

**Face your challenge,
Be smart**



**THEORETICAL
EXAMINATION**

**JULY 20, 2013
MOSCOW, RUSSIA**

General Directions

- Write down your name and code number on each page.
- You have 5 h 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 **38** 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.

Physical Constants, Units, Formulas and Equations

Avogadro's constant	$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$
Universal gas constant	$R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Speed of light	$c = 2.9979 \times 10^8 \text{ m} \cdot \text{s}^{-1}$
Planck's constant	$h = 6.6261 \times 10^{-34} \text{ J} \cdot \text{s}$
Faraday constant	$F = 96485 \text{ C} \cdot \text{mol}^{-1}$
Gravity of Earth	$g = 9.81 \text{ m} \cdot \text{s}^{-2}$
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

1 nanometer (nm) = 10^{-9} m

1 Da = 1 atomic mass unit

1 electron volt (eV) = $1.6022 \cdot 10^{-19} \text{ J} = 96485 \text{ J} \cdot \text{mol}^{-1}$

Energy of a light quantum with wavelength λ	$E = hc / \lambda$
Energy of one mole of photons	$E_m = hcN_A / \lambda$
Gibbs energy	$G = H - TS$
Relation between equilibrium constant and standard Gibbs energy	$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$
Relation between standard Gibbs energy and standard emf	$\Delta G^\circ = -nFE^\circ$
Clapeyron equation for phase transitions	$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$
Integrated Clausius-Clapeyron equation for phase transitions involving vapor	$\ln \frac{p_2}{p_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$
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>
Volume of a sphere of radius R	$V = \frac{4}{3} \pi R^3$
Surface area of a sphere of radius R	$S = 4\pi R^2$
Hydrostatic pressure	$p = \rho gh$

Problem 1. Clathrate gun (8 points)

Question	1	2	3	4	5	6	Total
Marks	2	1	3	5	6	2	19

The only gun that is able to kill all living people in one shot

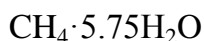
On the floors of oceans and seas there are vast reserves of methane in the form of clathrate compounds called methane hydrates. These reserves can be mined and serve as a source of energy or of raw materials for organic synthesis. However, scientists are seriously worried about the possibility of spontaneous decomposition of hydrates caused by the raising ocean temperature. It is believed that if a sufficient amount of methane is released into the atmosphere, then the oceans will warm up quicker due to the greenhouse effect, further accelerating the decomposition of clathrates. Due to the explosion of the resulting methane-air mixture and/or changes in the composition of the atmosphere, all living creatures may become extinct. This apocalyptic scenario is called a clathrate gun.



Upon decomposition of 1.00 g of a methane hydrate with a fixed composition at 25 °C and atmospheric (101.3 kPa) pressure, 205 mL of methane is released.

1. Determine n (not necessarily integer) in the formula of methane hydrate, $\text{CH}_4 \cdot n\text{H}_2\text{O}$.

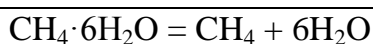
By the ideal gas law, the amount of methane $\nu = \frac{pV}{RT} = \frac{101300 \cdot 205}{10^6 \cdot 8.314 \cdot 298.15} = 8.38 \cdot 10^{-3} \text{ mol}$, then the amount of water in hydrate $\nu = \frac{1 - 8.38 \cdot 10^{-3} \cdot 16}{18} = 4.81 \cdot 10^{-2} \text{ mol}$. The ratio of amounts of water and methane is $4.81 \cdot 10^{-2} / 8.38 \cdot 10^{-3} \approx 5.75$, i.e. the composition of methane hydrate is $\text{CH}_4 \cdot 5.75\text{H}_2\text{O}$ or $x\text{CH}_4 \cdot 5.75x\text{H}_2\text{O}$, where x is any natural number.



2p

Real methane hydrate has a non-stoichiometric composition close to $\text{CH}_4 \cdot 6\text{H}_2\text{O}$. At atmospheric pressure, methane hydrate decomposes at -81°C . However, under high pressures (e.g. on the ocean floor) it is stable at much higher temperatures. Decomposition of methane hydrate produces gaseous methane and solid or liquid water depending on temperature.

2. Write down the equation of decomposition of 1 mole of $\text{CH}_4 \cdot 6\text{H}_2\text{O}$ producing solid water (ice) $\text{H}_2\text{O}(\text{s})$.



1p

The enthalpy of this process equals $17.47 \text{ kJ}\cdot\text{mol}^{-1}$. Assume that the enthalpies do not depend on temperature and pressure, the volume change upon decomposition of hydrate is equal to the volume of released methane, and methane is an ideal gas.

3. At what external pressure does decomposition of methane hydrate into methane and ice take place at -5°C ?

Decomposition of methane hydrate can be viewed as a phase transition, which obeys Clausius-Clapeyron equation: $\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$. $\Delta V = \frac{RT}{p} + \frac{6M(H_2O_{(s)})}{\rho(H_2O_{(s)})} - \frac{M(CH_4 \cdot 6H_2O)}{\rho(CH_4 \cdot 6H_2O)}$. The difference between two last terms is negligibly small in comparison with the first term. Thus, we can write the following equation: $\frac{1}{p} dp = \frac{\Delta H}{RT^2} dT$. The dependence of the pressure from temperature is thus given by $p = p_0 \exp\left(\frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)$. Substituting $T_0 = 192.15 \text{ K}$, $T = 268.15 \text{ K}$, $p_0 = 1 \text{ atm}$, we find that $p = 22 \text{ atm}$ or 2.2 MPa .

$$p = 2.2 \text{ MPa}$$

3p

4. What is the minimum possible depth of pure liquid water at which methane hydrates can be stable?

To answer this question, you should first deduce at which minimum temperature methane hydrate can coexist with liquid water. Choose the correct answer.

☒ 272.9 K ☐ 273.15 K ☐ 273.4 K 2p

At the minimum possible depth, the sum of pressures of atmosphere and water column is equal to the dissociation pressure of methane hydrate. The temperature should be as low as possible, but it cannot be less than the melting point of water at the corresponding pressure. Thus, the temperature and pressure should correspond to the point of coexistence of water, ice, methane hydrate and gaseous methane. Since the melting point of water decreases with increasing pressure, the correct answer is 272.9 K .

Substituting $T = 272.9 \text{ K}$ into the equation from the previous question, we obtain $p = 2.58 \text{ MPa}$. The height of the water column can be calculated using a formula

$$h = \frac{P - P_{atm}}{g\rho(H_2O)}, \text{ where } g = 9.8 \text{ m}\cdot\text{s}^{-2}. \text{ From here } h \approx 250 \text{ m}.$$

$$h = 250 \text{ m}$$

3p (1p for the correct pressure, 1p for a correct formula for h , 1p for a correct answer)

Large methane hydrate stocks on the floor of Baikal lake, the largest freshwater lake in Russia and in the world, have been discovered in July 2009 by the crew of a deep-submergence vehicle «Mir-2». During the ascent from the depth of 1400 m methane hydrate samples started to decompose at the depth of 372 m .

5. Determine the temperature in Baikal lake at the depth of 372 m. The enthalpy of fusion of ice is $6.01 \text{ kJ}\cdot\text{mol}^{-1}$.

From the Hess's law, the enthalpy of the process $\text{CH}_4\cdot 6\text{H}_2\text{O} = \text{CH}_4 + 6\text{H}_2\text{O(l)}$ is equal to $17.47 + 6\cdot 6.01 = 53.53 \text{ kJ}\cdot\text{mol}^{-1}$.

2p

From the previous question we know that at $T_0 = 272.9 \text{ K}$ and $p_0 = 2.58 \text{ MPa}$ there is an equilibrium between methane, water and methane hydrate.

2p for the idea of starting from the triple point

Since that we can calculate the temperature of decomposition T at pressure $p = 9.8\cdot 1000\cdot 372 + 101000 = 3746600 \text{ Pa}$ using the equation $\frac{1}{T} = \frac{1}{T_0} + \frac{R}{\Delta H} \ln \frac{p_0}{p}$. We obtain

$T = 277.3 \text{ K}$, or about 4°C (which is in agreement with the measured temperature of Baikal water at such depth).

2p

$$T = 277.3 \text{ K}$$

Total 6p

Total amount of methane in hydrates on Earth is no less than $5\cdot 10^{11}$ tons.

6. By how many degrees would the Earth atmosphere heat up, if such amount of methane is burned by reacting with atmospheric oxygen? The enthalpy of combustion of methane is $-889 \text{ kJ}\cdot\text{mol}^{-1}$, the total heat capacity of the Earth's atmosphere is about $4\cdot 10^{21} \text{ J}\cdot\text{K}^{-1}$.

