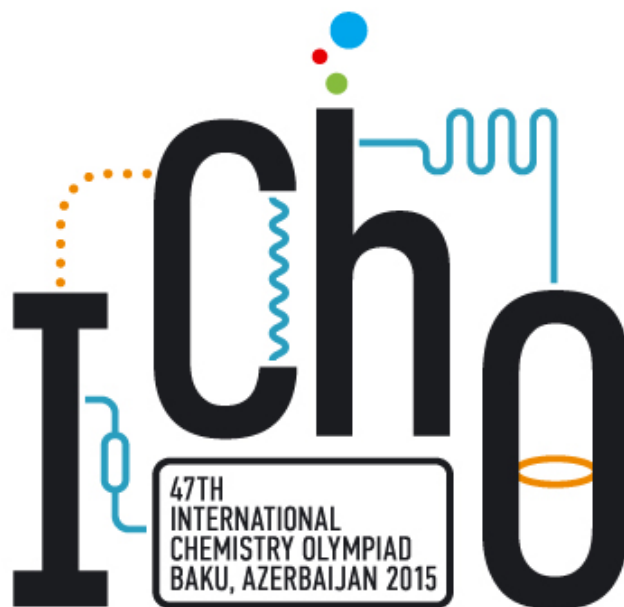


Life is a huge lab



**THEORETICAL
EXAMINATION**

ANSWERS and GRADING SCHEMES

JULY 25, 2015

BAKU, AZERBAIJAN

General Directions

- Write down your name and code number on each page.
- You have 5 hours to fulfill the tasks. Failure to stop after the STOP command may result in zero points for the current task.
- Write down answers and calculations within the designated boxes. Give your work where required.
- Use only the pen and calculator provided.
- If you need draft paper use the back side of the paper. It will not be marked.
- There are **40** pages in the booklet including the answer boxes, Cover Sheet and Periodic Table.
- The official English version is available on demand for clarification only.
- Need to go to the restroom – raise your hand. You will be guided there.
- **After the STOP signal** put your booklet in the envelope (don't seal), leave at your table. Do not leave the room without permission.
- You have additional 15 minutes to read the whole set.
-
- Formulas necessary for solution of some problems can be found on the next page.

Physical Constants, Units, Formulas and Equations

Universal gas constant	$R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Standard pressure	$p^\circ = 1 \text{ bar} = 10^5 \text{ Pa} = 750 \text{ mmHg}$
Atmospheric pressure	$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} = 760 \text{ mmHg}$
Zero of the Celsius scale	273.15 K

Reversible adiabatic process for an ideal gas	$pV^{1+R/C_V} = \text{const}$
Work made on an ideal gas in an adiabatic process	$W = nC_V(T_2 - T_1)$
Dependence of internal energy on temperature	$U(T_2) = U(T_1) + C_V(T_2 - T_1)$
Relation between molar isobaric and isochoric heat capacities for an ideal gas	$C_p = C_V + R$
Gibbs energy	$G = H - TS$
Relation between equilibrium constant and standard Gibbs energy	$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$
Dependence of Gibbs energy of reaction on concentration or pressure	$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{prod}}}{a_{\text{reag}}},$ <p>$a = c / (1 \text{ mol/L})$ for the substances in solution, $a = p / (1 \text{ bar})$ for gases</p>
Change of Gibbs energy per unit volume in time for the system with two chemical reactions 1 and 2 with rates r_1 and r_2	$\frac{\Delta G_{\text{Syst}}}{\Delta t} = \Delta G_1 r_1 + \Delta G_2 r_2$

Problem 1. New and well-forgotten old refrigerants
(8 points)

Question	1			2			3	4				Total
	1.1	1.2	1.3	2.1	2.2	2.3		4.1	4.2	4.3	4.4	
Marks	4	2	2	1	1	1	3	10	2	6	1	33

The problem of choosing a refrigerant for refrigeration and air conditioning systems attracted the attention of scientists and technologists throughout the last century. It has been suggested that during this time refrigerants progressed through four generations. Ammonia, which was ascribed to the first generation, had been used in most of the oldest refrigeration units. It was later replaced by chlorofluorocarbons (CFCs) – derivatives of methane and ethane with the hydrogen atoms replaced by fluorine and chlorine.

In Baku, at "Bakkonditioner" factory, production of the first Soviet serial household air conditioners BK-1500 had been launched. A second-generation refrigerant chlorodifluoromethane CHF_2Cl was used in them. In this problem, we compare various refrigerants in terms of thermodynamics.



First air conditioner of Baku factory in a souvenir shop in the Old City ("Icheri Sheher")

Thermodynamic properties of various refrigerants

Refrigerant	"Generation"	$\Delta H_{\text{vap}} / \text{kJ} \cdot \text{mol}^{-1}$ (at 280 K)	$C_{V(\text{gas})} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
NH_3	1	21.3	26.7
CHF_2Cl	2	20.0	48.8
$\text{CF}_3\text{CH}_2\text{F}$	3	22.1	79
$\text{CF}_3\text{CF}=\text{CH}_2$	4	19.1	120

Consider a model refrigeration cycle consisting of 4 steps schematically shown below in the pressure (p) – internal energy (U) coordinates.

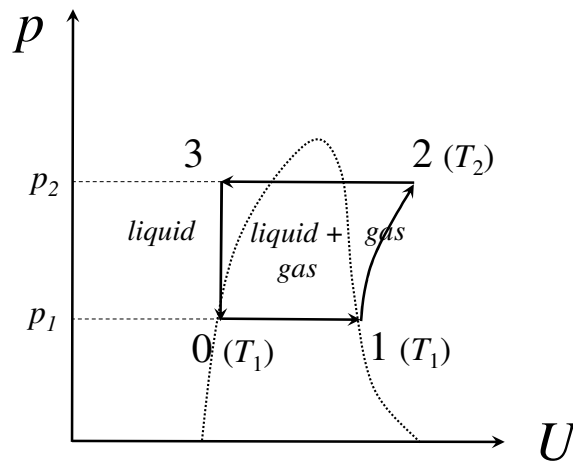


Diagram 1. Dashed line indicates the phase boundaries

During the first step of the cycle (line 0-1 in diagram 1), a liquid refrigerant is boiling at constant pressure p_1 and temperature T_1 (boiling temperature) until it completely evaporates. At this step, the refrigeration unit absorbs heat from surrounding objects. At the second step, the refrigerant undergoes reversible adiabatic compression and heats up to temperature T_2 (line 1-2). After that the compressed refrigerant is cooled in a condenser at constant pressure p_2 (line 2-3) and then returns to the initial state (line 3-0).

Let the cycle involve 1 mole of refrigerant, which is initially (point 0) completely liquid, $T_1 = 280$ K, $T_2 = 380$ K, assume that the vapor of any refrigerant behaves like an ideal gas. The thermodynamic characteristics of refrigerants are listed in the table above.

1.1. For each of refrigerants, ammonia and chlorodifluoromethane, calculate the amount of heat Q absorbed by refrigeration unit during heat exchange (line 0-1) and the work W required to compress its vapor adiabatically (line 1-2).

Calculations

Note: here and below in this problem, only correct VALUES are marked except 4.1, 4.3

Ammonia

$$Q = \nu \Delta H_{\text{vap}} = 21.3 \text{ kJ}; \quad \text{1p}$$

$$W = \nu C_{V(\text{gas})}(T_2 - T_1) = 2.67 \text{ kJ}. \quad \text{1p}$$

$$Q = 21.3 \text{ kJ}$$

$$W = 2.67 \text{ kJ}$$

Chlorodifluoromethane

$$Q = \nu \Delta H_{\text{vap}} = 20.0 \text{ kJ}; \quad \text{1p}$$

$$W = \nu C_{V(\text{gas})}(T_2 - T_1) = 4.88 \text{ kJ}. \quad \text{1p}$$

$$Q = 20.0 \text{ kJ}$$

$$W = 4.88 \text{ kJ}$$

1.2. Which quantity(ies) remain(s) constant during the adiabatic compression step? Indicate by the circle(s).

U H S G V

2p for the correct answer

Minus 1p for every incorrect option, total – no less than 0.

To compare the energy efficiency of refrigeration cycles with different parameters and refrigerants, the coefficient of performance (COP) is used, which is defined as a ratio of heat removed from a cooled system to the work of compressor: $COP = Q/W$.

1.3. Calculate the values of COP in a considered cycle for ammonia and chlorodifluoromethane.

Calculations

Ammonia

$$COP = Q/W = 7.98 \quad \mathbf{1p}$$

$$COP = 7.98$$

Chlorodifluoromethane

$$COP = Q/W = 4.10 \quad \mathbf{1p}$$

$$COP = 4.10$$

2.1. Why was ammonia replaced by CFCs in household refrigeration units? (Choose only one option)

- a) to increase the energy efficiency of refrigeration cycles
- b) because the density of ammonia is less than that of air under the same conditions
- c) for user safety reasons

c

1p

A search for replacement of CFCs as refrigerants started when it was shown that their use can cause irreparable damage to the protective ozone layer of the atmosphere. The third, ozone-friendly generation of refrigerants came on the scene. Its typical representatives are fluoroalkanes.

2.2. What is the cause of the damage made by CFCs to the ozone layer? (Choose only one option)

- a) ozone molecule easily adds to C–F bond
- b) C–F bond is easily broken by radiation, which leads to the formation of free radicals
- c) ozone molecule easily adds to C–Cl bond
- d) C–Cl bond is easily broken by radiation, which leads to the formation of free radicals

d

1p

However, under the 1997 Kyoto Protocol, fluoroalkanes also had to be replaced because they accumulate in the atmosphere and rapidly absorb infrared radiation, causing a rise in temperature of the atmosphere (the greenhouse effect). The refrigerants of the fourth generation such as 2,3,3,3-tetrafluoropropene $\text{CF}_3\text{CF}=\text{CH}_2$ have been suggested and are coming into use.

2.3. Why does this compound enhance the greenhouse effect less than fluoroalkanes? (Choose only one option)

- a) it is more reactive and easier to decompose
- b) it easily reacts with ozone
- c) it is better soluble in water

a

1p

3. Calculate the values of the *COP* in the refrigeration cycle considered above for two refrigerants of the third and fourth generations – $\text{CF}_3\text{CH}_2\text{F}$ and $\text{CF}_3\text{CF}=\text{CH}_2$. Did the energy efficiency improve in comparison with CHF_2Cl ? Choose “Yes” or “No”.

Calculations

$\text{CF}_3\text{CH}_2\text{F}$

$$COP = \Delta H_{\text{vap}} / (C_{V(\text{gas})}(T_2 - T_1)) = 2.80$$

1p

$$COP = 2.80$$

Yes

No

0.5p



$$\text{COP} = \Delta H_{\text{vap}} / (C_{V(\text{gas})}(T_2 - T_1)) = 1.59$$

1p

$$\text{COP} = 1.59$$

Yes

No

0.5p

Unlike household appliances, industrial refrigeration systems are often still using ammonia. It does not contribute to the greenhouse effect nor does it destroy the ozone layer. Industrial units can have a huge size and a large cost. Prior to their construction, they should be carefully modeled taking into account many different factors. In real systems, some part of the refrigerant at the start of the heat exchange with the environment is in the vapor phase (point 0 in the diagram below), and at the end (point 1) it is always overheated above the boiling point.

