The 5th Olympiad of Metropolises

Chemistry

Theoretical Problems

December 19, 2020

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}
Speed of light	$c = 2.998 \cdot 10^{8}$ m·s^{-1}
Planck constant	$h = 6.626 \cdot 10^{-34}$ J·s
Zero of the Celsius scale:	273.15 K
Light-year	$9.46 \cdot 10^{15}$ m

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. Artificial bones **(10 marks)**

Question	1	2	3	4	**Sum**
Points	3	5	1	1	**10**
Result					

For better biocompatibility, the bone implants made of titanium are coated with bioactive films based on calcium salts of orthophosphoric acid, for example, tricalcium phosphate $Ca_3(PO_4)_2$. In recent years, the attention of scientists has been attracted by materials based on octacalcium phosphate X, which is characterized by high integration with bone tissue. Synthesis of X is carried out in several stages. In the first stage, 400 ml of a 0.2M calcium nitrate solution is quickly added to 400 ml of a 0.2M solution of ammonium hydrogen phosphate with continuous stirring. The resulting white precipitate Y is filtered off. When kept at 150 ° C for 24 hours, precipitate Y converts into Z, and the weight of solid is decreased by 20.9%.

1. Determine the formulas of substances Y and Z. Write down the reaction equation for the formation of Y.

Calculation.

Y –

Z –

Reaction equation:

When the resulting product Z is exposed to an excess of sodium acetate solution, the substance gradually changes transforming into a crystalline octacalcium phosphate X which mass is 9.82 g. After the reaction, the solution above the precipitate becomes acidic.

When dried in a desiccator with phosphoric anhydride, the mass of X decreases by 9.2%. Write down the reaction equations if it is known that the solution above the precipitate does not precipitate with a sodium hydroxide solution.

2. Determine the formula of X and write down the reaction of its formation from Z.

Calculation

X –

Reaction equation:

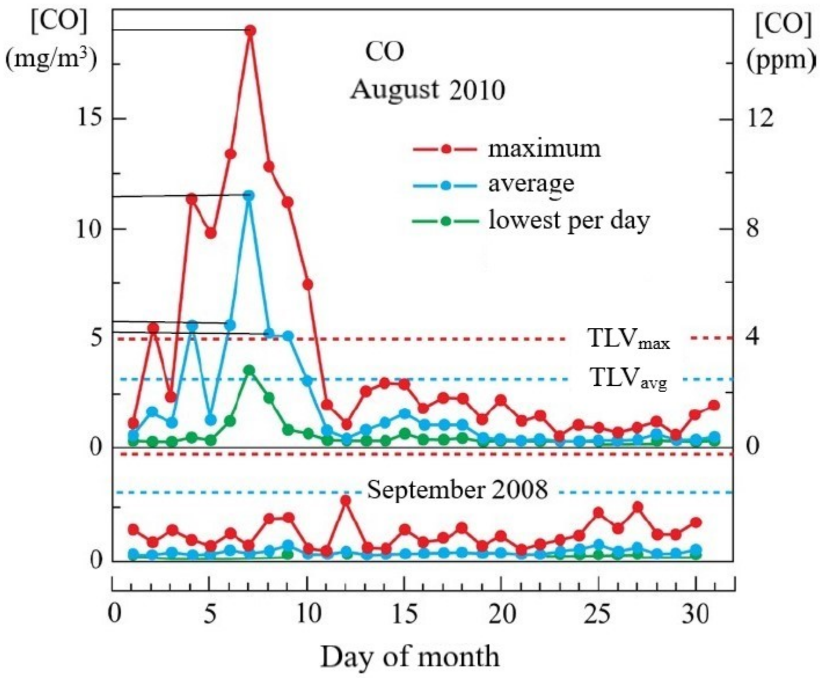
3. The solution above the precipitate gives a yellow precipitate R with silver nitrate. Write down the reaction equation.

4. High integration of X in the organism is caused by the fact that it gradually transforms into a more stable crystalline substance, which is part of the bone tissue. Write down the formula of this substance.

Problem 2. Carbon monoxide on Earth and in space **(10 marks)**

Question	1	2	3	4	5	6	7	**Sum**
Points	1	1.5	0.5	1	1	3	2	**10**
Result								

August 2010 in Moscow was marked by an unprecedented smog. Due to peat fires and the lack of air mixing in the atmosphere, the concentration of poisonous gases in the air exceeded the threshold limit values for several days in a row. The graph below shows the change in the content of carbon monoxide CO (in mg/m^3 and in parts per million by volume, ppm) in the atmosphere of Moscow during August 2010. The horizontal lines show the threshold limit values – the one-time limit (TLV_{max} – red horizontal line) and the average daily limit (TLV_{avg} – blue horizontal line).