Upon burning of methane, $\frac{500\cdot 10^9\cdot 10^3}{0.016}\cdot 889\cdot 10^3 = 2.78\cdot 10^{22} \text{ J}$ of heat is released. Earth atmosphere will heat up by $2.78\cdot 10^{22} / 4\cdot 10^{21} \approx 7 \text{ K}$.

$$\Delta T = 7 \text{ K}.$$

2p

Problem 2. Break down photosynthesis – the Hill reaction (7 points)

Question	1	2	3			4		5	6	Total
			a	b	c	a	b			
Points	1	2	2	2	3.5	1	2	3	2.5	19

In the history of photosynthesis research, there were some breakthrough experiments which added much to our knowledge of this very complex process. One of such experiments was performed in 1930s by an English biochemist Robert Hill. In this problem, we consider some of his data together with the data of more recent experiments.

1. In plants, under illumination, carbon dioxide is reduced to carbohydrates (denote as {CH₂O}) and oxygen is produced. Write the overall equation of photosynthesis in plants.

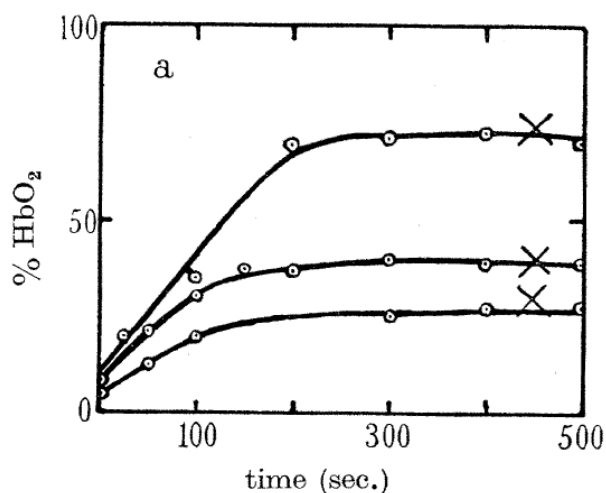
$\text{H}_2\text{O} + \text{CO}_2 = \{\text{CH}_2\text{O}\} + \text{O}_2$	1 p
(0 p for the unbalanced reaction)	
Total:	1 p

Much of the photosynthesis takes place in chloroplasts – organelles found in plant cells and containing chlorophyll – the light-absorbing substance. Hill isolated chloroplasts from the cells by grinding the leaves in the sucrose solutions. The cell-free chloroplasts did not produce oxygen under illumination even in the presence of CO₂. However, upon adding potassium ferrioxalate K₃[Fe(C₂O₄)₃] (with the excess of potassium oxalate) to the chloroplast suspension Hill observed oxygen liberation under illumination even without CO₂.

2. Hill's experiment enabled to determine the source of oxygen during photosynthesis. Write the formulas of the oxidant and the reducing agent in the photosynthesis inside the plant cells and in the cell-free chloroplasts (the Hill reaction).

Natural photosynthesis		Hill reaction	
Oxidant	Reducing agent	Oxidant	Reducing agent
CO ₂ (0.5 p)	H ₂ O (0.5 p)	K ₃ [Fe(C ₂ O ₄) ₃] (0.5 p)	H ₂ O (0.5 p)
			Total: 2 p

Hill measured the amount of evolved oxygen using muscle haemoglobin (Hill denoted it Hb) which binds all molecular oxygen in a 1:1 ratio to form HbO₂. The initial concentration of Hb was 0.6·10⁻⁴ M. Kinetic curves corresponding to different ferrioxalate concentrations are shown in the figure (the upper curve corresponds to 2.0·10⁻⁴ M).



The fraction of bound haemoglobin HbO₂ (with respect to the initial amount of Hb) as function of time.

Crosses denote the end of reaction

(Figure 2a from the original Hill's paper: *R. Hill. Oxygen produced by isolated chloroplasts. – Proc. R. Soc. B, 1939, v. 127, pp. 192-210*)

3. a. From the figure, estimate the Fe / O₂ mole ratio at the end of reaction. Do not take into account the iron from Hb.
- b. Write the equation of Hill reaction assuming that it proceeds with a high yield.
- c. Using the table of standard electrode potentials, determine the Gibbs energy of the Hill reaction at $T = 298$ K, oxygen pressure 1 mm Hg, pH = 8 and standard concentrations of other species. Is this reaction spontaneous at such conditions?

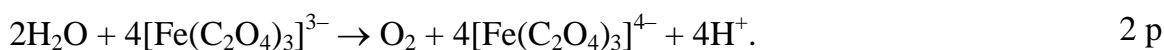
Half-reaction	E° , V
$\text{O}_2 + 4\text{H}^+ + 4e \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{CO}_2 + 4\text{H}^+ + 8e \rightarrow \{\text{CH}_2\text{O}\} + \text{H}_2\text{O}$	-0.01
$\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$	+0.77
$\text{Fe}^{3+} + 3e \rightarrow \text{Fe}^0$	-0.04
$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} + e \rightarrow [\text{Fe}(\text{C}_2\text{O}_4)_3]^{4-}$	+0.05
$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{4-} + 2e \rightarrow \text{Fe} + 3\text{C}_2\text{O}_4^{2-}$	-0.59

a. Calculations

The upper curve in the saturation limit gives ~ 75% of HbO₂

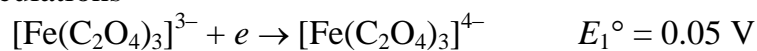
$$n(\text{Fe}) / n(\text{O}_2) = c(\text{Fe}) / c(\text{HbO}_2) = 2.0 \cdot 10^{-4} / (0.75 \cdot 0.6 \cdot 10^{-4}) = \mathbf{4.4 : 1} \quad 2 \text{ p}$$

b. Ratio ~ 4:1 shows that Fe(III) is reduced to Fe(II), which in the presence of excess oxalate exists as a complex:



(1 p if Fe is given as Fe^{3+} , without ligands)

c. Calculations



$$\text{emf: } E^\circ = E_1^\circ - E_2^\circ = -1.18 \text{ V}$$

(0 p if $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$ half-reaction is used)

1 p

$$\Delta G = \Delta G^\circ + RT \ln(p_{\text{O}_2} [\text{H}^+]^4) = -4 \cdot 96500 \cdot (-1.18) + 8.314 \cdot 298 \cdot \ln\left(\frac{1}{750} (10^{-8})^4\right) =$$

$$= 2.57 \cdot 10^5 \text{ J/mol} = 257 \text{ kJ/mol}$$

2 p

The reaction is

spontaneous

not spontaneous

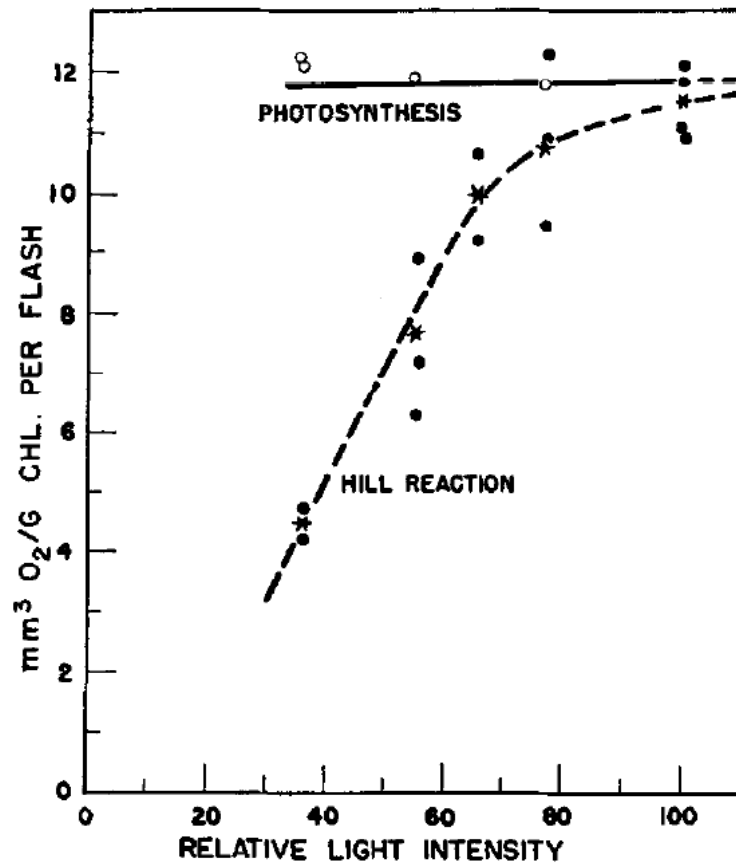
☐☒

0.5 p

The reaction is highly endoergic and, hence, not spontaneous. Light is necessary.

Now, the name “Hill reaction” denotes photochemical oxidation of water by any oxidant other than carbon dioxide which is sensitized by plant cells or isolated chloroplasts.