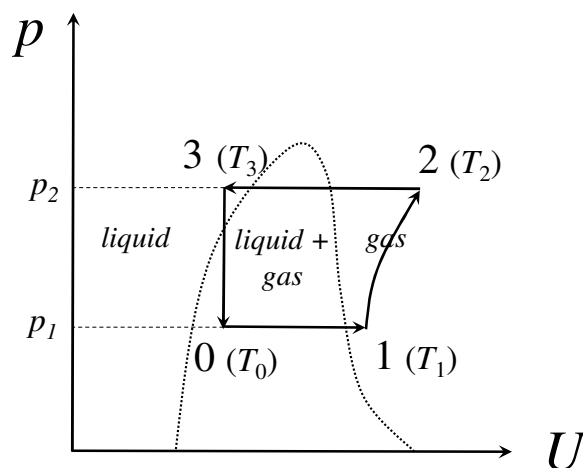


Diagram 2. Dashed line indicates the phase boundaries

Consider a cycle with 1 mole of ammonia. Its thermodynamic properties are the following: enthalpy of vaporization $\Delta H_{\text{vap}} = 23.35 \text{ kJ} \cdot \text{mol}^{-1}$ at $T_{\text{vap}} = 239.8 \text{ K}$ (boiling temperature at 1 bar pressure). Heat capacity of the liquid phase $C_{V(\text{liq})} = 77 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, of the gas phase $C_{V(\text{gas})} = 26.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Assume that the heat capacities are temperature-independent and the vapor behaves like an ideal gas. The temperature dependence of the saturated vapor pressure of ammonia can be described by the empirical equation:

$$\log(p/\text{bar}) = 4.87 - 1114 / (T/\text{K} - 10.4).$$

During the first step of the cycle (line 0-1 in diagram 2), the equilibrium mixture of liquid refrigerant and its vapor receives heat from the environment at constant pressure $p_1 = 3.0 \text{ bar}$. The refrigerant completely evaporates and overheats up to the temperature $T_1 = 275 \text{ K}$. In the beginning of the process (point 0), the molar fraction of gaseous ammonia is $x = 0.13$.

4.1. Calculate the initial temperature of refrigerant T_0 , its volume change ΔV and the amount of heat Q absorbed by refrigeration unit during this step. Take into account that the dependence of ΔH_{vap} from the temperature **cannot** be neglected.

Calculations:

$$T_0 = 10.4 + 1114 / (4.87 - \log p_1) = 264 \text{ K} \quad \mathbf{2p}$$

$$T_0 = 264 \text{ K}$$

$$\Delta V = (vRT_1 / p_1) - (xvRT_0 / p_1) = 6.7 \text{ L} \quad \mathbf{3p}$$

$$\Delta V = 6.7 \text{ L}$$

$$\begin{aligned} Q &= \Delta H = \Delta U + p_1 \Delta V = \Delta U(\text{liquid fraction}) + \Delta U(\text{gas fraction}) + p_1 \Delta V = \\ &= \Delta U(\text{vaporization of liquid fraction at } T_0) + \Delta U(\text{heating evaporated liquid fraction up to } T_1) + \\ &+ \Delta U(\text{gas fraction}) + p_1 \Delta V = \\ &= v(1-x)(\Delta H_{\text{vap}} - RT_{\text{vap}} + (C_{V(\text{gas})} - C_{V(\text{liq})})(T_0 - T_{\text{vap}})) + vC_{V(\text{gas})}(T_1 - T_0) + p_1 \Delta V = 19.8 \text{ kJ} \end{aligned}$$

or

$$Q = v(1-x)(\Delta H_{\text{vap}} + (C_{V(\text{gas})} + R - C_{V(\text{liq})})(T_0 - T_{\text{vap}})) + v(C_{V(\text{gas})} + R)(T_1 - T_0) = 19.8 \text{ kJ}$$

5p

(3p for a correct equation for calculation and 2p for correct value)

$$Q = 19.8 \text{ kJ}$$

Then the refrigerant is reversibly and adiabatically compressed. It heats up to the temperature $T_2 = 393 \text{ K}$ (line 1-2).

4.2. Find the work W required for compression and the COP of the system. If you were not able to find Q in 4.1, use $Q = 20.15 \text{ kJ}$.

Calculations:

$$W = vC_{V(\text{gas})}(T_2 - T_1) = 3.15 \text{ kJ} \quad \mathbf{1p}$$

$$W = 3.15 \text{ kJ}$$

$$COP = Q/W = 6.3 \quad \mathbf{1p}$$

$$COP = 6.3$$

At the next step corresponding to the line 2-3 in diagram, the compressed refrigerant is cooled in a condenser at constant pressure. Then it returns to the initial state through adiabatic expansion with zero work (line 3-0).

4.3. Determine the temperature T_3 at point 3 to which the refrigerant is cooled in a condenser.

Calculations:

The internal energies of the refrigerant are equal in points 0 and 3. Thus,

$$x \cdot (\Delta H_{\text{vap}} - RT_{\text{vap}} + (C_{V(\text{gas})} - C_{V(\text{liq})})(T_0 - T_{\text{vap}})) + C_{V(\text{liq})} (T_0 - T_3) = 0,$$

$$T_3 = 298 \text{ K}.$$

6p

(3p for a correct equation and 3p for correct value)

$$T_3 = 298 \text{ K}$$

In the production of refrigeration units it is necessary to consider climatic factors. If a condenser is cooled by atmospheric air, the temperature T_3 increases as the air temperature increases.

4.4. How will the *COP* change if T_3 increases while T_0 , T_1 , T_2 remain the same?

- a) Increase
- b) Remain the same
- c) Decrease

c

1p

Comment: It will decrease because the length of 0-1 line decreases or because x (see 4.3) increases and less liquid is in the equilibrium mixture at T_0 , so less heat Q is necessary to evaporate it!

Problem 2. Coupling of chemical reactions

(7 points)

Question	1			2		3	Total
	1.1	1.2	1.3	2.1	2.2		
Marks	4	6	4	3	6	2	25



I. Prigogine (left)



N. Shilov



W. Ostwald

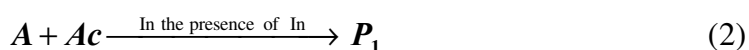
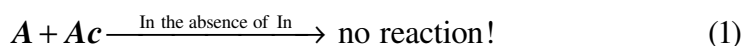
When in the system one reaction allows another one to proceed they say that these two reactions are coupled. Ilya Prigogine, Nobel prize winner in chemistry (1977) in his books widely used the concept of “coupled reactions”. Coupling of reactions is an essential feature of living systems, including human body.

How one reaction makes another one to occur? In this problem we are going to discuss several possible mechanisms of coupling.

(I) “Chemical coupling”

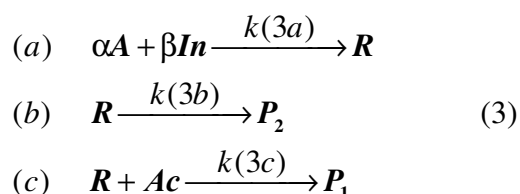
“On Chemical coupling” was the title of the dissertation defended by Russian chemist N. Shilov in 1905. N. Shilov was the graduate student of famous professor W. Ostwald. Dr. Shilov described the following set of reactions.

The substance A does not react with Ac . In the presence of the third reagent (called inductor), In , however, the reaction of A with Ac takes place:



In is not a catalyst! Its concentration decreases in the course of the reactions.

According to the scheme proposed by Shilov, Ac reacts not with A itself, but with the intermediate product R of the reaction of A with In . There is another, competing reaction of R that forms P_2 .



α and β are stoichiometric coefficients. Other stoichiometric coefficients and **reaction order with respect to all reactants in all three reactions are unity.**

In the Shilov's experiments the ratio of the consumed amounts of Ac and In , $I = \frac{\Delta n_{Ac}}{\Delta n_{In}}$ increased up to the constant value with the increasing initial concentration $[Ac]_0$ at $[In]_0 = \text{const.}$

1.1. What was this limiting constant value of I at $[Ac]_0 \rightarrow \infty$, $[In]_0 = \text{const.}$?

Brief explanation

The value of I should increase with the increase of $[Ac]_0$ at $[In]_0 = \text{const.}$, because the larger fraction of the intermediate product R will enter the reaction (3c). The maximum value of I will be achieved if all R reacts in (3c), therefore $I_\infty = 1/\beta$.

$$I_\infty = 1/\beta \quad \quad \quad \mathbf{4 \text{ points}} \quad (2 \text{ points if only } I_\infty = 1/\beta \text{ is given!})$$

1.2. Derive an expression for I using the steady-state approximation if necessary. Plot the graph of I vs $[In]_0$ at $[Ac]_0 = \text{const.}$ Assume that In was completely consumed and Ac was in excess..

Calculations

Shilov's mechanism includes the initial reaction



and two competitive reactions

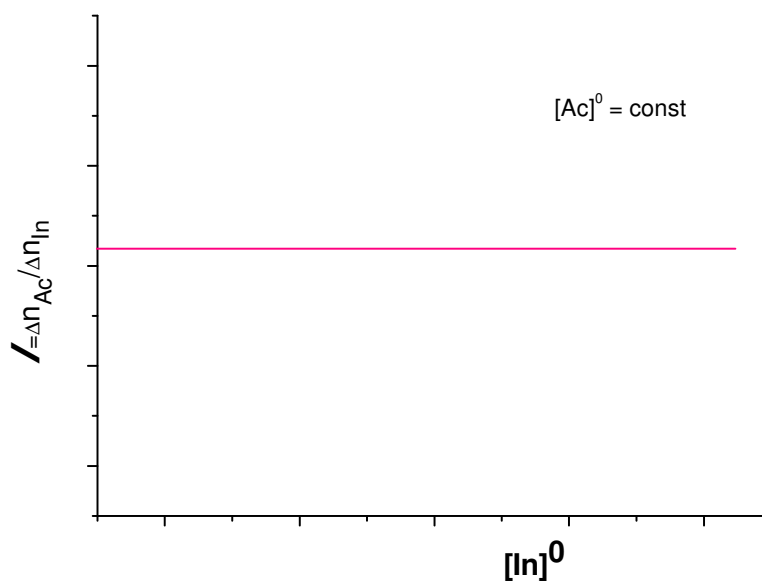


The rates of conversion of In and Ac are determined by the rates of the reactions (3a) and (3c), respectively:

$$\frac{r(3c)}{r(3a)} = \frac{k(3c)[R][Ac]}{k(3a)[A][In]} = \frac{k(3c)[Ac] \times \frac{k(3a)[A][In]}{k(3c)[Ac] + k(3b)}}{k(3a)[A][In]} = \frac{k(3c)[Ac]}{k(3c)[Ac] + k(3b)}$$

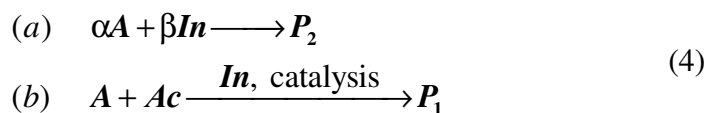
in steady-state approximation for $[R]$. We see that the ratio of two rates does not depend on the initial concentration $[In]_0$ and I will also not depend on it. This gives the straight line parallel to the $[In]_0$ axis on the graph.

Graph



6 points (2 points for the graph + 4 points for the steady-state equations)

What if Shilov's mechanism is not valid and In is a conventional catalyst of the reaction (2)? Simultaneously In reacts with A and its concentration decreases. The reaction scheme in this case is



1.3. What is the limiting value of I for the reaction scheme (4) at $[Ac]_0 \rightarrow \infty$, $[In]_0 = \text{const}$?