Using the graph answer the following questions.

1. How many times did the maximum CO content in August exceed the one-time limit TLV_{max}?

2. How many times did the average CO content during the three most gas-polluted days (August 6-8) exceed the average daily limit TLV_{avg}?

Carbon monoxide is a greenhouse gas, but it does not live long in the atmosphere, on average about 2 months.

3. Write the equation of the possible reaction leading to the removal of CO from the atmosphere.

CO is the second most abundant molecule in the universe. Due to intense radiation in the IR range, it was detected even in the solar atmosphere, where the minimum temperature is 4000 K. Microwave CO radiation with a wavelength of 2.6 mm proved to be a very convenient tool for studying the structure of large molecular clouds formed by molecular hydrogen, because in the Universe the ratio of CO : H_2 = $6 \cdot 10^{-5}$ is approximately the same under various conditions. In addition, this radiation causes cooling of the clouds and can lead to gravitational collapse and the birth of new stars.

4. Explain very briefly why CO molecules can exist at high temperatures. Draw the structural formula of CO and give the formulas of three particles isoelectronic to CO.

Structural formula of CO:

Isoelectronic particles:

5. Suggest the nuclear and chemical reactions which led to the formation of CO on the Sun. Write the reaction equations.

Microwave radiation arises due to the transitions between rotational energy levels, which in a diatomic molecule are described by the formula:

$$E_J = BJ(J + 1)$$

where $J = 0, 1, 2 \ldots$ is a rotational quantum number, B is a rotational constant. $B = 3.82 \cdot 10^{-23}$ J for CO. Transitions are possible only between the neighboring rotational levels for which the rotational quantum number differs by 1.

6. Determine the initial and final values of J corresponding to the radiative transition in CO with a wavelength of 2.6 mm.

Calculation

$J_{\text{init}} =$

$J_{\text{final}} =$

7. Calculate the mass of CO in a spherical molecular cloud of diameter 100 light-years with a particle density of 200 cm^{-3}.

Calculation

$m =$

The necessary formula.

Relation between the energy of the transition ΔE and the wavelength λ: $\Delta E = \dfrac{hc}{\lambda}$

Problem 3. Detective stories of people and plants **(10 marks)**

Question	1	2	3	4	5	6	7	**Total**
Points	1	1.5	1	1	1	2.5	2	**10**
Result								

The history of this poisonous substance is associated with many famous names and includes many proven facts, doubtful statements and just fiction. Compound **A**, containing 60.0 wt.% of the alkali metal, was first obtained by "hard-luck" Karl Wilhelm Scheele in 1782. Scheele was the discoverer of a number of chemical elements and several organic acids (tartaric, citric, lactic, uric, oxalic).

1. Write down the formulas of two elements, discovered by Scheele.

2. Write down the structures of three acids, discovered by Scheele.

Tartaric acid	Lactic acid	Oxalic acid

At the beginning of the twentieth century, **A** was freely sold in pharmacies. It was used for poisoning rats and some insects, for example, wasps. **A** was placed into a "stain", which was filled then with plaster. The slow reaction of **A** with water vapor and carbon dioxide led to the formation of a volatile liquid **B**, which killed the insects. In detective stories (from A. Christie, for example) a detective or a doctor, having sniffed something, usually says that the victim was poisoned with substance **A**, since the contents smell like bitter almonds. This is the smell of liquid **B**, which Joseph Louis Gay-Lussac first received in its pure form in 1811.