In another experiment (1952), quinone in an acid solution was used as an oxidant in the Hill reaction initiated by light flashes in the *Chlorella* algae. Experimental data are shown in the figure. The volume of oxygen (in mm^3 , at temperature 10°C and pressure 740 mmHg) per one gram of chlorophyll per one flash was determined as a function of light intensity for natural photosynthesis and for isolated chloroplasts. It was found that the maximum yield of oxygen is the same for natural photosynthesis and the Hill reaction.



(Figure 1 from: H. Ehrmantraut, E. Rabinovitch. *Kinetics of Hill reaction*. – *Archives of Biochemistry and Biophysics*, 1952, v. 38, pp. 67-84)

- 4 a. Determine the reaction order of a photochemical Hill reaction with respect to light intensity at low and high intensity. For each case choose one of three values:

Reaction order:

Low intensity

0 ☐ 1 ☒ 2 ☐

High intensity

0 ☒ 1 ☐ 2 ☐

(0.5 p – for each correct choice, total – 1p)

- b. How many chlorophyll molecules participate in the formation of one oxygen molecule in the saturation limit of the Hill reaction? (The molecular mass of chlorophyll is about 900 Da).

Calculations

$$n(\text{Chl}) / n(\text{O}_2) = 1/900 / [(12 \cdot 10^{-6} \cdot (740/760) \cdot 101.3) / (8.314 \cdot 283)] = 2200 \quad 2 \text{ p}$$

 (1 p if similar ratio is obtained with other gas conditions, for example 1 atm or room temperature, 0.5 p for the correct amount of Chl, 1 p for the correct amount of oxygen)

The quantum requirement of the light redox reactions is defined as the average number of light photons (not necessarily integer) needed for the transfer of one electron from a reducing agent to an oxidant. The isolated chloroplasts were irradiated during 2 hours by a monochromatic light (wavelength 672 nm) with the energy input 0.503 mJ/s, and the total volume of oxygen formed was 47.6 mm³ (under the same conditions as in question 4).

5. Calculate the quantum requirement for the Hill reaction.

Calculations	
Total energy absorbed: $E = 0.503 \cdot 10^{-3} \cdot 3600 \cdot 2 = 3.62 \text{ J}$	
Energy of one mole of photons: $E_m = hcN_A / \lambda =$ $= 6.63 \cdot 10^{-34} \cdot 3.00 \cdot 10^8 \cdot 6.02 \cdot 10^{23} / (672 \cdot 10^{-9}) = 1.78 \cdot 10^5 \text{ J/mol}$	
$n(\text{phot}) = E / E_m = 2.03 \cdot 10^{-5} \text{ mol}$	1 p
$n(\text{O}_2) = PV / RT = (740/760) \cdot 101.3 \cdot 47.6 \cdot 10^{-6} / (8.314 \cdot 283) =$ $2.00 \cdot 10^{-6} \text{ mol.}$	1 p
Formation of one O ₂ molecules requires the transfer of 4 electrons: $n(e) = 8.00 \cdot 10^{-6} \text{ mol}$	
Quantum requirement: $n(\text{phot}) / n(e) = 2.5.$	1 p
Total:	3 p

6. Try to make conclusions from the above experiments (questions 2-5). For each of the following statements **choose either “Yes” or “No”**.

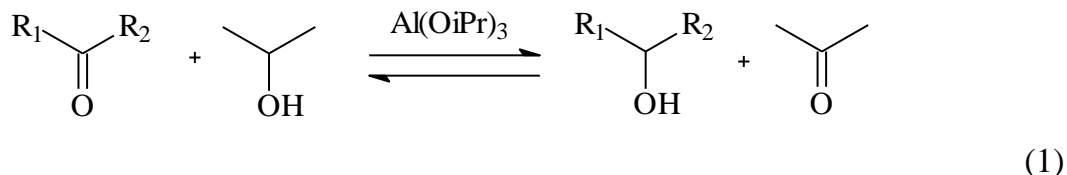
	Yes	No
In natural photosynthesis, water oxidation and CO ₂ reduction are separated in space.	✓	
In chloroplasts, O ₂ is produced from CO ₂ .		✓
Oxidation of water in chloroplasts requires light illumination.	✓	
Most of chlorophylls in chloroplasts participate directly in the photochemical O ₂ production.		✓
In isolated chloroplasts, every absorbed photon causes transfer of one electron.		✓

(0.5 p for each correct answer, total – 2.5 p)

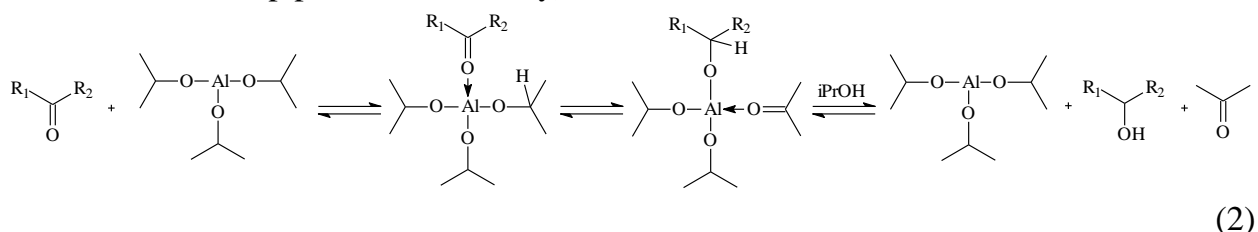
Problem 3. Meerwein-Schmidt-Ponndorf-Verley reaction (8 points)

Question	1a	1b	2	3	4	Total
Marks	7	3	8.5	6	8	32.5

Meerwein-Schmidt-Ponndorf-Verley (MSPV) reaction is a useful tool for reduction of carbonyl compounds to alcohols. The reaction is the reduction of carbonyl compounds by low molecular weight alcohols in the presence of alkoxides of aluminium or other metals:



The mechanism of the reaction includes coordination of carbonyl compound by aluminium alkoxide, hydride transfer in the inner sphere of the complex and subsequent transalkoxylation. It can be schematically represented as follows (transalkoxylation is shown as a one-step process for brevity):



The reaction is reversible and shifting the equilibrium to the desired product requires some excess of the reductant. In some cases (e.g. in the case of reduction of aromatic aldehydes and ketones) the equilibrium constant is so large that the reverse reaction can be neglected.

The table below contains standard entropies and standard enthalpies of formation of liquid substances at 298 K. The boiling points of the substances at 1 bar are also given.

Substance	$\Delta_f H^\circ_{298}$, kJ/mol	S°_{298} , J/(mol·K)	t_{vap} , °C
Acetone	−248.4	200.4	56
Isopropanol	−318.1	180.6	82
Cyclohexanone	−271.2	229.0	156
Cyclohexanol	−348.2	203.4	161

1a. Calculate the minimum isopropanol:cyclohexanone mass ratio which is required to reach a 99% yield of reaction at 298 K. Assume that a) the reaction mixture eventually gets at equilibrium and b) no products are initially present.

The reaction enthalpy is:

$$\begin{aligned} \Delta_r H^\circ_{298} &= \Delta_f H^\circ_{298}(\text{C}_3\text{H}_6\text{O}) + \Delta_f H^\circ_{298}(\text{C}_6\text{H}_{12}\text{O}) - \Delta_f H^\circ_{298}(\text{C}_3\text{H}_8\text{O}) - \Delta_f H^\circ_{298}(\text{C}_6\text{H}_{10}\text{O}) \\ &= (-248.4) + (-348.2) - (-318.1) - (-271.2) = -7.3 \text{ kJ/mol}, \end{aligned}$$