Brief explanation

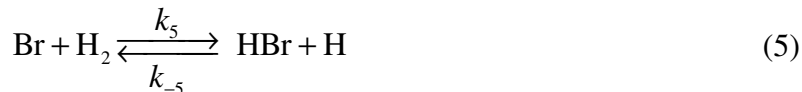
In this case I will permanently increase with the increase of $[Ac]_0 \rightarrow \infty$ at $[In]_0 = \text{const}$. The rate of the reaction (4b) may be so high that conversion of In in reaction (4a) will be negligible. Hence $I \rightarrow \infty$ if $[Ac]_0 \rightarrow \infty$ at $[In]_0 = \text{const}$.

$$I_\infty = \infty \text{ (infinity)}$$

4 points (2 points if only $I_\infty = \infty$ (infinity) is given).

(II) «Kinetic coupling»

The standard Gibbs energy of the gas-phase reaction



is positive, $\Delta G^\circ(5) = 66 \text{ kJ}\cdot\text{mol}^{-1}$ at $T = 600 \text{ K}$.

2.1. What is the ratio of the rates of forward and reverse reactions, $\frac{r_5}{r_{-5}}$, at this temperature, standard pressures of H_2 and HBr and equal pressures of H and Br ?

Calculations

The standard Gibbs energy of reaction (5) at 600K is 66 kJ/mol. The equilibrium constant is

$$K = e^{-66000/8.314/600} = 1.8 \cdot 10^{-6} = k_5 / k_{-5}. \quad \text{1 point}$$

Reaction is considered at standard pressures of all the reactants and products. The ratio of the rates of forward and reverse reactions is

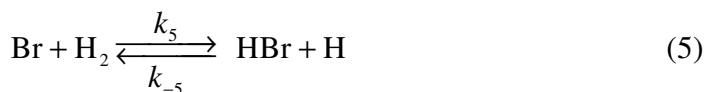
$$\frac{r_5}{r_{-5}} = \frac{k_5[\text{Br}][\text{H}_2]}{k_{-5}[\text{HBr}][\text{H}]} = \frac{k_5}{k_{-5}} = 1.8 \cdot 10^{-6}$$

$$\frac{r_5}{r_{-5}} = 1.8 \cdot 10^{-6} \quad \text{2 points}$$

Total – 3 points

If you could not answer this question, for further calculations use reference value $r_5/r_{-5} = 3.14 \cdot 10^{-7}$.

Reaction (5) proceeds in the forward direction due to the reaction (6) which simultaneously occurs in the system:



k_5 , k_{-5} , k_6 are rate constants of forward and reverse reaction (5) and forward reaction (6), respectively.

This is the *kinetic coupling* of two reactions.

Let pressures of neutral molecules keep standard values $p(\text{H}_2) = p(\text{Br}_2) = p(\text{HBr}) = 1 \text{ bar}$, and pressures of radicals $p(\text{H})$, $p(\text{Br})$ reach steady-state values. Rate constant k_6 is 10 times larger than k_{-5} .

2.2. Calculate $\Delta G(5)$ and $\frac{r_5}{r_{-5}}$ under such conditions.

Calculations

The steady-state condition is the same for both radicals, e.g. for radical H

$$\frac{d[\text{H}]}{dt} = k_5[\text{Br}][\text{H}_2] - k_{-5}[\text{HBr}][\text{H}] - k_6[\text{H}][\text{Br}_2] = 0$$

$$\frac{[\text{H}]}{[\text{Br}]} = \frac{k_5[\text{H}_2]}{k_{-5}[\text{HBr}] + k_6[\text{Br}_2]}$$

The concentrations of all the neutral molecules are the same (they correspond to the pressure of 1 bar), therefore

$$\frac{[\text{H}]}{[\text{Br}]} = \frac{k_5}{k_{-5} + k_6} = \frac{k_5 / k_{-5}}{1 + k_6 / k_{-5}} = \frac{1.8 \cdot 10^{-6}}{1 + 10} = 1.6 \cdot 10^{-7} \quad \text{2 points}$$

The Gibbs energy of reaction (5) under such conditions is:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{H}][\text{HBr}]}{[\text{Br}][\text{H}_2]} = 66 + 8.314 \cdot 10^{-3} \cdot 600 \cdot \ln(1.6 \cdot 10^{-7}) = -12 \text{ kJ} \cdot \text{mol}^{-1}$$

2 points

The ratio of rates is:

$$\frac{r_5}{r_{-5}} = \frac{k_5[\text{Br}][\text{H}_2]}{k_{-5}[\text{HBr}][\text{H}]} = \frac{k_5}{k_{-5}} \frac{[\text{Br}]}{[\text{H}]} = \frac{k_5}{k_{-5}} \frac{1 + k_6 / k_{-5}}{k_5 / k_{-5}} = 1 + \frac{k_6}{k_{-5}} = 11 \quad \text{2 points}$$

$$\Delta G(5) = -12 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\frac{r_5}{r_{-5}} = 11$$

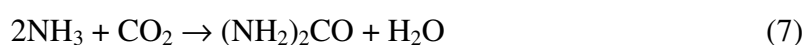
Total – 6 points

(III) "Second law of thermodynamics restricts coupling"

According to the Second Law of thermodynamics, two simultaneously occurring chemical reactions should decrease the system's Gibbs energy G_{Syst} , $\frac{\Delta G_{\text{Syst}}}{\Delta t} < 0$.

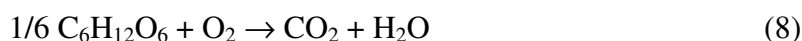
One of these reactions may have positive Gibbs energy and still proceed in the forward direction due to the coupling with the second reaction. This second reaction must have negative Gibbs energy and the requirements of the Second law must be fulfilled! Consider the example.

The synthesis of urea under specific conditions



$$\Delta G(7) = 46.0 \text{ kJ} \cdot \text{mol}^{-1}$$

is supposed to be coupled with the complete oxidation of glucose (under the same conditions)



$$\Delta G(8) = -481.2 \text{ kJ} \cdot \text{mol}^{-1},$$

$$r(8) = 6.0 \cdot 10^{-8} \text{ M} \cdot \text{min}^{-1}.$$

Both reactions are presented schematically. No other reactions are considered.

3. What is the maximum rate of the reaction (7) permitted by the Second Law if this reaction is coupled to reaction (8)?

Calculations

According to the Second law the following condition has to be met:

$$\frac{\Delta G_{\text{Syst}}}{\Delta t} = \Delta G(7) \times r_7 + \Delta G(8) \times r_8 \leq 0$$

therefore

$$r_7 \leq \frac{-\Delta G(8)}{\Delta G(7)} r_8 = \frac{481.2}{46.0} \cdot 6.0 \cdot 10^{-8} = 6.3 \cdot 10^{-7} \text{ M} \cdot \text{min}^{-1}$$

This is the maximum possible rate of the coupled reaction.

$$r_7(\text{max}) = 6.3 \cdot 10^{-7} \text{ M} \cdot \text{min}^{-1}$$

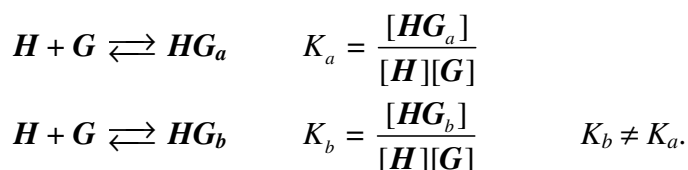
2 points

Problem 3. Two binding centers – competition or cooperation?

(7 points)

Question	1		2				Total
	1.1	1.2	2.1	2.2	2.3	2.4	
Marks	3	2	8	3	6	6	28

Many chemical reactions in living organisms include the formation of “host-guest” complexes where the host molecule reversibly binds one or several guest molecules. Consider a host molecule H with two binding centers – say, a and b which have different affinities for the guest molecules G :



where HG_a and HG_b denote a complex where guest is bound to a center and b center, respectively. K_a and K_b are the binding constants for the centers a and b , brackets denote molar concentrations.

Attachment of one G molecule to H can change the binding ability of the second centre. This change is described by the “interaction factor” β which reflects the influence of one binding center on another and is defined as follows:



where HG_2 is the completely bound complex.

1.1. Determine the range of values (or one value, if necessary) of β which correspond to three possible ways of interaction between binding centers: a) cooperation (binding by one center facilitates subsequent binding); b) competition (first binding complicates the second); c) independence (no interaction).

Cooperation: $\beta > 1$	1 pt (0.5 pt – for value, not range)
Competition: $0 < \beta < 1$	1 pt (0.5 pt without zero; 0.5 pt – for value, not range)
Independence: $\beta = 1$	1 pt
Total 3 pts	

1.2. Find the equilibrium constant for the process: $HG_b + G \rightleftharpoons HG_2$ in terms of binding constant(s) and interaction factor.

Calculations:

$$K = \frac{[HG_2]}{[HG_b][G]} = \frac{[HG_2]}{[HG_a][G]} \cdot \frac{[HG_a]}{[HG_b]} = \beta K_b \cdot \frac{K_a}{K_b} = \beta K_a$$

$K = \beta K_a$ 2 pts

2.1. The solution was prepared with the initial concentrations $[H]_0 = 1 \text{ M}$ and $[G]_0 = 2 \text{ M}$. After the reactions were completed, the concentration of H decreased by 10 times and that of G by 4 times. For these host and guest, $K_b = 2K_a$. Determine the concentrations of all other species in the solution and find the binding constant K_a and the factor β .

Calculations:

From $K_b = 2K_a$ it follows: $[HG_b] = 2[HG_a]$ **1 pt**

Material balance with respect to H : $[H] + [HG_a] + [HG_b] + [HG_2] = [H]_0 = 1 \text{ M}$, or
 $0.1 + 3[HG_a] + [HG_2] = 1 \text{ M}$ **0.5 pt**

Material balance with respect to G : $[G] + [HG_a] + [HG_b] + 2[HG_2] = [G]_0 = 2 \text{ M}$, or
 $0.5 + 3[HG_a] + 2[HG_2] = 2 \text{ M}$. **0.5 pt**

Solving the system of two equations, we find: $[HG_a] = 0.1 \text{ M}$, $[HG_2] = 0.6 \text{ M}$, hence $[HG_b] = 0.2 \text{ M}$.

$$K_a = \frac{[HG_a]}{[H][G]} = \frac{0.1}{0.1 \cdot 0.5} = 2$$

$$\beta = \frac{[HG_2]}{[HG_a][G]K_b} = \frac{0.6}{0.1 \cdot 0.5 \cdot 4} = 3$$

$$[HG_a] = 0.1 \text{ M}$$

$$[HG_b] = 0.2 \text{ M}$$

$$[HG_2] = 0.6 \text{ M}$$

(**1 pt** for $[HG_a]$, **2 pts** for $[HG_2]$, and $[HG_b]$ is not marked if $[HG_b] = 2[HG_a]$ was given **1 pt**, otherwise **1 pt**)

$$K_a = 2$$

1 pt

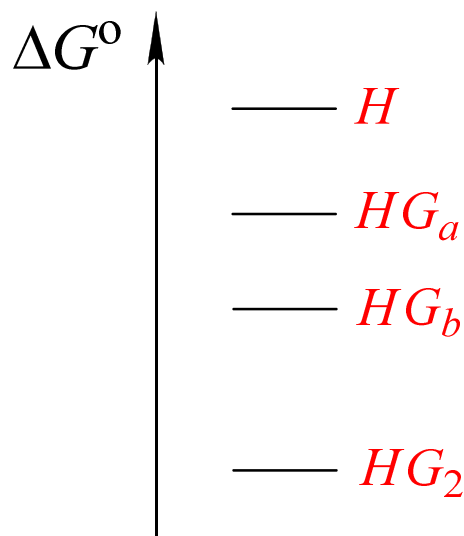
$$\beta = 3$$

2 pts

Total 8 pts

If you could not answer this question, for further calculations use reference values $K_a = 3.14$ and $\beta = 2.72$.