3. Write down the formulas of **A** and **B**.

A	**B**

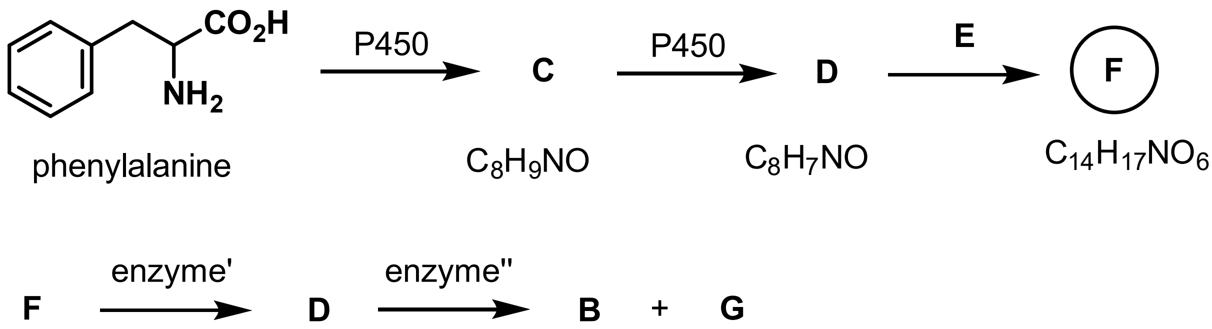
In one of the historical legends, **A** was taken out of a box, grinded and placed into cakes and sweet red wine, all this was offered to the victim. The person ate pastries, drank wine, but remained alive. According to one version, **A** simply decomposed during storage. According to another one, **A** reacted with substances in the food and formed relatively harmless products.

4. Write down one chemical equation for each version.

5. Which of the acids, discovered by Scheele, can be synthesized by the type 2 reaction? Which compound should react with A in this case?

Structural formula of the acid	Structural formula of starting compound for this acid synthesis

It turned out that compounds **A** and **B** are used not only by criminals, but also by some plants, which thus protect themselves from herbivores. Plant enzymes generate **B** in the form of its derivatives, which are stable as long as the plant is intact. If the integrity is violated, the same enzymes decompose these derivatives with the release of **B**, discouraging the animal's desire to feast on this plant. After ripening, the plant stops producing enzymes that generate **B**. This self-sacrifice is needed so that animals can eat the plant and spread its seeds. For example, under the action of cytochrome P450 in plants, the following transformations occur, which generate the plant's "secret weapon" from phenylalanine, and when damaged, the plant generates compound **B**:



6. Decipher the scheme: write down the structural formulas of compounds **C**–**G**.

C	**D**	**E**

F	G

Another plant enzyme is actively involved in the generation of salts of acid **B**: ACC oxidase, which oxidizes 1-aminocyclopropanecarboxylic acid (a non-proteinogenic α-amino acid generated from threonine) to form ethylene. If we assume that molecular oxygen acts as the only oxidizing agent in this reaction, then the products are also water and the anion **H**, which can exist in media with low dielectric constant, but rapidly decomposes in more polar media with the formation of acid **B** or its salts. Generation of **H** is extremely important for the plant to remove **B** from the catalytic site of the enzyme, since the interaction between them leads to enzyme deactivation. Recently, a salt of anion **H** with cation **I** was prepared for the first time. The salt contains 7.57 wt.% of phosphorus. It was stable enough to be characterized by physicochemical methods. In particular, according to NMR data, the salt contains only three types of hydrogen atoms in a ratio of 2: 2: 1, but 6 types of carbon atoms.

7. Write down the structural formulas of cation **H** and anion **I**.

H	I

Problem 4. Chemical clock **(10 marks)**

Question	1	2	3	4	Sum
Points	2	5	2	6	15
Result					

A chemical clock, or a clock reaction, is a chemical system in which there is a definite delay between mixing of reactants and an onset of a certain visual effect. One of the most common examples of such reactions is an iodine clock, in which iodine which is being continuously generated from iodide is immediately consumed by the reducing agent. After the reducer is spent, the iodine still being formed gives a distinctive coloration to the solution which can be enhanced by an addition of starch. In a well-known recipe of iodine clock, hydrogen peroxide is used as an oxidizer and thiosulfate as a reducer in an acetate buffer. The reactions which take place in this clock and their respective rate laws are as follows:

$$H_2O_2 + 2I^- = 2OH^- + I_2 \qquad r_1 = k_1[H_2O_2][I^-]$$

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-} \qquad r_2 = k_2[I_2][S_2O_3^{2-}]^2$$

Iodide is usually taken in large excess, so most of iodine is present in a form of a triiodide ion, but this fact will be neglected throughout the problem. At room temperature, the rate constants are:

$$k_1 = 0.011\ L\cdot mol^{-1}\cdot s^{-1}, \qquad k_2 = 1.3\cdot 10^6\ L^2\cdot mol^{-2}\cdot s^{-1}.$$

1. In an alkaline medium, the reaction between thiosulfate and iodine leads to the formation of sulfate (that's why the acetate buffer is required in a clock). Write down the net ionic equation of this reaction.