<p>the reaction entropy is:</p> $\Delta_r S^\circ_{298} = S^\circ_{298}(\text{C}_3\text{H}_6\text{O}) + S^\circ_{298}(\text{C}_6\text{H}_{12}\text{O}) - S^\circ_{298}(\text{C}_3\text{H}_8\text{O}) - S^\circ_{298}(\text{C}_6\text{H}_{10}\text{O}) =$ $= 200.4 + 203.4 - 180.6 - 229.0 = -5.8 \text{ J}/(\text{mol}\cdot\text{K})$ <p>and the reaction Gibbs energy is:</p> $\Delta_r G^\circ_{298} = \Delta_r H^\circ_{298} - T \Delta_r S^\circ_{298} = -5.6 \text{ kJ/mol}$ <p>The equilibrium constant equals</p> $K = \exp(-\Delta_r G^\circ_{298}/RT) = 9.6$ <p>The expression for equilibrium constant is as follows:</p> $K = \frac{x(\text{C}_3\text{H}_6\text{O})x(\text{C}_6\text{H}_{12}\text{O})}{x(\text{C}_3\text{H}_8\text{O})x(\text{C}_6\text{H}_{10}\text{O})} = \frac{\nu(\text{C}_3\text{H}_6\text{O})\nu(\text{C}_6\text{H}_{12}\text{O})}{\nu(\text{C}_3\text{H}_8\text{O})\nu(\text{C}_6\text{H}_{10}\text{O})},$ <p>where x is the molar fraction of a substance in the equilibrium mixture, ν is an amount of a substance in the mixture. Denote the initial amount of cyclohexanone as y. 99% of cyclohexanone must react. Hence, in equilibrium the amounts of $\text{C}_6\text{H}_{10}\text{O}$ and $\text{C}_6\text{H}_{12}\text{O}$ are $0.01y$ and $0.99y$, respectively. Denote the initial amount of isopropanol z. Due to the reaction stoichiometry the amounts of $\text{C}_3\text{H}_6\text{O}$ and $\text{C}_3\text{H}_8\text{O}$ in equilibrium are $0.99y$ and $(z - 0.99y)$, respectively. Substituting these amount into the expression for equilibrium constant one gets:</p> $K = \frac{0.99y \cdot 0.99y}{0.01y \cdot (z - 0.99y)} = \frac{98.01}{\left(\frac{z}{y} - 0.99\right)} = 9.6$ <p>The solution is:</p> $\frac{z}{y} = 11.2$ <p>Hence, the mole ratio $\nu(\text{C}_3\text{H}_8\text{O}) : \nu(\text{C}_6\text{H}_{10}\text{O})$ is 11.2. The mass ratio can be calculated as follows:</p> $m(\text{C}_3\text{H}_8\text{O}) : m(\text{C}_6\text{H}_{10}\text{O}) = \nu(\text{C}_3\text{H}_8\text{O}) \cdot M(\text{C}_3\text{H}_8\text{O}) / (\nu(\text{C}_6\text{H}_{10}\text{O}) \cdot M(\text{C}_6\text{H}_{10}\text{O})) =$ $= 11.2 \cdot 60 / 98 = 6.9$ <p>Answer:</p> $m(\text{C}_3\text{H}_8\text{O}) : m(\text{C}_6\text{H}_{10}\text{O}) = 6.9$	<p>2p</p> <p>1p</p> <p>3p</p> <p>1p</p> <p>Total: 7p</p>
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1b. Choose the appropriate way(s) to increase the cyclohexanol yield.

Warning: erroneously ticked boxes will result in penalty points

Increase the temperature up to 50°C using a reflux	
Increase the temperature up to 60°C, evaporating (distilling) the acetone	V
Add some ethanol to the reaction mixture	V

Add some ethanal to the reaction mixture	
Correct answer	1.5p
Penalty for every wrongly ticked box	-1.5p
Total:	3p

2. Often the rate-limiting step in the MSPV reaction is the hydride transfer or the alcoholysis of the alkoxide after hydride transfer. For these two cases, using the above mechanism (2), derive an expression for the rate of reaction as a function of current concentrations of a carbonyl compound, isopropanol and a catalyst. In both cases determine the rate orders in the reactants and the catalyst. Assume that all reaction steps before the limiting step are fast and reversible. Use equilibrium approximation, if necessary. For brevity use the following notation: **A** for carbonyl compound, **B** for isopropanol, **C** for catalyst. Denote intermediates as you wish.

Rate-limiting step is the hydride transfer

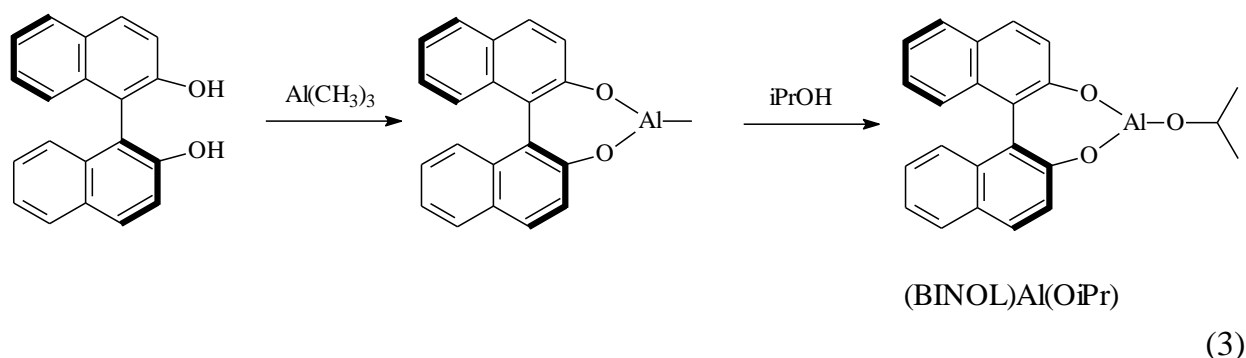
Kinetic scheme:	
$A + C \rightleftharpoons A \cdot C$ fast, K	
$A \cdot C \rightarrow A' \cdot C'$ rate-determining, k	
Expression for equilibrium constant:	
$K = \frac{[A \cdot C]}{[A][C]}$	0.5p
The rate of the RDS is:	0.5p
$r = k[A \cdot C]$	
Final expression:	
$r = k[A \cdot C] = kK[A][C]$	1.5p
Answer:	
Order in carbonyl compound: 1	0.5p
Order in isopropanol: 0	0.5p
Order in the catalyst: 1	0.5p
Total:	4p

Rate-limiting step is the transalkoxylation of the alcoholate by isopropanol

Kinetic scheme:	
$A + C \rightleftharpoons A \cdot C$ fast, K_1	
$A \cdot C \rightleftharpoons A' \cdot C'$ fast, K_2	
$A' \cdot C' + B \rightarrow P$ rate-determining, k	
Expression for equilibrium constants:	

$K_1 = \frac{[A \cdot C]}{[A][C]}$	0.5p
$K_2 = \frac{[A' \cdot C']}{[A \cdot C]}$	0.5p
The rate of reaction is: $r = k[A' \cdot C'][B]$	0.5p
Final expression: $r = k[A' \cdot C'][B] = kK_1K_2[A][B][C]$	1.5p
Answer: Order in carbonyl compound: 1 Order in isopropanol: 1 Order in the catalyst: 1	0.5p 0.5p 0.5p
Total:	4.5p

MSPV reaction can be used to obtain chiral alcohols, if the chiral catalyst is employed. For instance, Campbell et al. used the catalyst based on the chiral 2,2'-dihydroxy-1,1'-binaphthyl (BINOL), which is synthesized *in situ* from binaphtol and trimethylaluminium:



The chirality of BINOL is due to the sterically hindered rotation around the C-C bond. Though perfectly stable at room temperature, BINOL may racemize when heated.

3. Which of the phenols below can form stable (at room temperature) enantiomers so that they can be used in the same fashion to produce a chiral catalyst?

Warning: erroneously ticked boxes will result in penalty points

Substance	Can be used	Substance	Can be used
	v		

	V		V
Each correct choice Penalty for every wrongly ticked box			2p -2p Total: 6p

4. *Enantiomeric excess*, *ee*, is used to characterize the enantiomeric purity of the substance. This quantity equals ratio of the difference of concentrations of enantiomers *R* and *S* to their sum:

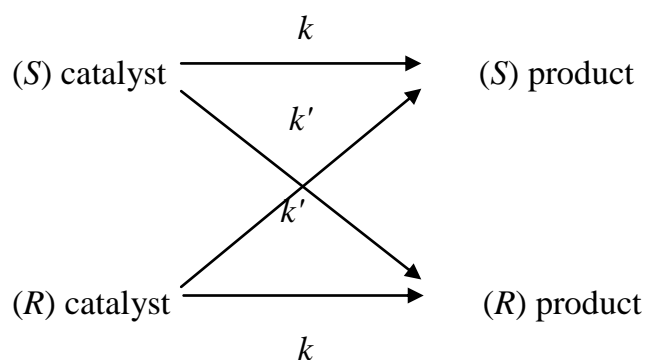
$$ee = \frac{[R] - [S]}{[R] + [S]}$$

Enantiomeric excess of the pure *R* isomer is unity, *ee* of the racemic mixture is zero.

When using the enantiomerically pure (BINOL)Al(OiPr) as a catalyst for reduction of α -bromoacetophenone, the *ee* of the product equals 81%. What is the *ee* of the product if the catalyst *ee* equals 50%? Provide your calculation with an illustration or derivation of the final formula.