2.2. Find the correct order of standard molar Gibbs energies of formation of host H and all host-guest complexes from H and G . In the scheme below, write the corresponding chemical formula near every line.



1 pt – for the highest $\Delta G^\circ(H)$,

1 pt – for the lowest $\Delta G^\circ(HG_2)$

1 pt – for $\Delta G^\circ(HG_a) > \Delta G^\circ(HG_b)$

Total 3 pts

2.3. Some amount of G was added to 1 mole of H and the mixture was dissolved in water to obtain 1 liter of the solution. The number of the totally bound molecules HG_2 in the solution is equal to the total number of single-bound molecules HG . Find the initial amount of G (in mol). The constants K_a and K_b and the factor β are the same as in question 2.1.

Calculations:

1) $[HG_2] = [HG_a] + [HG_b] = 3[HG_a]$

$$\frac{[HG_2]}{[HG_a][G]} = \beta K_b = 12, \quad \frac{3}{[G]} = 12, \quad [G] = 0.25 \text{ M}$$

2) Material balance with respect to H : $[H] + 3[HG_a] + [HG_2] = 1 \text{ M}$

$$[H] + 6[HG_a] = 1 \text{ M}$$

$$[H] + 12[H][G] = 1 \text{ M}$$

$$[H] = 0.25 \text{ M.}$$

3) $[HG_a] = K_a[H][G] = 0.125 \text{ M.}$

$$[HG_2] = 3[HG_a] = 0.375 \text{ M.}$$

4) Material balance with respect to G : $[G]_0 = [G] + 3[HG_a] + 2[HG_2] = 1.375 \text{ M}$

$$n_0(G) = 1.375 \text{ mol}$$

Correct determination of $[G]$, $[H]$, $[HG_a]$, $[HG_2]$ – **1 pt** for each concentration

$n_0(G)$ – **2 pts**

Total 6 pts

2.4. What would be the equilibrium composition of the solution if: a) $\beta = 0$; b) β is very large ($\beta \rightarrow \infty$). The constants K_a and K_b as well as the initial concentrations of H and G are the same as in question 2.1.

$$\beta = 0$$

Calculations:

In this case, no HG_2 is formed.

Material balance with respect to H : $[H] + [HG_a] + [HG_b] = 1 \text{ M}$, or

$$[H] + 3[HG_a] = 1 \text{ M}$$

Material balance with respect to G : $[G] + [HG_a] + [HG_b] = 2 \text{ M}$, or

$$[G] + 3[HG_a] = 2 \text{ M}$$

Equilibrium constant:

$$K_a = \frac{[HG_a]}{[H][G]} = 2$$

Solving the system of three equations, we get:

$$[H] = 0.129 \text{ M} \quad [G] = 1.129 \text{ M} \quad [HG_a] = 0.290 \text{ M} \quad [HG_b] = 0.580 \text{ M}$$

$$[HG_2] = 0$$

1 pt for each concentration except HG_b , maximum – **4 pts**

$$\beta \rightarrow \infty$$

Calculations (or arguments):

In this case, formation of HG_2 is practically irreversible, so only HG_2 is present in the solution.

$$[H] = 0 \quad [G] = 0 \quad [HG_a] = 0 \quad [HG_b] = 0$$

$$[HG_2] = 1 \text{ M}$$

2 pts

(any calculation which gives similar result – full mark)

Total 6 pts

Problem 4. From one yellow powder to another: A simple inorganic riddle**(6 points)**

Question	1	2	3	4	Total
Marks	8	8	3	5	24

The yellow binary compound X_1 was completely dissolved in concentrated nitric acid by heating, the gas evolved is 1.586 times denser than air. Upon adding an excess of barium chloride to the solution formed a white solid X_2 precipitates. It was filtered. The filtrate reacts with an excess of silver sulfate solution forming a precipitate of two solids X_2 and X_3 , also separated from solution by filtration. To the new filtrate the solution of sodium hydroxide was being added drop-wise until the solution became nearly neutral (about pH 7). At this time a yellow powder X_4 (77.31 wt.% of Ag) crystallized from the solution. The mass of X_4 is nearly 2.4 times larger than that the mass of the first portion of X_2 .

1. Determine the chemical formulae of $\text{X}_1 - \text{X}_4$.

Calculations:

The precipitate X_2 formed by addition of barium chloride in acidic medium is barium sulfate BaSO_4 . **1 pt**

The precipitate X_3 formed by addition of silver sulfate is silver chloride AgCl **1 pt**

The yellow precipitate X_4 formed by addition of alkali can be mercury oxide HgO or silver phosphate Ag_3PO_4 . The ratio of molar masses $\text{X}_4 : \text{X}_2$ is 0.931 for $\text{HgO} : \text{BaSO}_4$ which is not valid and 1.798 for $\text{Ag}_3\text{PO}_4 : \text{BaSO}_4$ which gives 2.4 being multiplied by 4/3. So, the molar ratio is $4\text{Ag}_3\text{PO}_4 : 3\text{BaSO}_4$ which corresponds to $\text{P} : \text{S} = 4:3$, i.e. to formula of X_1 P_4S_3 .

$\text{X}_1 = \text{P}_4\text{S}_3$

$\text{X}_2 = \text{BaSO}_4$

$\text{X}_3 = \text{AgCl}$

$\text{X}_4 = \text{Ag}_3\text{PO}_4$

2 pts for Ag_3PO_4

4 pts for P_4S_3 (**0 pts** without calculations)

Total – 8 pts

2. Determine the chemical formula of the gas and provide equations for all reactions in ionic or non-ionic form.

Calculation

The gas evolved has a molar mass $1.586 \times 29 = 46$ g/mol, that is NO_2 . **1 pt**

Chemical formula of the gas _____

Dissolution of X_1

$\text{P}_4\text{S}_3 + 38\text{HNO}_3 = 4\text{H}_3\text{PO}_4 + 3\text{H}_2\text{SO}_4 + 38\text{NO}_2 + 10\text{H}_2\text{O}$ **2 pt**

Formation of X_2



Formation of X_2 and X_3



Addition of NaOH and formation of X_4



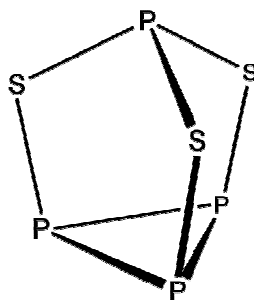
(neutralization of H_3PO_4 and subsequent reaction with Ag_2SO_4 will also be accepted)

(50% of points for non-balanced reactions with correct products)

Total – 8 pts

3. In the structural unit of X_1 all atoms of only one element are in equivalent positions. Draw the structure of X_1 .

Phosphorus sulfide P_4S_3 is a molecular cage



3 pts

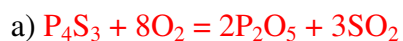
(Any reasonable structures with correct valencies of sulfur and phosphorus will also be accepted.

1 pt for the structure with non-equivalent atoms of both elements)

4. Predict the products of X_1 interaction with:

- a) excess oxygen;
- b) excess of hot concentrated sulfuric acid;
- c) solid $KClO_3$ with grinding.

Write down the reaction equations.



1 pt



(oxidation of sulfide to S instead of SO_2 is full mark)



(50% of points for non-balanced reactions with correct products)

Total – 5 pts

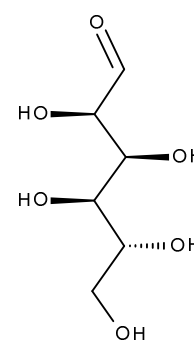
Problem 5. Indispensable glucose**(8 points)**

Question	1						2					Total
	1.1	1.2	1.3	1.4	1.5	1.6	2.1	2.2	2.3	2.4	2.5	
Marks	2	3	6	4	6	1	2	2	4	2	2	34

Carbohydrates are the most important providers of energy for living cells. Monosaccharide glucose is a source of energy for the living cell, but for persons who suffer from diabetes glucose may be dangerous. High level of glucose may lead to cardiovascular diseases and even death. That is why people avoid consuming too much carbohydrates and glucose particularly.

1. Determination of reducing sugars in fruit juice

One of the technique for determination of reducing sugars in different samples includes the use of Fehling's reagent. A 10.00-mL aliquot of fruit juice (assuming the initial sample contained only glucose and fructose) was transferred into a titration flask and Fehling's reagent was added. This reagent was prepared by mixing 50.00 mL of 0.04000 M copper sulfate (solution A) and potassium-sodium tartrate and sodium hydroxide (solution B). Solution C thus obtained, was then heated and red precipitate was formed.



Glucose

1.1. Write the balanced ionic equation of chemical reaction occurring upon heating of the solution C. Use Cu^{2+} for initial copper solution.

$\text{C}_6\text{H}_{12}\text{O}_6 + 2 \text{Cu}^{2+} + 5\text{OH}^- = \text{C}_6\text{H}_{11}\text{O}_7^- + \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$	2 points
If $\text{C}_6\text{H}_{12}\text{O}_7$ instead of $\text{C}_6\text{H}_{11}\text{O}_7^-$	1 point
Hereinafter if an equation is not balanced, then points/2.	

After that 10 mL of 10% solution of potassium iodide and 1 M sulfuric acid were added to the flask. The mixture was covered with watch glass and was then placed in a dark place. An excess of iodine was then titrated with 0.05078 M sodium thiosulphate solution. 11.87 mL of the titrant was required to reach the endpoint.