2. In one experiment, the following solutions were mixed: 20 mL of 2M KI, 10 mL of an acetate buffer, 10 mL of 0.1M $Na_2S_2O_3$, 10 mL of 0.1M H_2O_2, and a drop of a starch solution. Calculate the time delay between the mixing and the color appearance at room temperature. If needed, use reasonable assumptions and symbolic notation such as => (therefore), >> (much greater), ≈ (roughly equal), const (constant) etc.

3. How will the time delay change if a 0.05M solution of KI is taken in the previous experiment instead of a 2M one (keeping the same volume)? Mark an appropriate box.

☐ The coloration appears immediately

☐ The time delay decreases

☐ The time delay does not change

☐ The time delay increases

☐ The coloration does not appear at all

Shortly after the start, the iodine clock approaches a stationary state in which the rates of iodine formation and consumption are equal. As a result, the iodine concentration is non-zero at all times, even before the color becomes observable. In some cases, this stationary concentration can be large enough to make iodine visible long before all thiosulfate is consumed.

4. In another experiment, the following solutions were mixed at room temperature: 20 mL of 2M KI, 10 mL of an acetate buffer, 10 mL of 0.001M $Na_2S_2O_3$, 10 mL of 0.001M H_2O_2, and a drop of a starch solution. Assuming the stationary state in the clock, estimate the time delay before the color appearance and find the fraction of unreacted thiosulfate at that moment. Assume that iodine is detectable at concentrations above 10^{-4} M. If needed, use reasonable assumptions and symbolic notation as described above.

Problem 5. Energy saving acids **(10 marks)**

Question	1	2	3a	3b	4	**Sum**
Points	2	2	4	1	6	**15**
Result						

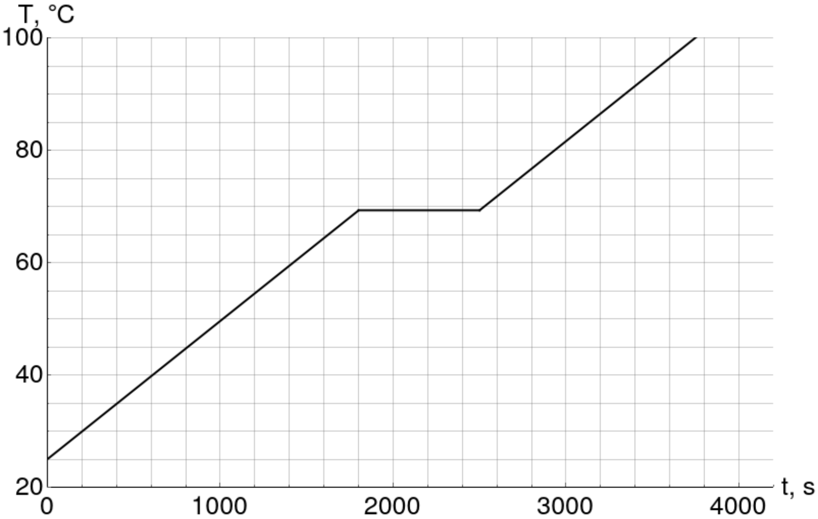
It is hard to imagine winter life of large cities located in continental climate, such as Moscow, without central heating. Most of the heating systems use fossil fuels, such as natural gas or coal. Thus, saving of heat energy is a challenging problem for improving ecology of cities and reducing of carbon footprint.

An interesting mechanism of heat saving is based on materials which undergo phase transition near the room temperature. During daytime a building panel is heated by sunlight and the substance within it melts. At night, the reverse phase transition accompanied by release of heat takes place due to cooling of the room. Saturated fatty acids, such as monoprotic acid **X**, are perspective materials for these building blocks due to low melting temperatures and low cost.

1. Draw the structure of **X**, if complete neutralization of 1.00 g of acid required 14.08 ml of 0.250 M sodium hydroxide solution.

Calculation Structure of **X**

In order to determine the heat of fusion of **X**, 0.125 mol of it were slowly heated in the adiabatic calorimeter equipped by the 10 W heating unit. The plot of temperature T versus time t is shown in the figure below.