Solution 1

The total kinetic scheme is:



4p

According to the scheme, the $R:S$ ratio is

$$\frac{[(R) - \text{product}]}{[(S) - \text{product}]} = \frac{k[(R) - \text{catalyst}] + k'[(S) - \text{catalyst}]}{k[(S) - \text{catalyst}] + k'[(R) - \text{catalyst}]}$$

After inserting this expression into ee definition one gets:

$$\begin{aligned} ee_{\text{product}} &= \frac{[(R) - \text{product}] - [(S) - \text{product}]}{[(R) - \text{product}] + [(S) - \text{product}]} = \frac{\frac{[(R) - \text{product}]}{[(S) - \text{product}]} - 1}{\frac{[(R) - \text{product}]}{[(S) - \text{product}]} + 1} = \\ &= \frac{(k[(R) - \text{catalyst}] + k'[(S) - \text{catalyst}]) - (k[(S) - \text{catalyst}] + k'[(R) - \text{catalyst}])}{(k[(R) - \text{catalyst}] + k'[(S) - \text{catalyst}]) + (k[(S) - \text{catalyst}] + k'[(R) - \text{catalyst}])} = \\ &= \frac{[(R) - \text{catalyst}] - [(S) - \text{catalyst}]}{[(R) - \text{catalyst}] + [(S) - \text{catalyst}]} \times \frac{k - k'}{k + k'} = ee_{\text{catalyst}} \frac{k - k'}{k + k'} \end{aligned}$$

That is, the ee of the product is proportional to the ee of the catalyst:

$$ee_{\text{product}} = ee_{\text{catalyst}} \frac{k - k'}{k + k'}$$

Applying numbers one gets:

$$ee_{\text{product}} = 0.50 \cdot 0.81 = 0.41$$

Solution 2

$$50\% ee \equiv \begin{cases} 50\% \text{ rac.} \\ 50\% R \end{cases}$$

$$R \text{ cat.} \rightarrow 90.5\% R + 9.5\% S$$

$$\text{rac. cat.} \rightarrow 50\% R + 50\% S$$

$$\% \text{ of } R \text{ prod.} = 0.5 \times 0.905 + 0.5 \times 0.5 = 0.7025$$

$$\% \text{ of } S \text{ prod.} = 0.5 \times 0.095 + 0.5 \times 0.5 = 0.2975$$

$$ee \text{ prod.} = 0.7025 - 0.2975 = 0.405$$

Answer: 41%

Total: 8p

4p

Problem 4. A simple inorganic experiment (6 points)

Question	1	2	3	Total
Marks	5	12	7	24

Compound **A** which contains metal **X** is a colorless crystalline solid and highly soluble in water. It is used as a reagent in analysis and gives in alkali media a binary compound **B** containing 6.9 % (mass) of oxygen. Under heating **A** decomposes with a mass loss of 36.5%.

1. Determine the metal **X** and compounds **A**, **B**.

(a) The general formula of a binary compound is XO_n . The molar ration of X and O should be $93.1/X : 6.9/16 = 1 : n$, where X is a molar mass of metal X and $n = 0.5; 1; 1.5; 2$ etc.	1 p
$n = 0.5$ gives $X = 107.9$ that is of silver. X – Ag, B – Ag_2O .	2 p
(b) The heating of silver salts generally results in reduction of the metal. According to the mass loss, the molar mass of A is 170 g/mol, that is silver nitrate: A – $AgNO_3$.	2 p
Total:	5 p

2. Upon adding some amount of sodium thiosulphate to the solution of **A** the color immediately becomes red, then changes to reddish-brown, and after some minutes a dark-brown precipitate **C** forms (reaction 1). The solution over it is colorless. Being heated on air at 600°C, **C** gives a grey powder **X** (reaction 2), so as 0.90 g of residue can be obtained from 1.10 g of **C**. A gas evolved by heating **C** in vacuum (reaction 3) can be absorbed by calcium hydroxide suspension (reaction 4). Being stored for a long time under saturated solution of barium perchlorate in 0.1 M $HClO_4$, the color of the precipitate becomes lighter, while the use of magnesium perchlorate doesn't give such effect. What is **C**? Write the equations of the reactions (1 – 4).

(a) The residue formed by heating on air is metallic silver, as the silver compounds readily decompose. Substance C contains silver and probably sulphur and oxygen as it evolves sulphur oxide by heating in vacuum.	1 p
1.10 g of C contains 0.90 g of Ag, so 1 mol of Ag is in 132 g of C . The mass of the elements other than Ag is $132 - 108 = 24$ g, which corresponds to $1/2S$ and $1/2O$. So, the empirical formula is $AgS_{1/2}O_{1/2}$ or Ag_2SO .	2 p
(b) The light brown color of the precipitate after the addition of barium salt means the formation of barium sulphate which is unsoluble in acids. The sulphate groups on the surface of the precipitate are substituted by perchlorate-ions from solution. So, basing on the formula Ag_2SO and assuming the presence	1 p

of sulphate, the formula $\text{Ag}_8\text{S}_3\text{SO}_4$ can be suggested.	3 p
(c) The equations are listed below:	
Equation 1:	
$16\text{AgNO}_3 + 6\text{Na}_2\text{S}_2\text{O}_3 + 6\text{H}_2\text{O} \rightarrow 2[\text{Ag}_8\text{S}_3]\text{SO}_4\downarrow + 4\text{Na}_2\text{SO}_4 + 4\text{NaNO}_3 + 12\text{HNO}_3$	2 p
Penalty for the unbalanced equation:	- 1 p
Equations 2 – 4:	
$[\text{Ag}_8\text{S}_3]\text{SO}_4 + 2\text{O}_2 \rightarrow 8\text{Ag} + 4\text{SO}_2$	1 p
$[\text{Ag}_8\text{S}_3]\text{SO}_4 \rightarrow 2\text{Ag}_2\text{S} + 4\text{Ag} + 2\text{SO}_2.$	1 p
$\text{SO}_2 + \text{Ca}(\text{OH})_2 = \text{CaSO}_3 + \text{H}_2\text{O}$ or	
$2\text{SO}_2 + \text{Ca}(\text{OH})_2 = \text{Ca}(\text{HSO}_3)_2$	1 p
Penalty for each of the unbalanced equations 2 – 4:	- 0.5 p
Total:	12 p

3. The compound **C** being stored under the mother liquor (containing an excess of **A**) its color changes to yellow due to the transformation into **D**. If barium ions are added to the suspension of **C** in the mother liquor, a mixture of **D** and of a white precipitate forms. Propose the formula of **D**, taking into account that it contains 77.5% (mass) of **X**. Give the equation of **D** formation.

We can assume that the sulphate-ions in C are substituted by nitrate-ions.	2 p
For a formula unit containing n silver atoms, molar mass is $108n / 0.775 = 139.35n$. For $n = 3$ we get $M = 418$ that corresponds to $418 - 108 \cdot 3 = 94$ that is $\text{NO}_3 + \text{S}$. So, D is $[\text{Ag}_3\text{S}]\text{NO}_3$.	3 p
Equation:	
$[\text{Ag}_8\text{S}_3]\text{SO}_4 + \text{AgNO}_3 + 2\text{NaNO}_3 \rightarrow 3[\text{Ag}_3\text{S}]\text{NO}_3 + \text{Na}_2\text{SO}_4$	2 p
Penalty for the unbalanced equation:	-1 p
Total:	7 p

Problem 5. Simple estimates of graphene properties (7 points)

Question	1a	1b	2	3	Total
Marks	2	2.5	4	5.5	14

Graphene is a two-dimensional, one atom thick carbon material (Fig.1 a). Many layers of graphene stack together to form graphite (Fig. 1b).

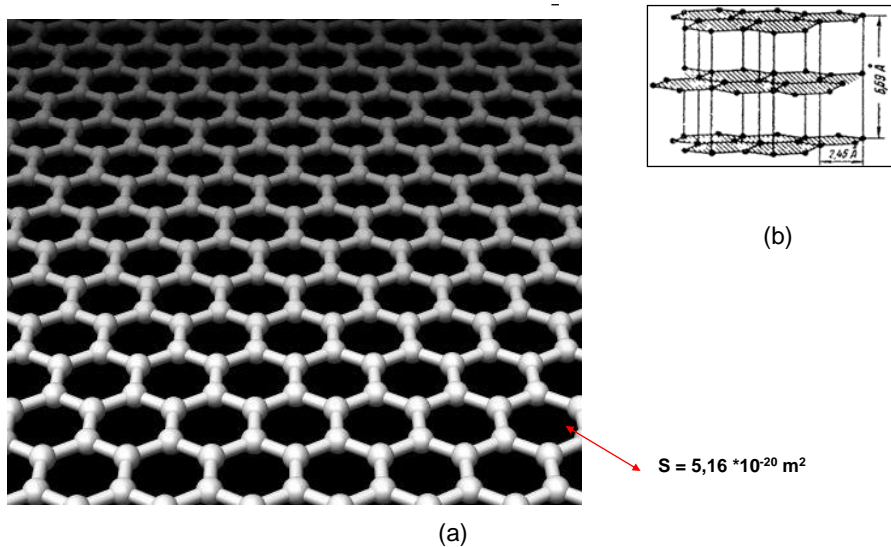


Fig. 1. (a) The structure of graphene. Spheres are carbon atoms. They are arranged in hexagons. The area of one carbon hexagon is $5.16 \cdot 10^{-20} \text{ m}^2$. (b) Crystal lattice of graphite. Three graphene layers are shown

Such atomic structure was long considered to be unstable. However, in 2004 Andrey Geim and Konstantin Novoselov have reported production of the first samples of this unusual material. This groundbreaking invention was awarded by Nobel prize in 2010.