1.2. Write the balanced equation(s) in molecular or ionic form for all the reactions taking place in the flask.

$2\text{CuSO}_4 + 4\text{KI} = 2\text{CuI} + \text{I}_2 + 2\text{K}_2\text{SO}_4$ $\text{or } 2\text{Cu}^{2+} + 4\text{I}^- = 2\text{CuI} + \text{I}_2$ $\text{KI} + \text{I}_2 = \text{KI}_3$ $\text{or } \text{I}^- + \text{I}_2 = \text{I}_3^-$ $\text{C}_6\text{H}_{11}\text{O}_7^- + \text{H}_2\text{SO}_4 = \text{C}_6\text{H}_{12}\text{O}_8 + \text{HSO}_4^-$ $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$ $\text{or } 2\text{S}_2\text{O}_3^{2-} + \text{I}_2 = 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$	<p>2 points</p> <p>not marked</p> <p>not marked</p> <p>1 point</p>
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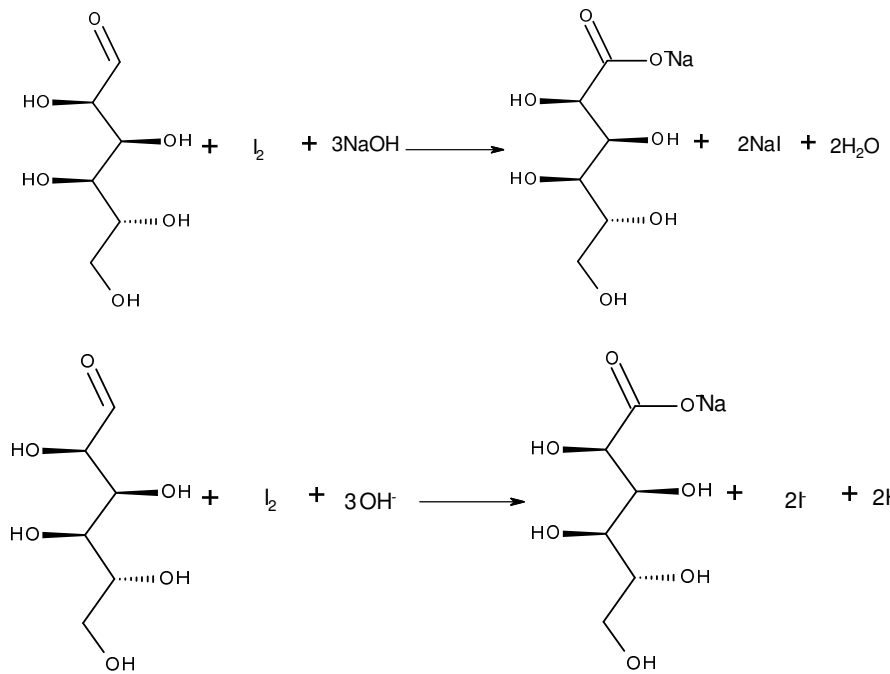
1.3. Consider all fructose was transformed into glucose under the experimental conditions; calculate the total mass content of sugars (in g/L) in a fruit juice. $M_w = 180.16 \text{ g/mol}$.

<p>Total amount of copper(II) is $50.00 \text{ mL} * 0.04000 \text{ M} = 2.0000 \text{ mmol}$.</p> <p>Obviously, there is an excess of iodine and the remaining iodine was titrated with sodium thiosulphate: $11.87 \text{ mL} * 0.05078 \text{ M} = 0.6028 \text{ mmol}$.</p> <p>$2.0000 - 0.6028 \text{ mmol} = 1.3972 \text{ mmol}$ of copper(II) was required to oxidize the sugars.</p> <p>$v(\text{sugars}) = v(\text{Cu}^{2+})/2 = 0.6986 \text{ mmol}$ in 10.00 mL</p> <p>$C(\text{sugars}) = 0.6986 \text{ mmol}/10.00 \text{ mL} = 0.06986 \text{ M}$</p> <p>mass content = $180.16 \text{ g/mol} * 0.06986 \text{ M} = 12.6 \text{ g/L}$</p>	<p>6 points</p>
---	------------------------

A new 10.00-mL aliquot of the same juice was treated with a 10.00-mL portion of acidified potassium iodate(V) solution (0.01502 M) and 10 mL of 10% solution of potassium iodide. After the mixture turned brown, an excess of sodium hydroxide solution was added. The flask was then covered with a watch glass and put into a dark place. The obtained solution was acidified and titrated with 0.01089 M solution of sodium thiosulphate. The average titrant volume used for titration was 23.43 mL . Note that fructose is not converted into glucose under these conditions.

1.4. Write all the balanced equations for the described reactions in molecular or ionic form.

$\text{KIO}_3 + 5\text{KI} + 3\text{H}_2\text{SO}_4 = 3\text{I}_2 + 3\text{K}_2\text{SO}_4 + 3\text{H}_2\text{O}$ $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ = 3\text{I}_2 + 3\text{H}_2\text{O}$	<p>2 points</p>
<p>Only glucose was oxidized with iodine</p>	<p>2 points</p>

 <p>or</p>	
$H^+ + OH^- = H_2O$	not marked
$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$	not marked

1.5. Calculate the mass content of each sugar (in g/L) in the juice.

Total amount $v(I_2) = 3v(IO_3^-) = 3 \cdot 0.01502 \text{ M} \cdot 10 \text{ mL} = 0.4506 \text{ mmol}$	1 pt	6 points
$v(S_2O_3^{2-}) = 23.43 \text{ mL} \cdot 0.01089 \text{ M} = 0.2552 \text{ mmol}$	1 pt	
$v(S_2O_3^{2-})/2 = v(I_2) = 0.1276 \text{ mmol}$	1 pt	
$0.4506 \text{ mmol} - 0.1276 \text{ mmol} = 0.3230 \text{ mmol}$ of iodine was used to oxidize glucose		
$C(\text{glucose}) = 0.3230 \text{ mmol} / 10.00 \text{ mL} = 0.03230 \text{ M}$	1 pt	
mass content of glucose = $180.16 \text{ g/mol} \cdot 0.03230 \text{ M} = 5.82 \text{ g/L}$	1 pt	
mass content of fructose = $12.6 - 5.82 = 6.78 \text{ g/L}$	1 pt	

1.6. One bread exchange unit (1 BEU) corresponds to the content of 12 g of digestible carbohydrates in product. How many BEU are in one glass (200 mL) of juice?

$0.2 \text{ L} \cdot 5.82 \text{ g/L} = 1.16 \text{ g}$ of digestible carbohydrates, it is 0.1 BEU	1 point
Or $0.2 \text{ L} \cdot 12.6 \text{ g/L} = 2.52 \text{ g}$, it is 0.2 BEU	1 point

2. Diagnosis of diseases

The derivative of glucose, 2-deoxy-2- (^{18}F) fluoro-D-glucose (FDG), is the most common radiopharmaceuticals for diagnosis of cancer using positron emission tomography. The first step of FDG preparation is to produce a radionuclide fluoro-18 by nuclear reaction in a cyclotron. The next step is the radiochemical synthesis. Fluorine-18 is introduced into D-glucose molecule by

nucleophilic substitution. 2-deoxy-2-(^{18}F)fluoro-D-glucose once injected into the patient actively accumulates in cells of malignant tumors; this process is accompanied by decomposition of fluorine-18. This radionuclide is a β^+ emitter – nucleus emits a positron (anti-electron). Positron interacts with an electron and after that annihilation occurs, which can be detected. This allows determining precisely the tumor sizes and type.

2.1. Complete the nuclear reactions leading to various fluorine isotopes.

- a) $^{18}\text{O} + {}^1_1\text{H} \rightarrow \dots + ^{18}\text{F}$ n 0.5 points
- b) $\dots + {}^2_1\text{D} \rightarrow ^{18}\text{F} + \alpha$ ^{20}Ne 0.5 points
- c) $^{19}\text{F} + {}^2_1\text{D} \rightarrow ^{20}\text{F} + \dots$ ${}^1_1\text{H}$ 0.5 points
- d) $^{16}\text{O} + \dots \rightarrow ^{18}\text{F} + {}^1_1\text{H} + n$ α or ${}^4_2\text{He}$ 0.5 points

2.2. The decay mode of unstable light nuclei depends on the ratio between the number of neutrons and protons in them. If this ratio is greater than that for a stable isotope then the nucleus decays in a β^- -mode, if it is smaller – in a β^+ -mode.

Determine the type of decay for the nuclei in the table:

Nucleus	^{11}C	^{20}F	^{17}F	^{14}C
Decay mode	β^+	β^-	β^+	β^-
	0.5 points	0.5 points	0.5 points	0.5 points

When nuclear reaction (a) is used for fluorine-18 preparation, the target material is presented as water enriched with H_2^{18}O . The presence of usual water H_2^{16}O leads to a side nuclear reaction with ^{16}O , leading to the formation of isotope ^{17}F .

2.3. It is known that within five minutes after completion of irradiation of the target the ratio of radioactivities of ^{18}F and ^{17}F is 10^5 . Assuming that irradiation time is short, the radioactivity of each isotope is proportional to the nuclear reaction yield and the mole fraction of a component in the irradiated target, **calculate** the mass fraction of H_2^{18}O in the target. $t_{1/2}(^{18}\text{F}) = 109.7$ minutes, $t_{1/2}(^{17}\text{F}) = 65$ seconds. The ratio between nuclear reactions yields is $\eta_{^{18}\text{O}-^{18}\text{F}} / \eta_{^{16}\text{O}-^{17}\text{F}} = 144.7$.

Radioactivity is:

$$A = \lambda N, \text{ where } N \text{ is the number of atoms, } \lambda = \ln 2 / t_{1/2}$$

1 point

The initial ratio of radioactivities:

$$\frac{A_0(^{18}\text{F})}{A_0(^{17}\text{F})} = \frac{\lambda(^{18}\text{F})}{\lambda(^{17}\text{F})} \cdot \frac{\eta(^{18}\text{O} \rightarrow ^{18}\text{F})}{\eta(^{16}\text{O} \rightarrow ^{17}\text{F})} \cdot \frac{\chi(\text{H}_2^{18}\text{O})}{\chi(\text{H}_2^{16}\text{O})} = \frac{65/60}{109.7} \cdot 144.7 \cdot \frac{\chi(\text{H}_2^{18}\text{O})}{\chi(\text{H}_2^{16}\text{O})} = 1.43 \frac{\chi(\text{H}_2^{18}\text{O})}{\chi(\text{H}_2^{16}\text{O})}$$

After 5 minutes the ratio changed due to radioactive decay of fluorine:

$$\frac{A_{300}(^{18}\text{F})}{A_{300}(^{17}\text{F})} = \frac{A_0(^{18}\text{F}) \cdot \exp\left(-\frac{\ln 2}{109.7} \cdot 5\right)}{A_0(^{17}\text{F}) \cdot \exp\left(-\frac{\ln 2}{65} \cdot 300\right)} = 23.75 \cdot \frac{A_0(^{18}\text{F})}{A_0(^{17}\text{F})} = 33.94 \cdot \frac{\chi(\text{H}_2^{18}\text{O})}{\chi(\text{H}_2^{16}\text{O})} = 10^5$$

1 point

$$\frac{\chi(\text{H}_2^{18}\text{O})}{\chi(\text{H}_2^{16}\text{O})} = 2947$$

1 point

Mass fraction of H_2^{18}O is:

$$\omega(\text{H}_2^{18}\text{O}) = \frac{2947 \cdot 20}{2947 \cdot 20 + 18} = 0.9997$$

1 point

$$\omega(\text{H}_2^{18}\text{O}) = 0.9997 = 99.97\%.$$

Total – 4 points

2.4. Calculate the yield of labeling D-glucose with fluorine-18, if initial radioactivity of a fluorine-18 sample was 600.0 MBq and radioactivity of the obtained 2-deoxy-2- (^{18}F) fluoro-D-glucose is 528.2 MBq. Synthesis time is 3.5 minutes.

During the synthesis, the radioactivity will decrease:

$$A_{3.5} = A_0 \cdot \exp\left(-\frac{\ln 2}{109.7} \cdot 3.5\right) = 586.9 \text{ MBq}$$

1 point

$$\eta = 528.2 / 586.9 = 0.900 = 90.0\%$$

1 point

2.5. Biological half-life (through the excretory organs) of 2-deoxy-2- (^{18}F) fluoro-D-glucose is 120.0 minutes. How much radioactivity (in MBq) will remain in the patient ten hours after injection of FDG with the initial radioactivity of 450.0 MBq.