2. Determine the melting temperature and the enthalpy of fusion of acid **X**.

Melting temperature of **X**

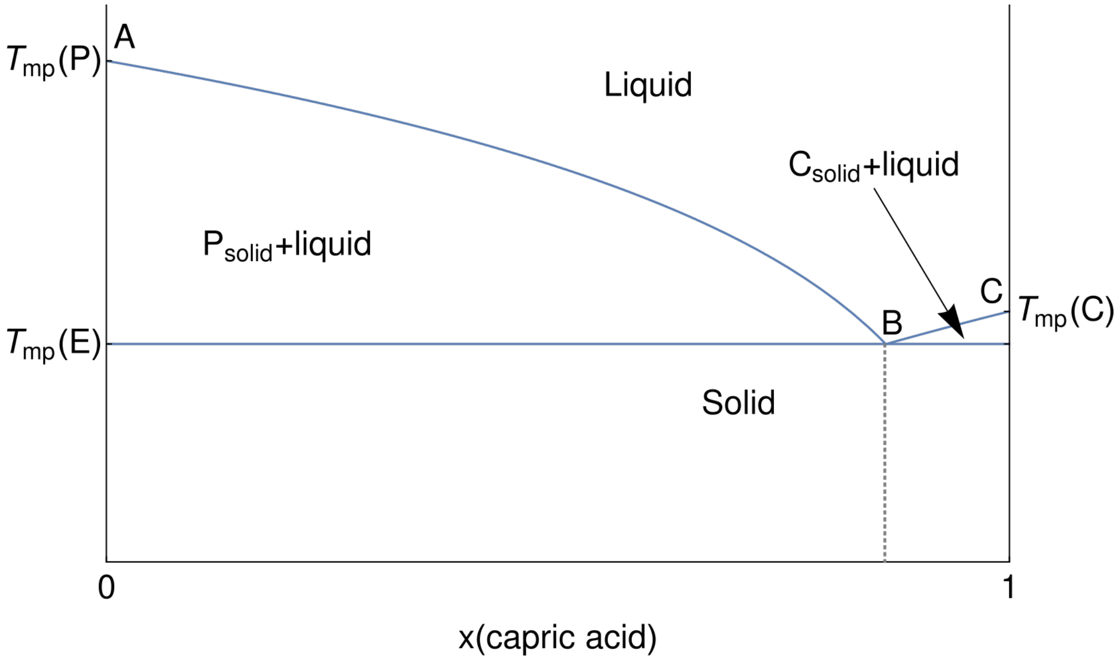
Enthalpy of fusing of **X**

Usually, it is difficult to find the pure acid with the melting temperature close to the room temperature. However, it is possible to control the melting temperature using mixtures of homologous acids instead of pure ones. Melting temperature of these mixtures can be estimated using colligative properties of solutions.

3. a. Calculate the melting temperatures of the binary eutectic mixtures of capric acid ($C_9H_{19}COOH$) with lauric ($C_{11}H_{23}COOH$) and myristic ($C_{13}H_{27}COOH$) acids. Mass fraction of capric acid is 61.5 % in the former mixture and 73.5 % in the latter one. The enthalpy of fusion of pure capric acid is 27.2 kJ/mol, the melting temperature is 31.5 °C.

   b. Which of these mixtures is better suitable for the room with the daytime temperature 25 °C and the night time temperature 22 °C?

The phase diagram of the mixture containing capric (C) and palmitic (P) acids is shown in the figure below. It demonstrates dependence of phase composition on the mole fraction of capric acid.



The lines A-B and B-C are described by the equation:

$$\ln x = \frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T^{\circ}} - \frac{1}{T}\right),$$

where x is the mole fraction, $\Delta_{\text{fus}}H$ is the molar enthalpy of fusion, T° is the melting temperature of a pure acid. All quantities refer to palmitic acid for the curve A-B and to capric acid for the curve B-C.

4. Determine the coordinates (temperature and mole fraction of capric acid) of the eutectic point (point B). The entalpy of fusion of palmitic acid is 54.4 kJ/mol, and its melting temperature is 63 °C.

Temperature at point B =

Mole fraction of capric acid at point B =

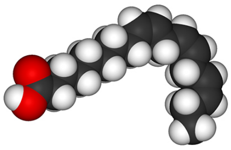
The necessary formulas.

Freezing-point depression of a solvent on the addition of a solute:
$\Delta T = K_c m$, where m is molality [moles of solute per kilogram of solvent],

$$K_c = \frac{RT_{\text{mp}}^2 M}{\Delta_{\text{fus}} H},$$

where T_{mp}, M, and $\Delta_{\text{fus}}H$ are melting point, molar mass and enthalpy of fusion of a pure solvent.