Experimental studies of graphene are still restricted. Production of massive portions of the new substance still is a challenging synthetic problem. Many properties of graphene were *estimated*. Usually, there is not enough information for rigorous calculations, so we have to make assumptions and neglect unimportant factors. In this problem, you will estimate the adsorption properties of graphene.

1a. Estimate the specific surface of graphene open for adsorption in units m^2/g . Consider that graphene plane is separated from any other solid or liquid substance.

The area of a hexagon is $S = 5.16 \cdot 10^{-20} \text{ m}^2$.

Calculations:

The number of hexagons per gram of carbon, n , is

$$n = N_A \cdot \frac{3}{6} \cdot \frac{1}{12} = 6.022 \cdot 10^{23} \cdot 0.5 \cdot \frac{1}{12} = 2.51 \times 10^{22} \quad 1 \text{ pt}$$

The area per gram is

$$S_{total} = S \cdot n \cdot 2 = 5.16 \cdot 10^{-20} \cdot 2.51 \cdot 10^{22} \cdot 2 = 2590 \frac{\text{m}^2}{\text{g}} \quad 1 \text{ pt}$$

In case of two-dimensional material both sides of the layer are open for adsorption and have to be taken into consideration. The total area of hexagons should be multiplied by two!

But! NO penalty – for missing the coefficient 2.

Total: 2 pts

The single layer of nitrogen molecules adsorbed on the outer surface of graphite is shown in Fig. 2. Assume that the same arrangement of nitrogen molecules is formed on a graphene surface.

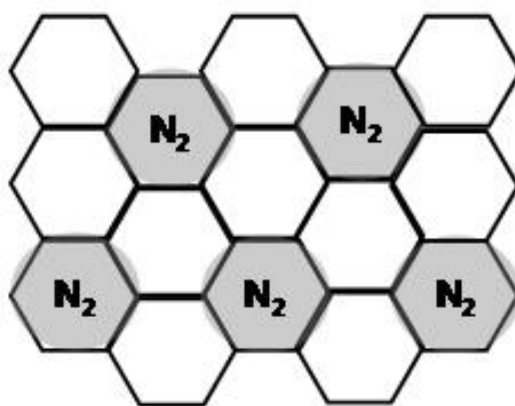


Fig. 2. Nitrogen molecules N_2 (grey circles) on the outer surface of graphite

1b. How many grams of nitrogen can be adsorbed on 1 gram of graphene assuming that the graphene layer is placed onto the surface of a solid support? Estimate the volume occupied by these nitrogen molecules after the complete desorption from 1 g of graphene (pressure 1 bar, temperature 298 K).

Graphene is on the solid support and only one side of the plane works. One molecule of nitrogen falls on 6 atoms of carbon (three hexagons) (see fig.2). 0.5 pt

Mass of nitrogen adsorbed per gram of graphene:

$$\frac{m_{N_2}}{m_C} = \frac{1 \times 28}{6 \times 12} = 0.39; \quad m_{N_2} = 0.39 \text{ g} \quad 1 \text{ pt}$$

The volume of nitrogen is

$$V_{N_2} = \frac{(m / M) RT}{p} = \frac{(0.39 / 28) \cdot 8.314 \cdot 298}{100} = 0.34 \text{ dm}^3. \quad 1 \text{ pt}$$

Total: 2.5 pts

Let us consider adsorption as a common chemical equilibrium



(A_{gas} are molecules A in the gaseous state, A_{ads} are the same molecules on the surface)

with the equilibrium constant K :

$$K = \frac{n_{A_{\text{ads}}} (\text{mol/m}^2)}{p_{A_{\text{gas}}} (\text{bar})}$$

(such assumption holds if a small number of molecules is adsorbed on the surface)

Adsorption properties of graphene can be estimated from the data for adsorption on a regular three-dimensional graphite. The enthalpy of adsorption (ΔH° of reaction (1)) of any molecule A on graphene is on average by 10% less negative compared to that on graphite. On graphite, the adsorbed molecule is bound more strongly due to the interaction with the lower graphene layers in the lattice (Fig. 1b) and hence the enthalpy of adsorption is more negative. The standard entropies of adsorption on graphene and graphite are assumed to be the same.

2. How many moles, n , of CCl_4 are adsorbed on 1 g of graphene at $p(\text{CCl}_4) = 10^{-4}$ bar if $2.0 \cdot 10^{-7}$ mol of CCl_4 are adsorbed on 1 m^2 of graphite at $p(\text{CCl}_4) = 6.6 \cdot 10^{-5}$ bar? Assume that graphene is placed onto the surface of a solid support and the interaction of CCl_4 with the support does not change the enthalpy of adsorption of CCl_4 on graphene. The temperature in both cases is 293 K. ΔH° of adsorption of CCl_4 on graphite is -35.1 kJ/mol.

The equilibrium constant for the adsorption on graphite surface is

$$K(\text{graphite}) = \frac{n(\text{CCl}_4 \text{ on graphite})}{p(\text{CCl}_4)} = \frac{2.0 \cdot 10^{-7}}{6.6 \cdot 10^{-5}} = 3.0 \cdot 10^{-3} \text{ mol/m}^2/\text{bar} \quad 1 \text{ pt}$$

The equilibrium constant need to be re-calculated for the graphene surface. There is a 10% difference in enthalpies of adsorption on graphene and on graphite, respectively, while the entropies are the same, so

$$\frac{K(\text{graphene})}{K(\text{graphite})} = e^{-(\Delta H_{\text{graphene}} - \Delta H_{\text{graphite}})/RT} = e^{-3510/(8.314 \cdot 293)} = 0.24 \quad 2 \text{ pts}$$

$$K(\text{graphene}) = 0.24 K(\text{graphite}) = 7.2 \cdot 10^{-4} \text{ mol/m}^2/\text{bar}$$

The adsorption of CCl_4 on graphene is calculated based on the equilibrium constant for graphene surface and the area of graphene surface in m^2/g . One side of the

graphene layer works in this case, $S_{\text{total}} = 2590/2 = 1295 \frac{\text{m}^2}{\text{g}}$

$$\begin{aligned} n \{ \text{mol/g} \} &= K(\text{graphene}) \{ \text{mol/m}^2/\text{bar} \} \cdot p(\text{CCl}_4) \{ \text{bar} \} \cdot S(\text{graphene}) \{ \text{m}^2/\text{g} \} = \\ &= (7.2 \cdot 10^{-4}) \cdot 10^{-4} \cdot 1295 = 9.3 \cdot 10^{-5} \text{ mol/g} \end{aligned} \quad 1 \text{ pt}$$

NO penalty if the area is multiplied by two.

The area of the graphene surface (the number!) determined in question 1a is used here. Possible mistake in calculating this area will be considered only once. No double punishment!

Total: 4 pts

The graphene films are expected to be sensitive gas detectors. If 10^9 particles of a gas are adsorbed on 1 cm^2 of a graphene surface this is enough to measure an electrical resistivity change of the graphene layer and to detect the presence of a gas in the environment.

3. Determine the minimal content of ethane, C_2H_6 , in the air (in mol.%) at atmospheric pressure ($T = 293\text{K}$) at which a graphene sensor will detect this gas. The known data for the adsorption of alkanes on graphite are shown in Fig 3. Assume that air doesn't affect the adsorption properties of ethane.