Radioactivity is excreted by radioactive decay and through the excretory organs (e.g. kidneys). The excretion process may be considered as two competitive first-order reactions. Activity after one hour is:

$$A_{60} = A_0 \exp\left(-(\lambda_1 + \lambda_2)t\right) = 450 \cdot \exp\left(-\left(\frac{\ln 2}{109.7} + \frac{\ln 2}{120}\right) \cdot 600\right) = 0.32 \text{ MBq}$$

2 points.

Problem 6. Bread is the stuff of life

(8 points)

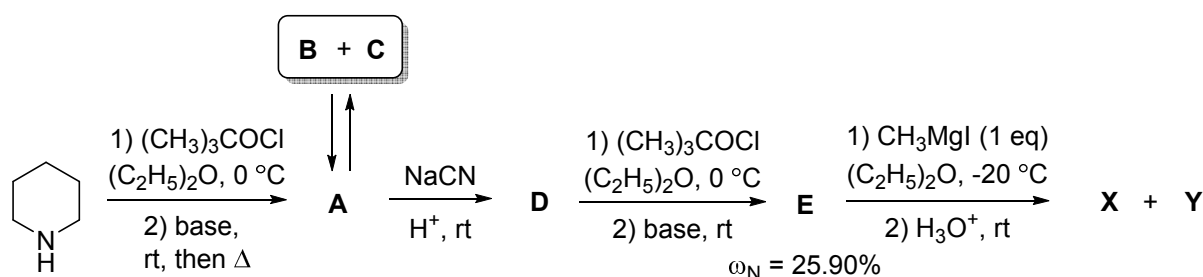
Question	1	2	3	Total
Marks	28	4	8	40

When you pass by the bakery, you are stopped by the smell of freshly baked bread. The hero of one of the novels said on a similar occasion: "If you tell me that this is not perfect, you are my enemy forever." The principle bread flavour component was identified in 1969 as compound **X** which occurs in equilibrium with its tautomer **Y** in a 2:1 ratio. Unfortunately, both forms are labile, and after some hours bread has no the same nice smell.




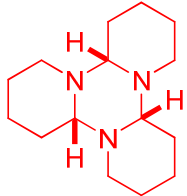

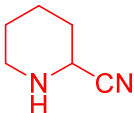
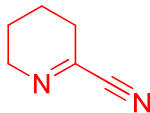

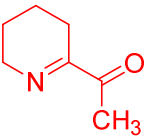
This tautomeric mixture of **X** and **Y** was synthesized in 1993 from piperidine by the reaction sequence given in Scheme 1. It is noteworthy that the initial ratio of **X** and **Y** was 1:4; on standing this ratio gradually changed to an equilibrium one.

Scheme 1.



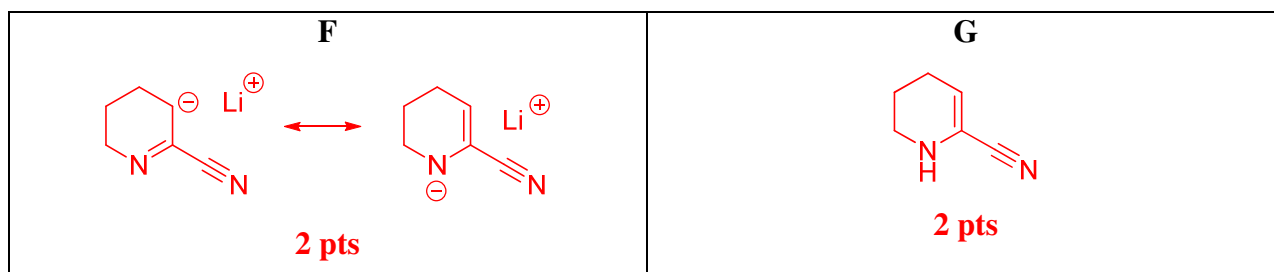
Compound **B** which is characterized by 3-fold axis of symmetry (*i.e.*, rotation by 120° results in a molecule indistinguishable from the original) occurs in equilibrium with its diastereomer **C**. The interconversion of these two forms proceeds *via* intermediate **A** which is also intermediate in **B** and **C** formation as well as their transformation to **D**. Compounds **A**, **B**, and **C** have the same elemental composition: $\omega_{\text{C}} = 72.24\%$, $\omega_{\text{H}} = 10.91\%$, $\omega_{\text{N}} = 16.85\%$.

1. Write down the structural formulae of compounds **A-E**, **X**, **Y**.

<p style="text-align: center;">A</p>  <p style="text-align: center;">4 pts (1pt for any reasonable isomer)</p>	<p style="text-align: center;">B</p>  <p style="text-align: center;">4 pts (Other reasonable structures with molecular formula (C₅H₉N)_n but without 3-fold axis of symmetry – 2 pts)</p>	<p style="text-align: center;">C</p>  <p style="text-align: center;">4 pts</p>
<p style="text-align: center;">D</p>  <p style="text-align: center;">4 pts</p>	<p style="text-align: center;">E</p>  <p style="text-align: center;">4 pts (1 pt for any reasonable isomer)</p>	<p style="text-align: center;">X</p>  <p style="text-align: center;">4 pts (other structures will be estimated only if they are consistent with both reaction schemes, 3 pts if in cell Y)</p>
<p style="text-align: center;">Y</p>  <p style="text-align: center;">4 pts (other structures will be estimated only if they are consistent with both reaction schemes, 3 pts if in cell X)</p>		

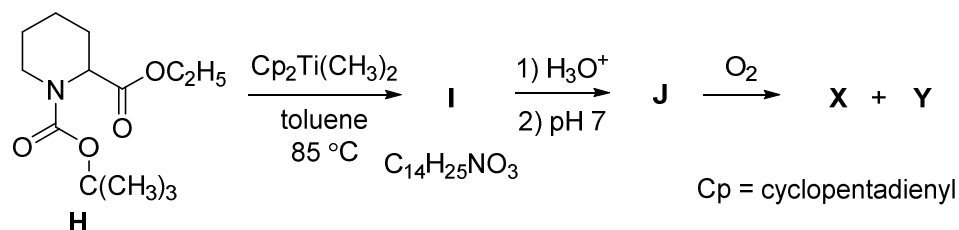
Treatment of compound **E** with $\text{CH}_3\text{Li}\cdot\text{LiBr}$ complex in $(\text{C}_2\text{H}_5)_2\text{O}$ at $0\text{ }^\circ\text{C}$ failed to produce the target products **X** and **Y**. Instead, a yellow precipitate **F** was initially formed. Aqueous workup of this precipitate led to the mixture of compound **E** and its tautomer **G**.

2. Write down the structural formulae of compounds **F** and **G**.

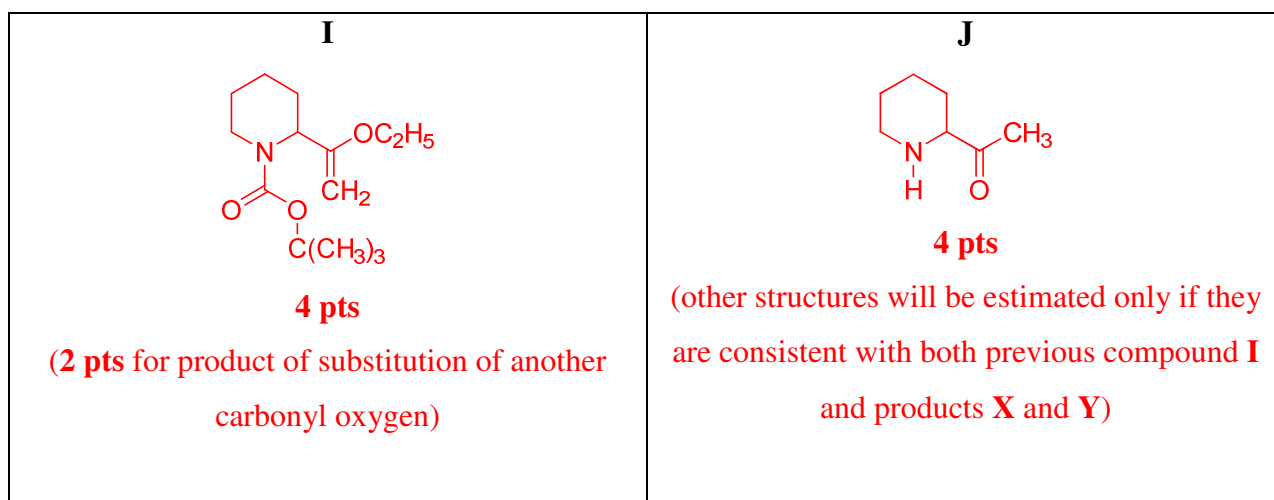


Another approach to compound **X** is based on the use of pipecolic acid derivative **H**. It was shown that **X** can be synthesized by reaction sequence presented in Scheme 2.

Scheme 2.



3. Write down the structural formulae of compounds **I** and **J**.



Problem 7. Not by bread alone

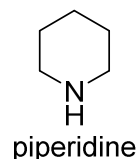
(8 points)

Question	1	2	3	4	Total
Marks	8	24	2	16	50

Pomegranate is called in Azerbaijan, which is famous for its vegetables, as the “king of all fruits”. Pomegranate is honored in various religions as a “fruit of Paradise”, symbol of righteousness, wealth, hope for eternal life.



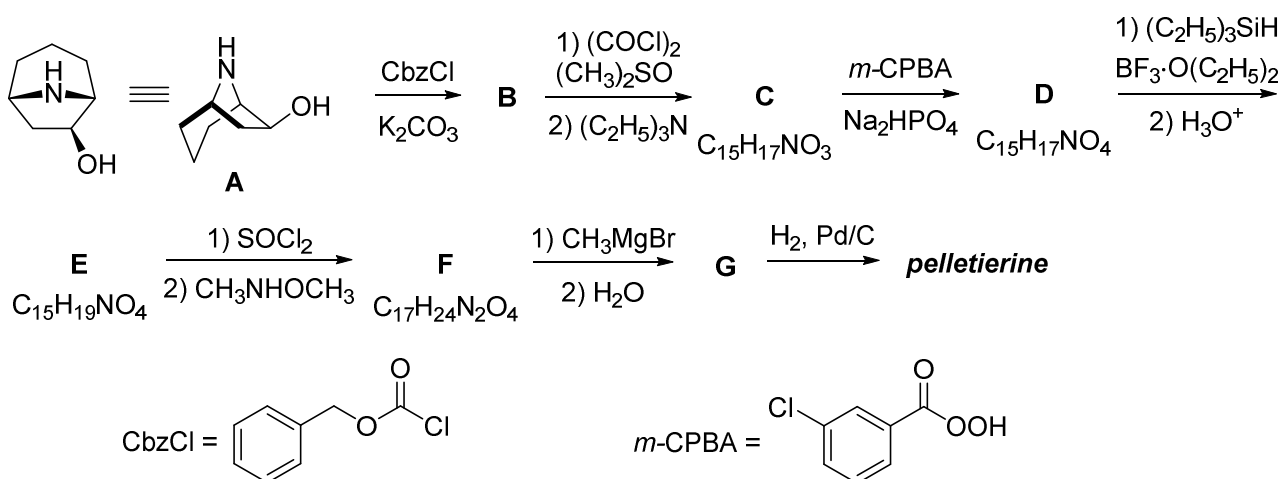
In 1878 alkaloid **pelletierine** was isolated from the bark of pomegranate tree (*Punica granatum* L., *Lythraceae*). This alkaloid is traditionally used as an anti-helminthic drug. Initially **X_W** (3-(piperidin-2-yl)propanal) was incorrectly proposed for pelletierine. But now it is accepted that natural pelletierine is (*S*)-1-(piperidin-2-yl)propan-2-one (**X_S**).