Problem 6. Reactive oxygen species (10 marks)



Question	1	2	3	4	5a	5b	5c	5d	6	7	**Sum**
Points	2	5	2	1	1	1	1	1	5	1	**20**
Result											

Incomplete reduction of oxygen in metabolic pathways leads to the formation of the so called Reactive oxygen species **X**, **Y**, and **Z**. The particle **X** is formed when molecular oxygen entraps one electron. **X** undergoes spontaneous dismutation (disproportionation) with H^+ yielding the compound **Y** and regenerating molecular oxygen.

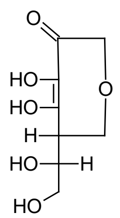
1. Determine **X** and **Y**, and write down equation of the formation of **Y**.

X	**Y**
Reaction:	

Normally, the negative influence of **Y** is suppressed by the tripeptuide **A**, composed of the residues of canonical α-amino acids (see the structures and codes at the end of the task). Analysis of **A** reveals that it contains two free carboxylic groups, both bound to α-carbon atoms. The N-terminal amino acid has the isoelectric point below 3.5 and molecular weight higher than 135 Da. The compound **B** and a dimer of the tripeptide **A** are formed as a result of redox reaction of **A** with **Y**. The amino acid residue involved in the dimer formation occupies the central position in the tripeptide, whereas the amino acid affording the last residue in **A** is free of chiral centers.

2. Write down equation of the reaction of **Y** with **A**, showing the structural formulae of **A** and the product of its dimerization.

L-ascorbate (the anion of L-ascorbic acid – see the fig.) helps avoiding the undesirable influence of **Y** in plant cells. L-ascorbate interacts with **X** affording monodehydroascorbate radical. In turn, the latter can undergo dismutation.



3. Write down equations of the monodehydroascorbate radical formation and dismutation.

4. Y can undergo enzymatic self-decomposition affording two safe products. Write down equation of self-decomposition of Y.

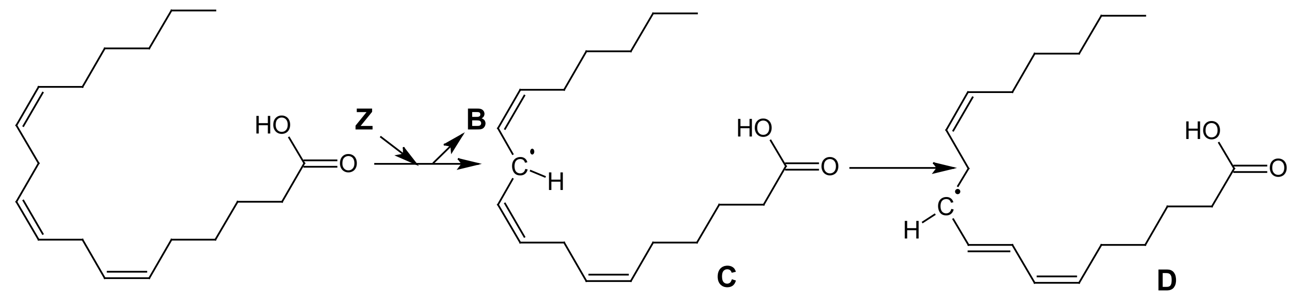
Y can interact with Fe^{2+} ions giving an extremely reactive species **Z**. One of products of this reaction can interact with **X**, which leads to much faster formation of **Z**.

5. a) Write down equation of the reaction between **Y** and Fe^{2+}
b) write down equation of the reaction between a product of the reaction 5a with **X**.
c) write down the overall equation of the reactions 5a and 5b.

