3(OH)_2(CO_3)_2 + H_2O(l)$ 2 points

$\Delta_rG^o(298\text{ K}) = 2*(-1389) + (-237) - (-394) - 3*(-883) = 28$ kJ/mol 6 points

$p_{CO2} = 1/K_p = \exp[28000/8.314/298] = 81000$ bar 8 points

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	$H_2O(l)$	$CO_2(g)$
$\Delta_fG^o(298\text{ K})$, kJ/mol	–883	–1389	–130	–237	–394

Calculations and estimates

From the previous answer it follows that at low pressure malachite is more stable than azurite. So, we need to decide which mineral is more stable tenorite (CuO) or malachite 4 points

Consider transformation of tenorite to malachite:

$2CuO + H_2O(l) + CO_2 \rightarrow Cu_2(OH)_2CO_3$ 2 points

$\Delta_rG^o(298\text{ K}) = -883 - 2*(-130) - (-237) - (-394) = 8.0$ kJ/mol 4 points

$K_p = 1 / p(CO_2) = 0.040$ 4 points

The partial pressure of CO_2 in the atmosphere: $p = 4 \cdot 10^{-4}$ bar 2 points

$Q = 1/(4 \cdot 10^{-4}) = 2500 > K_p$ => tenorite is more stable 4 points

The most stable mineral – tenorite

(Answer without calculations – 0 points)

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) $K_{sp}(M) = [Cu^{2+}]^2[OH^–]^2[CO_3^{2–}]$
$K_{sp}(A) = [Cu^{2+}]^3[OH^–]^2[CO_3^{2–}]^2$ 4 points (2x2)

Determine the concentrations of ions in the solution:
$[Cu^{2+}] = 0.05/20.05 = 0.0025$ M (dilution of the solution can be neglected) 2 points
Hydrogen carbonate is an ampholyte, so we can use a well-known approximate formula for H^+ concentration: $[H^+] = (K_1K_2)^{1/2} = 4.74·10^{–9}$ M 8 points
$[OH^–] = 10^{–14}/[H^+] = 2.11·10^{–6}$ M 2 points
Neglecting the dilution of the solution calculate the carbonate concentration $[CO_3^{2-}]$ at a given pH:
$[CO_3^{2–}] = c_0K_1K_2/([H^+]^2 + K_1[H^+] + K_1K_2) = 1.03·10^{–3}$ M 8 points
Compare with K_{sp}:
malachite: $(0.025)^2(2.11·10^{–6})^2(1.03·10^{–3}) = 2.9·10^{–20} >> K_{sp}(M)$ => precipitates 2 points
azurite: $(0.025)^3(2.11·10^{–6})^2(1.03·10^{–3})^2 =7.3·10^{–26} >> K_{sp}(A)$ => precipitates 2 points

b) The freshly precipitated substance contains a mixture of basic carbonates, because both solubility products are much less than the product of concentrations. Upon long standing, the formation of the most thermodynamically stable mineral is possible, i.e., malachite.

Both answers can be correct with the corresponding justification. 6 points

a) The precipitate **is formed**

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

Problem 6. Reserve battery (10 marks)

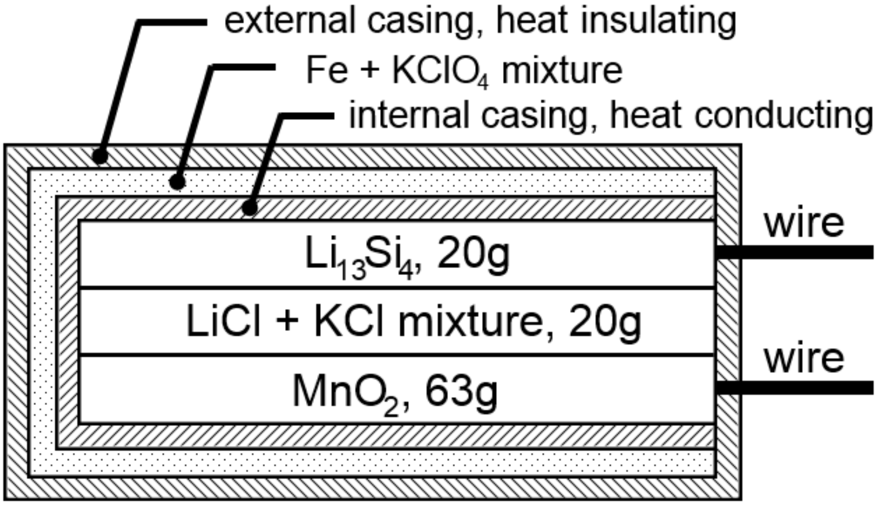
Question	1a	1b	1c	2	3	4	5	**Total**
Points	2	2	2	2	4	4	4	**20**
Result								

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.



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

---

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

$3Li_{13}Si_4 + 22MnO_2 = 4Li_7Si_3 + 11LiMn_2O_4$

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.

$4Fe + KClO_4 = 4FeO + KCl$

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.

$KClO_4 = KCl + 2O_2$

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 $Q = I \cdot t$

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

$n(Li_{13}Si_4) = 20/607.74 = 0.0987$ mol
$n(MnO_2) = 63/86.94 = 0.724$ mol

$n(Li_{13}Si_4)/3 = 0.0329 \text{ mol} = n(MnO_2)/22$ – stoichiometric relation

$n(e^-) = 0.362$ mol

$Q = n(e^-)F = 34958$ C = 9710 mA·h

Capacity = 9710 mA·h

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

Calculations

$\Delta_r H^o = 11\cdot(-1404) + 4\cdot(-294) - 3\cdot(-517) - 22\cdot(-520) = -3629$ kJ/mol

$\Delta_r S^o = 11\cdot(165) + 4\cdot(225) - 3\cdot(370) - 22\cdot(53) = 439$ J/(mol·K)

$\Delta_r G^o_{653} = -3916$ kJ/mol

$E^o = 3916000 / 96485 / 11 = 3.69$ V

emf = 3.69 V

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

The general scheme:
Isothermal reaction at 298K with heat removal – return of heat to the battery with heating of electrodes, electrolyte and combustion products.

$4Fe + KClO_4 = 4FeO + KCl$
$\Delta_r H^o = -1094$ kJ/mol

1 kg om mixture contains: 860 g Fe = 15.4 mol, 140 g $KClO_4$ = 1.01 mol
The heat released from 1 kg of mixture = 1094·1.01 = 1105 kJ/kg

Products of combustion of 1 kg of mixture : 11.36 mol Fe, 4.04 mol FeO, 1.01 mol KCl
The heat required for heating the products
$\Delta_{heat}H = 11.36\cdot27\cdot355 + 4.04\cdot61\cdot355 + 1.01\cdot83\cdot355 = 226$ kJ

$n(Li_{13}Si_4) = 20/607.74 = 0.0987$ mol
$\Delta_{heat}H = 0.0987\cdot372\cdot(380 - 25) = 13.03$ kJ

$n(MnO_2) = 63/86.94 = 0.724$ mol
$\Delta_{heat}H = 0.724\cdot54\cdot(380 - 25) = 13.88$ kJ

LiCl-KCl:
$\Delta_{heat}H = 20\cdot0.90\cdot(352 - 25) + 20\cdot230 + 20\cdot1.27\cdot(380 - 352) = 11.2$ kJ

Denote the mass of Fe + $KClO_4$ mixture as m kg. Then the heat balance is as follows:

$(1105 – 226)·m = 13.03 + 13.88 + 11.2$

$m = 0.043$ kg = 43 g

Mass of the mixture = 43 g

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	KCl
Anode	$LiCl$