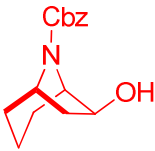
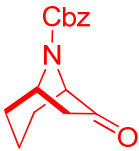
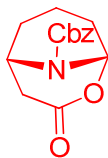
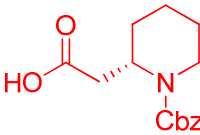
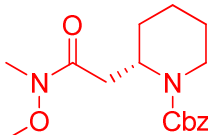
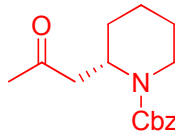
1. Write down the structural formulae of **X_W** and **X_S** (the latter – with the stereochemical information).

X_W (3-(piperidin-2-yl)propanal)	X_S (<i>S</i>)-1-(piperidin-2-yl)propan-2-one
<p>4 pts</p>	<p>4 pts (2 pts without stereochemistry)</p>

The synthesis of natural pelletierine (**X_S**) based on the transformation of nortropanol **A** was recently described.



2. Write down the structural formulae of compounds **B-G** with the stereochemical information.

<p style="text-align: center;">B</p>  <p style="text-align: center;">4 pts</p>	<p style="text-align: center;">C</p>  <p style="text-align: center;">4 pts</p>	<p style="text-align: center;">D</p>  <p style="text-align: center;">4 pts</p>
<p style="text-align: center;">E</p>  <p style="text-align: center;">4 pts</p>	<p style="text-align: center;">F</p>  <p style="text-align: center;">4 pts</p>	<p style="text-align: center;">G</p>  <p style="text-align: center;">4 pts</p>

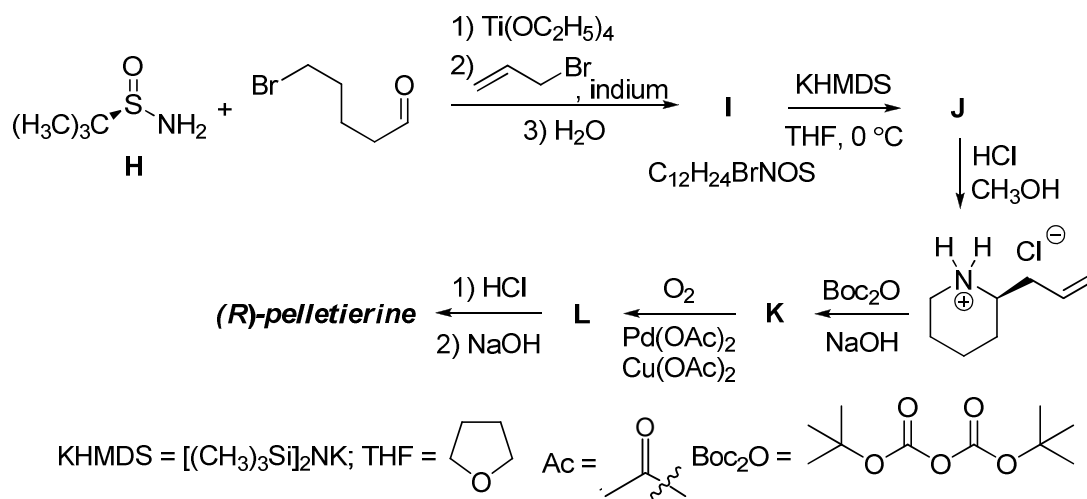
(For the structural formulae without stereochemistry (or with bad stereochemistry): 3 pts for each. Comments: a) for compound **B**, product of hydroxyl group acylation in **A** is estimated by 2 pts; b) for wrong isomeric structures of compounds **C-F** the mark will be in the range of 0-2 pts depending on the credibility of answer; c) for the wrong structures of compound **G** the mark will be in the range of 0-4 pts depending on the credibility of answer (4 pts will be given if under the specified conditions compound **G** can be obtained from **F** and can be transformed into (*S*)-1-(piperidin-2-yl)propan-2-one.)

3. Nortropanol **A** was used in this reaction as a single stereoisomer. How many stereoisomers can exist for compound **A** (including **A**)? Ignore nitrogen chirality.

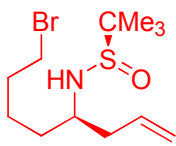

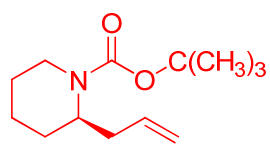
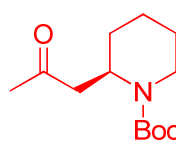
The number of possible stereoisomers of **A**: 4.

2 pts (0.5 pts for 8)

Enantiomer of **X_S** was synthesized using chiral *tert*-butanesulfinamide (**H**):



4. Write down the structural formulae of compounds **I-L** with the stereochemical information.

<p style="text-align: center;">I</p>  <p style="text-align: center;">4 pts</p>	<p style="text-align: center;">J</p>  <p style="text-align: center;">4 pts</p>
<p style="text-align: center;">K</p>  <p style="text-align: center;">4 pts</p>	<p style="text-align: center;">L</p>  <p style="text-align: center;">4 pts</p>

(For the structural formulae without stereochemistry (or with bad stereochemistry): 3 pts for each.

Wrong structures will be estimated depending on the credibility of answer.)

Problem 8. Oil for Life and Life after Oil

(8 points)

Question	1					2	3	4	Total
	1a	1b	1c	1d	1e				
Marks	1	4	4	3	12	5	13	13	55

Azerbaijan is known for its vast oil and gas fields. The first drilling for oil was done in Bibi-Heybat in 1846, 13 years before establishment of the first commercial oil well in Pennsylvania (USA). This remarkable date in the history of Azerbaijan is regarded as a starting point of contemporary oil industry, the leading sector of today's world economy. Currently, on-land and shelf sea oil production is being developed in Azerbaijan. Though serious precautions are taken, there is always a risk of hydrocarbon pollution of the environment during production, transportation, and processing of oil. In this task we will consider diverse technologies of oil spills clean up and specific features of metabolic pathways involved.



Application of complex solvents (dispersants) leading to capture of marine oil spills is among most promising clean up approaches. Organic substance **X** (11.94% of H by mass) is a typical component of such dispersants. Safety of **X** to human is fiercely debated. **X1** (54.53% of carbon by mass) composed of three elements and excreted with urine is the major metabolite of **X** in humans. The numbers of atoms of different elements in **X1** are three consecutive terms of a geometric progression (n, nq, nq^2), whereas the sum of these numbers does not exceed 25.

1a. Decide on the relationship (tick the correct variant) between the numbers of carbon and oxygen atoms in **X1**.

$n(C) > n(O)$ <input checked="" type="checkbox"/> 1 p	$n(C) < n(O)$ <input type="checkbox"/>	$n(C) = n(O)$ <input type="checkbox"/>	Data insufficient <input type="checkbox"/>
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1b. Derive the empirical formula of **X1** (hereafter always show your work where required). Be sure you prove the answer by calculations.

Your work

With regard to 1a, three variants ($n(\text{H}) > n(\text{C}) > n(\text{O})$, $n(\text{C}) > n(\text{H}) > n(\text{O})$, and $n(\text{C}) > n(\text{O}) > n(\text{H})$) are possible for **X1**. For each inequality, one can write down the corresponding formula using elements of a geometric progression (q is the progression common ratio), equations for calculation of mass fractions of carbon and its roots

Inequality	Formula	Equation	The first root (q_1)	The second root (q_2)
$n(\text{H}) > n(\text{C}) > n(\text{O})$	$\text{C}_{qn}\text{H}_{q^{2n}}\text{O}_n$	$\frac{12.01qn}{12.01qn + 1.008q^{2n} + 16.00n} = 0.5453$	2.00	7.93
$n(\text{C}) > n(\text{H}) > n(\text{O})$	$\text{C}_{q^{2n}}\text{H}_{qn}\text{O}_n$	$\frac{12.01q^2n}{12.01q^2n + 1.008qn + 16.00n} = 0.5453$	-1.21	1.32
$n(\text{C}) > n(\text{O}) > n(\text{H})$	$\text{C}_{q^{2n}}\text{H}_n\text{O}_{qn}$	$\frac{12.01q^2n}{12.01q^2n + 1.008n + 16.00qn} = 0.5453$	-0.06	1.66

There is only one positive integer root, thus the empirical formula is $\text{C}_2\text{H}_4\text{O}$.

problem formulation – 1p

derivation – 1p

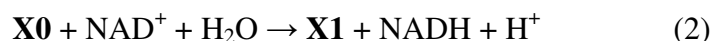
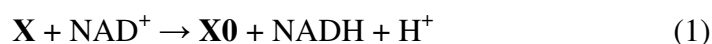
result – 2p

Total 4 pts

(alternative approaches are possible)

Empirical formula of **X1**: $\text{C}_2\text{H}_4\text{O}$

The biotransformation of **X** into **X1** occurs in two enzymatically catalyzed steps according to the hereunder reaction balanced equations (NAD^+ and NADH are the oxidized and reduced forms of nicotinamide adenine dinucleotide, respectively):



1c. Derive the molecular formula of **X**.

Your work

Since (1) and (2) are the reaction equations, one can write down the formula of **X** as: $\text{C}_{2n}\text{H}_{4n}\text{O}_n + 2\text{H} - 1\text{O} = \text{C}_{2n}\text{H}_{4n+2}\text{O}_{n-1}$. With an account for the known mass fraction of hydrogen:

$$\frac{1.008(4n+2)}{12.01 \cdot 2n + 1.008(4n+2) + 16.00(n-1)} = 0.1194. \text{ Finally, } n = 3, \text{ and the molecular formula of } \text{X} \text{ is}$$

$\text{C}_6\text{H}_{14}\text{O}_2$.

derivation – 2p

result – 2p

Total 4 pts

Molecular formula of **X**: $\text{C}_6\text{H}_{14}\text{O}_2$

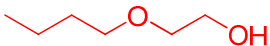
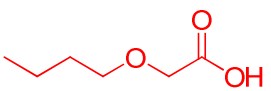
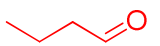
A minor metabolic transformation of **X** is catalyzed by cytochrome P450-dependent monooxygenase. This reaction leads to two compounds **X2** (51.56% of oxygen and 9.74% of hydrogen by mass) and **X3**.

1d. Derive the molecular formula of **X2** and draw its structure.