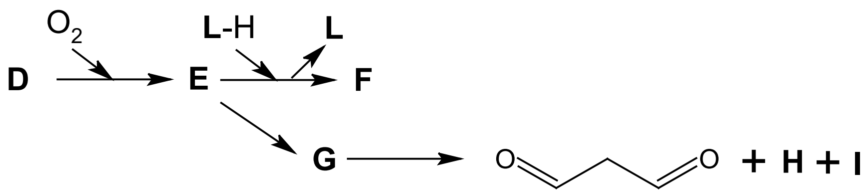
a)
b)
c)

d) what is the role of iron ions in the formation of **Z** according to the reaction 5c?
☐ oxidizer ☐ reducer ☐ catalysts ☐ enzyme ☐ energy source

Z can be potentially harmful by e.g. leading to lipid peroxidation. Let us consider the process using γ-linolenic (*cis*, *cis*, *cis* -6,9,12-octadecanoic) acid. Acid radicals **C˙ и D˙** are formed at the initial steps of the transformation induced by **Z**:



The subsequent transformations can be written as:

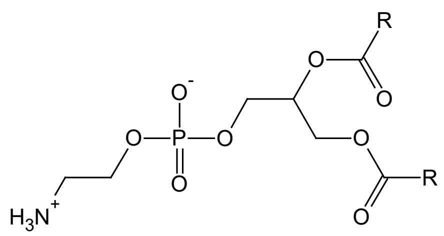


L-H is a hydrogen donor, **G** contains a five-membered cycle, and **H** and **I** are the products of decomposition of **G**, formed together with malondialdehyde.

6. Draw the structures of **E**-**I**.

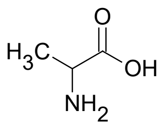
E	**F**	**G**
H	**I**	

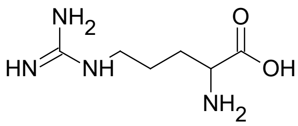
Malondialdehyde can produce inter- and intraprotein covalent links, as well as lead to covalent conjugates between proteins and phosphatidylethanolamine (see the fig.)

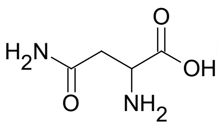


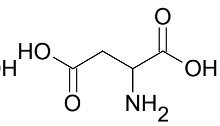
7. Draw the reaction of covalent malondialdehyde-based conjugation of a protein and phosphatidylethanolamine. Denote the protein by only the amino acid residue involved in the conjugation with dialdehyde. When choosing the amino acid residue, note that malondialdehyde forms linkages of the same type with both the protein and phosphatidylethanolamine.

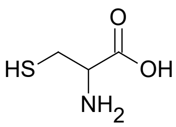
Canonical α-amino acids

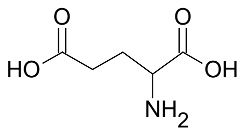

Alanine **(Ala)**

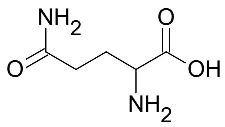

Arginine **(Arg)**

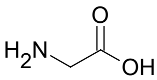

Asparagine **(Asn)**

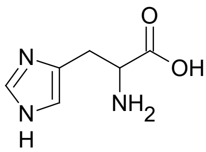

Aspartic Acid **(Asp)**

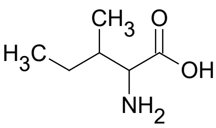

Cysteine **(Cys)**

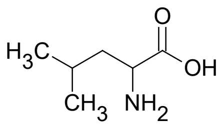

Glutamic Acid **(Glu)**

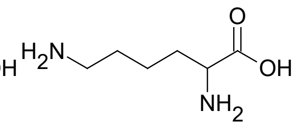

Glutamine **(Gln)**

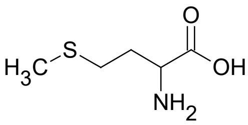

Glycine **(Gly)**

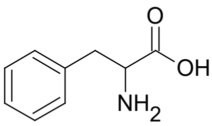

Histidine **(His)**

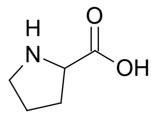

Isoleucine **(Ile)**

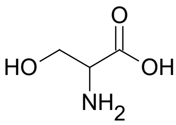

Leucine **(Leu)**

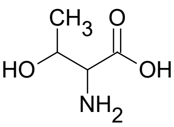

Lysine **(Lys)**

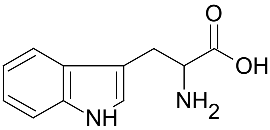

Methionine **(Met)**

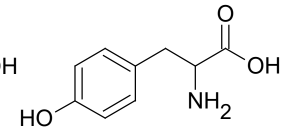

Phenylalanine **(Phe)**

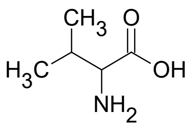

Proline **(Pro)**


Serine **(Ser)**


Threonine **(Thr)**


Tryptophan **(Trp)**


Tyrosine **(Tyr)**


Valine **(Val)**