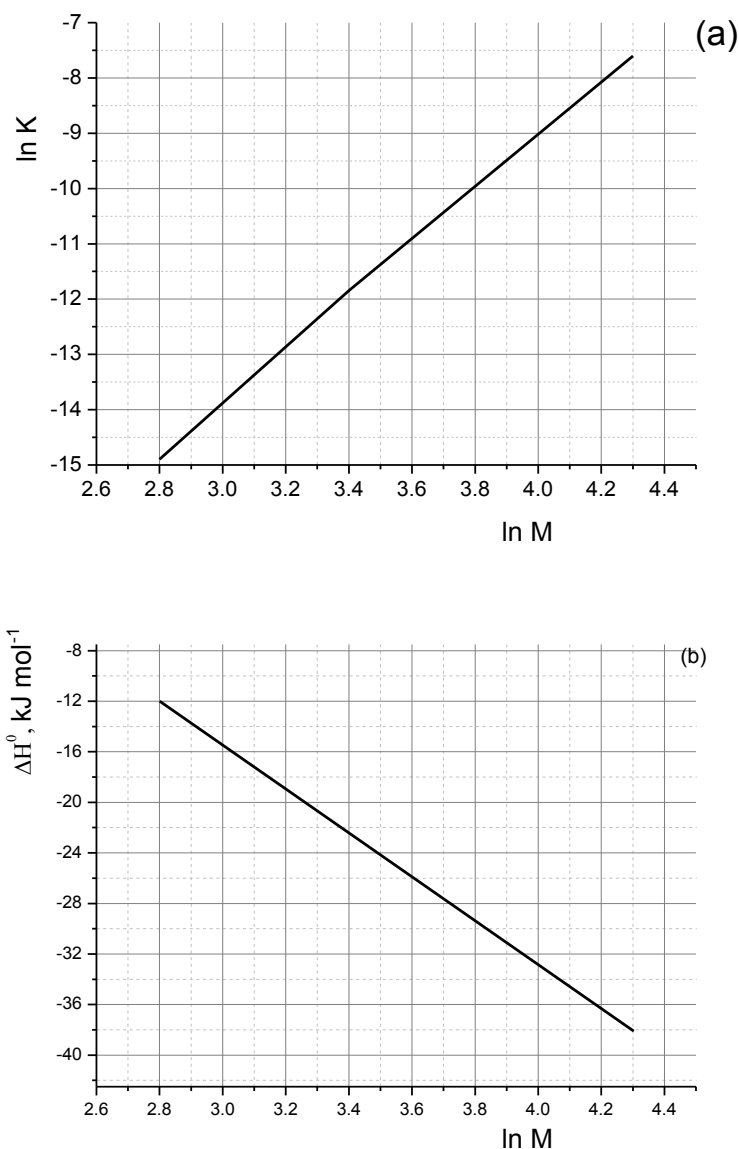


Fig. 3. Thermodynamic properties for adsorption of alkanes on a graphite surface. (a) $\ln K$ {mol/m²/bar} as a function of $\ln M$ (M – molecular mass of alkane in g/mol); (b) ΔH^0 of adsorption as a function of $\ln M$. Linear dependences are assumed in both cases

Your work:

The lower limit of detectable concentration of a substance on the graphene surface is

$$n\{\text{mol/m}^2\} = \left(\frac{10^9}{6.02 \cdot 10^{23}} \right) / 10^{-4} = 1.7 \times 10^{-11}$$

1 pt

The equilibrium constant and the enthalpy of adsorption of ethane on graphite are given in Fig.3:

$$M = 30; \ln M = 3.4; \ln K = -11.8, \Delta H^0 = -22.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$K_{\text{C}_2\text{H}_6} = 7.5 \cdot 10^{-6} \text{ mol/m}^2/\text{bar}$$

2 pts

This equilibrium constant needs to be re-calculated to the graphene surface (as in question 2).

$$K_{\text{C}_2\text{H}_6}(\text{graphene}) = K_{\text{C}_2\text{H}_6}(\text{graphite}) \times e^{-2250/(8.314 \cdot 293)} =$$

$$= 7.5 \cdot 10^{-6} \cdot 0.4 = 3.0 \cdot 10^{-6} \text{ mol/m}^2/\text{bar}$$

1 pt

The partial pressure of ethane is

$$p(\text{C}_2\text{H}_6) = \frac{n(\text{C}_2\text{H}_6 \text{ on graphene})}{K_{\text{C}_2\text{H}_6}(\text{graphene})} = \frac{1.7 \cdot 10^{-11}}{3.0 \cdot 10^{-6}} = 5.7 \cdot 10^{-6} \text{ bar}$$

1 pt

$$\text{Content of C}_2\text{H}_6: 5.7 \cdot 10^{-6} / 1.013 \cdot 100\% = 5.6 \cdot 10^{-4} \%$$

0.5 pts

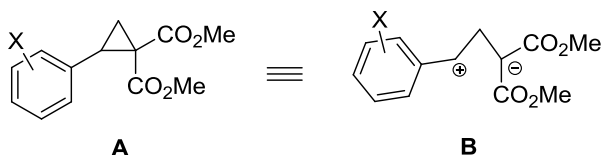
NO penalty if 1 bar is used here instead of atmospheric pressure.

Total : 5.5 pts

Problem 6. Cyclopropanes. So simple. So fancy... (7 points)

Question	1	2	3	Total
Marks	8	22	70	100

Cyclopropanes bearing donor and acceptor substituents at the neighboring C-atoms, for example, **A**, demonstrate high reactivity behaving similar to 1,3-zwitterion **B**.



Thus, **A1** (X = 4-OMe) undergoes the three-membered ring opening in the Lewis acid-catalyzed reaction with 1,3-dimethoxybenzene as a nucleophile giving the product **C**.

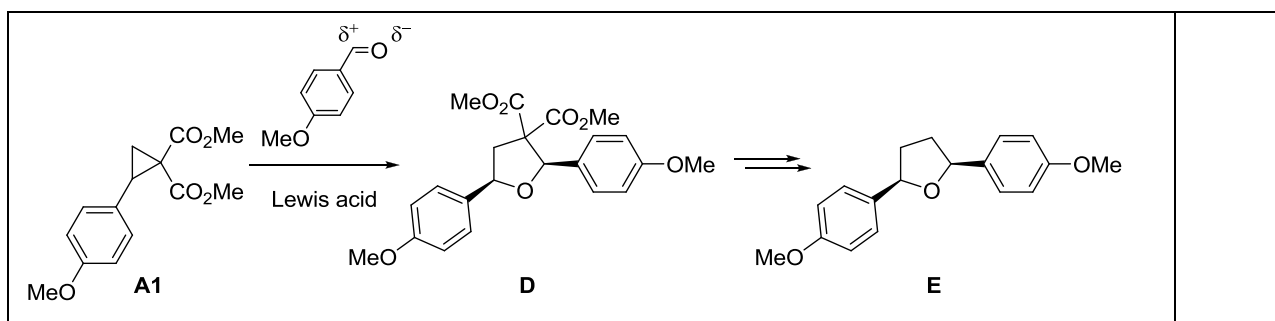
1. Write down structural formula of **C**.

<p>Reaction of A1 with 1,3-dimethoxybenzene as a nucleophile proceeds as Friedel-Crafts alkylation. Electrophiles attacks onto <i>ortho</i>-/<i>para</i>-position. Attack onto C4 position of arene proceeds easier than attack onto sterically more hindered C2 atom.</p>	<p>(2p)</p> <p>(4p)</p> <p>(2p)</p>
	<p>Structural formula of C: 8 p</p>

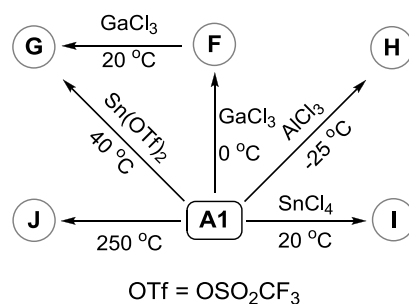
A1 participates in cycloadditions, annulations, oligomerizations, and other processes. Thus, [3+2]-cycloaddition between **A1** and 4-methoxybenzaldehyde leads to a five-membered ring in **D**. Complete decarboxylation of **D** produces **E** (C₁₈H₂₀O₃), the molecule of the latter having a plane of symmetry.

2. Write down structural formulae of **D** and **E** indicating their stereochemistry.

<p>A1 reacts similarly to 1,3-zwitterion B1. It is the 3-atom component.</p>	<p>(2p)</p>
<p>Therefore, 4-methoxybenzaldehyde is a two-atom component.</p>	<p>(2p)</p>
<p>Benzene ring is not prone to react as two-atom component. So, C=O group participates in the reaction. Accounting for its polarization, carbonyl oxygen reacts with a positive end of 1,3-zwitterion B1.</p>	<p>(4p)</p> <p>(4p)</p>
<p>Product has <i>cis</i>-geometry (see below)</p>	<p>(2p)</p>
<p>Therefore, D is <i>cis</i>-dimethyl 2,5-diaryltetrahydrofuran-3,3-dicarboxylate.</p>	<p>14 p</p>
<p>Decarboxylation of D produces 2,5-bis(4-methoxyphenyl)tetrahydrofuran E (accounting for its molecular formula). It has <i>cis</i>-arrangement of aryl groups as E has a plane of symmetry.</p>	<p>(4p)</p> <p>(4p)</p> <p>8 p</p>



Also, **A** can undergo various transformations in the absence of any reaction partners except catalysts. Some transformations typical of **A1** are shown in the Scheme below.



To determine the structures of **F-J**, a set of physico-chemical data was obtained (see Table for some results). It was found that:

- F** and **G** are structural isomers of **A1**;
- G** is formed as the most stable stereoisomer;
- H** and **I** are structural isomers;
- H** is formed as a single diastereomer with C_2 axis of symmetry (the molecule looks the same after rotation through the angle of 180°);
- I** is formed as a mixture of two diastereomers;
- J** is naphthalene derivative.