<p>Your work</p> <p>X2 is formed from X composed of three elements (C, H, and O) via a monooxygenase catalyzed reaction: $n(\text{C}) : n(\text{H}) : n(\text{O}) = \frac{100 - 51.56 - 9.74}{12} : \frac{9.74}{1.008} : \frac{51.56}{16.00} = 1 : 3 : 1$. 1p</p> <p>Since the number of hydrogen atom is necessarily even, the molecular formula of X2 is $\text{C}_2\text{H}_6\text{O}_2$. Other variants with a higher even number of hydrogen are not valid. Ethylene glycol $\text{HOCH}_2\text{CH}_2\text{OH}$ is the only stable substance with the molecular formula deciphered above.</p>	
Molecular formula of X2 : $\text{C}_2\text{H}_6\text{O}_2$ 1p	Structure of X2 : $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ 1p

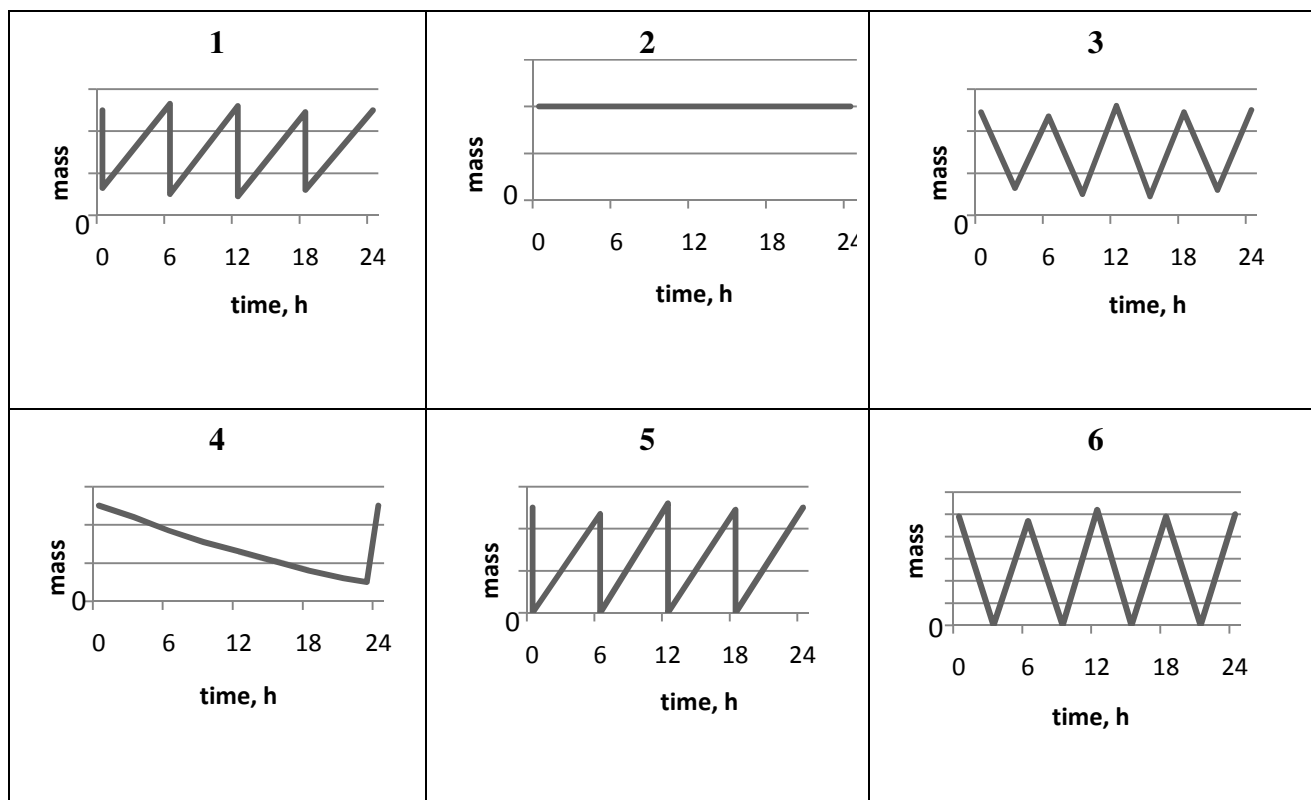
X contains only primary and secondary carbon atoms. **X0** and **X3** contain common functional group.

1e. Draw the structural formulae of **X**, **X1**, and **X3**.

 <p>X 4p</p> <p>If incorrect, but saturated 0.5p</p> <p>no branch 0.5p</p> <p>alcohol and ether 0.5p</p>	 <p>X1 4p</p> <p>If incorrect, but molecular formula 0.5p</p> <p>carboxyl 1p</p>	 <p>X3 4p</p> <p>If incorrect, but molecular formula 0.5p</p> <p>aldehyde 1p</p>
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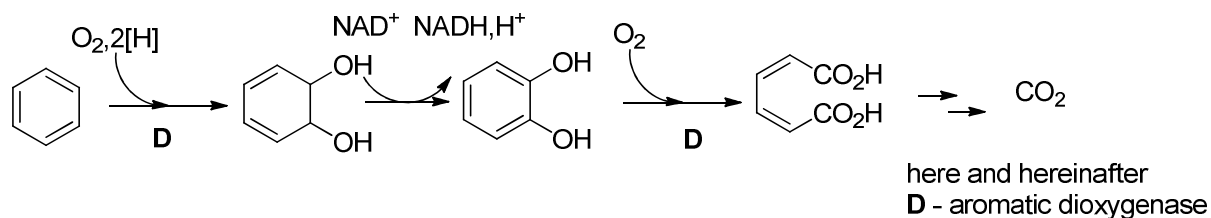
In a medical study, personnel permanently exposed to **X**-based solvents without proper protection was found to have a stationary concentration of **X** in blood.

2. **X1** is excreted with urine. Choose the graph of **X1** daily mass content in the body of a volunteer participated in this experiment. Write down the number of the correct graph.

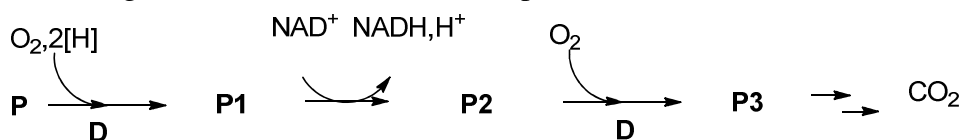


Number of graph: **1 (5 pts), if 5 (2.5 pts)**

The use of different bacteria is also considered as a promising way for the removal of hydrocarbon (even aromatic) contaminants from sea water and soil. Under aerobic conditions, benzene undergoes biodegradation as follows (first three steps are balanced):



Under the same conditions, a monocyclic aromatic hydrocarbon **P** (91.25% of carbon by mass) undergoes the following transformation (first three steps are balanced):



P3 gives a positive iodoform test. A 100 mg sample of **P3** requires 6.41 mL of 0.100 M KOH solution for complete neutralization.

3. Derive the structures of **P–P3**. Give the most stable tautomer of **P3**.

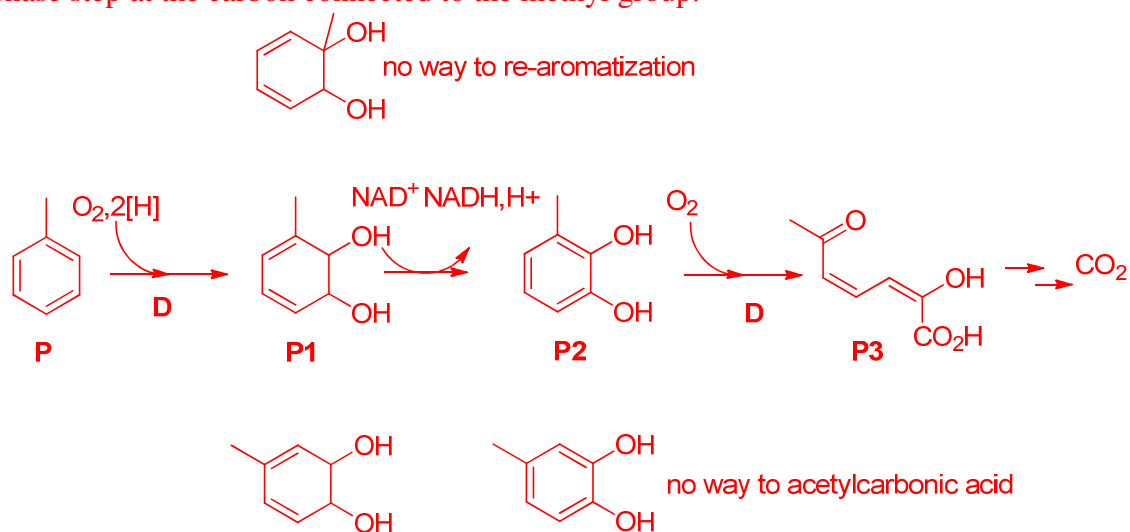
Your work

Dioxygenase incorporates two oxygen atoms in vicinal positions of the substrate, which can be followed by chemical bonds reorganization. The empirical formula of the hydrocarbon **P** is C_7H_8 ($C : H = \frac{91.25}{12.01} : \frac{100 - 91.25}{1.008} = 7 : 8$). Thus, it is toluene. **1p**

The molar mass of **P3** equivalent containing acidic group(s) is $\frac{100}{6.41 \cdot 0.100} = 156 \text{ g/mol}$. **1p**

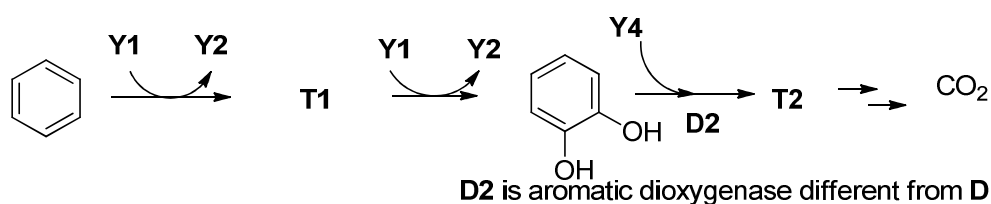
Two dioxygenase steps suggest the composition of $C_7H_8O_4$. **1p**

P3 must be a monocarboxylic acid if it still contains seven carbon atoms. Fragments containing a CH_3CO- group (or a $CH_3CH(OH)-$ group further transforming into CH_3CO- one) (**1p**) are involved into the iodoform reaction. This suggests splitting of the benzene moiety during the second oxygenase step at the carbon connected to the methyl group.

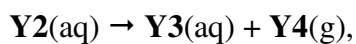


<p>P</p> <p>1p</p>	<p>P1</p> <p>3p (1p for isomer)</p>	<p>P2</p> <p>3p (1p for isomer)</p>	<p>P3</p> <p>2p (1 p for tautomer)</p>
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Microorganisms *Alicyclophilus* are capable of biodegradation of aromatic hydrocarbons even in soil. The process requires a suitable electron acceptor such as inorganic anion **Y1** (first three steps are balanced).


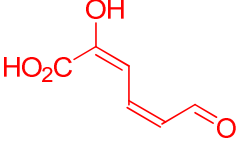


The intermediate anion **Y2** is enzymatically decomposed according to the balanced reaction equation:



wherein each of **Y3** and **Y4** is composed of atoms of only one element. **T2** does not contain two identical oxygen-containing functional groups. **T2** gives a precipitate when treated with the ammonia solution of Ag_2O , whereas **Y3** does not.

4. Deduce and give formulas of **Y1-Y4**. Draw the structures of **T1-T2**. Give the most stable tautomer of **T2**.

<p>Y1 ClO_3^- 1.5p (wrong central atom 0.5p)</p>	<p>Y2 ClO_2^- 1.5p (wrong central atom 0.5p)</p>	<p>Y3 Cl^- 1.5p (wrong element 0.5p)</p>
<p>Y4 O_2 1.5p</p>	<p>T1  2p</p>	<p>T2  5p If incorrect, but molecular formula 1p aldehyde 1p no identical 0.5p (5p for hemiacetal, 3p for other tautomers)</p>

The Periodic Table of the Elements

1 H Hydrogen 1.00794																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012182											5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050											13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium 52.147	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)