In the process leading to **I**, one molecule of **A1** demonstrates the described above common reactivity (analogous to that of **B**). The other molecule of **A1** behaves differently. Also, the latter behavior is demonstrated by cyclopropane **A2** (dimethyl 2-(3,4,5-trimethoxyphenyl)cyclopropane-1,1-dicarboxylate) when treated with SnCl_4 in CH_3NO_2 affording **K** as a mixture of two diastereomers. The major isomer has the center of symmetry. Similar reactivity is shown by **A2** in $\text{Sn}(\text{OTf})_2$ -catalyzed reaction with **G** furnishing **L**.

3. Write down the structural formulae of **F-J**, **L**, and of the major isomer of **K**.

	Ratio of the number of hydrogen-containing groups					Composition
	Non-aromatic				Aromatic	
	CH	CH ₂	CH ₃	OH		
F	1	1	1+1+1	0	4 in total	C 63.62%, H 6.11%
G	1+1+1	0	2+1	0	4 in total	C 63.62%, H 6.11%
H	1	1	1+1+1	0	4 in total	C 63.62%, H 6.11%
I	1+1+1	1+1	2+1+1+1+1	0	7 in total	C 63.62%, H 6.11%

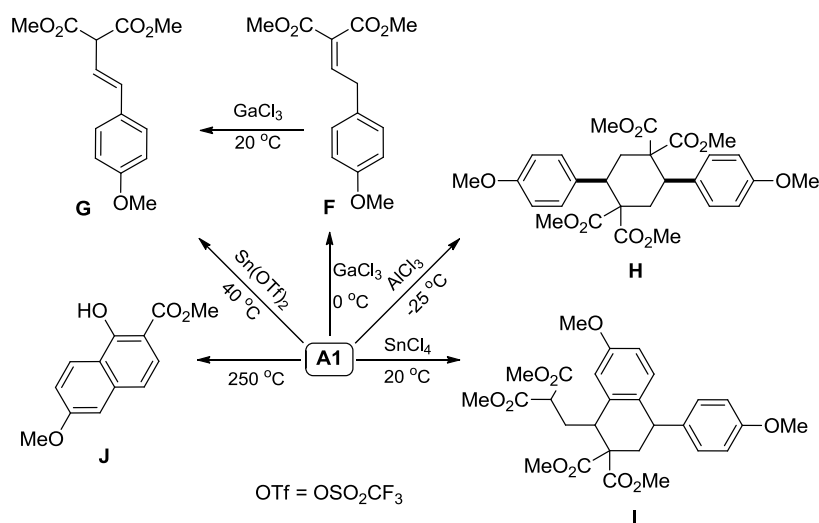
J	0	0	1+1	1	5 in total	C 67.22%, H 5.22%
K	1+1	1	2+1+1+1	0	1	C 59.24%, H 6.23%
L	1+1+1+1+1	1	2+2+1+1+1+1	0	5 in total	C 61.21%, H 6.18%

<p>F and G are isomers of A1. G has three CH groups instead of the cyclopropane fragment, two equivalent ester groups and unchanged aromatic fragment. So, G is $\text{ArCH=CHCH}(\text{CO}_2\text{Me})_2$ which is formed by cyclopropane-to-alkene isomerization as (<i>E</i>)-isomer (more stable than <i>Z</i>-isomer).</p>	(4p)
	(2p)
	6 p
<p>F has CH_2 and CH groups, two different ester groups and unchanged aromatic fragment. F is formed from A1 and undergoes secondary isomerization into G. Therefore, F is $\text{ArCH}_2\text{CH}=\text{C}(\text{CO}_2\text{Me})_2$.</p>	8 p
<p>I has twice as many protons as A1. It means that isomeric H and I are dimers of A1. Indeed, in problem it is directly stated that two molecules of A1 react when I is formed.</p>	(4p)
<p>H is highly symmetric. The aromatic fragment is not changed during its formation. So, H is a result of the symmetric dimerization of A1 when positive end of B1 of one molecule reacts with negative end of B1 of another molecule, and <i>vice versa</i>. Such dimerization produces cyclohexane. Its <i>cis</i>-isomer has C_2 axis of symmetry; <i>trans</i>-isomer has center of symmetry. Therefore, H is <i>cis</i>-isomer.</p>	(4p)
	(4p)
	12 p
<p>According to symmetry and table data, K is symmetric dimer of A2. Moreover, aromatic/non-aromatic protons ratio in K less than that in A2. Accounting for question 1, it is possible to deduce that benzylic carbon atom of one A2 molecules reacts as electrophiles with <i>ortho</i>-position of aromatic fragment (nucleophilic center) of another molecule, and <i>vice versa</i>. In this reaction A2 reacts as an equivalent of 1,3-zwitterion B2. Therefore, K is 9,10-dihydroanthracene derivative. The major isomer has the center of symmetry, <i>i.e.</i>, it has <i>trans</i>-arrangement of alkyl substituents.</p>	(4p)
	(4p)
	12 p
<p>I has 7 aromatic protons, <i>i.e.</i>, it has one aromatic proton less than H in which arene fragments are intact. In the process leading to I, one molecule of A1 reacts as an equivalent of B1, another A1 reacts as an equivalent of B2. In other words, one new C-C bond in I is formed <i>via</i> Friedel-Crafts alkylation of aromatic group in the first A1 molecule by positive end of 1,3-zwitterion producing from the second A1 molecule. Another C-C bond is formed <i>via</i> coupling of electrophilic benzylic carbon of the first A1 molecule with nucleophilic malonate carbon of the second A1 molecule. Therefore, I is tetraline derivative.</p>	(4p)
	(4p)
	12 p
<p>J has 12 protons. From composition data its molecular formula can be determined as $\text{C}_{13}\text{H}_{12}\text{O}_4$, <i>i.e.</i> it has one C atom, four H atoms, and one O atom less than A1. Moreover, J has no aliphatic hydrogens except the protons of methyl and OH groups. It is possible</p>	(4p)

if a new aromatic ring is formed *via* intramolecular Friedel-Crafts reaction. For it, **A1** is isomerized under heating into (Z)-isomer of **G** followed by intramolecular acylation of aromatic moiety producing 1-hydroxy-7-methoxynaphthalene-2-carboxylate (**J**).

(4p)

8 p



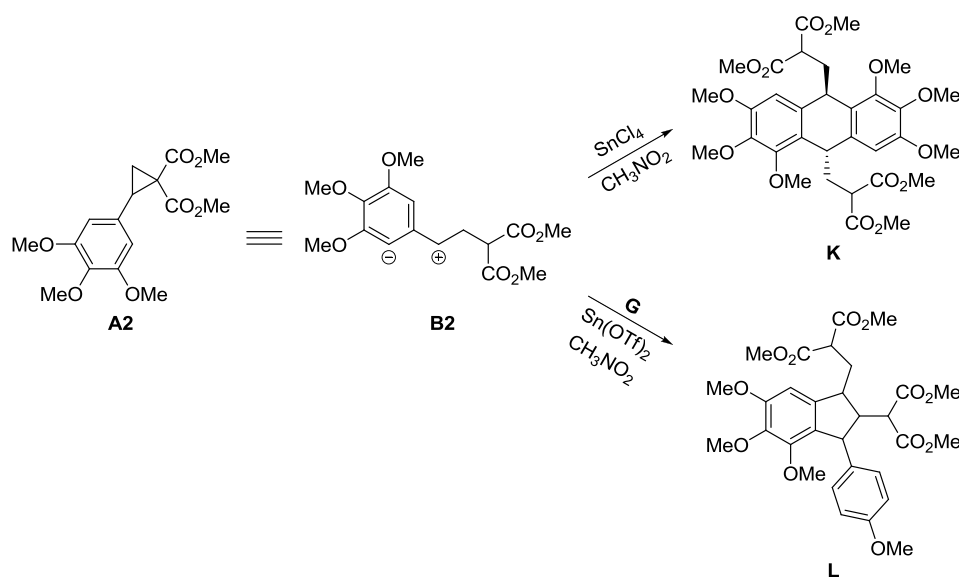
L has 36 protons. From composition data its molecular formula is C₃₀H₃₆O₁₂. It corresponds to combination of **A2** and **G**. Since **A2** reacts as an equivalent of **B2**, it can be supposed that electrophilic center of **B2** attacks C=C bond of **G** in accordance with Markovnikov's rule followed by reaction between the formed cationic center and *ortho*-carbon atom of trimethoxyphenyl substituent producing indane derivative **L**.

(4p)

(4p)

(4p)

12 p



In total, 100 points

Problem 7. Diverse permanganatometry (8 points)

Quest.	1	2	3	4	5	Total
Marks	2	2	14	7	9	34

The amount of many reducing agents can be determined by permanganatometric titration in alkaline medium allowing permanganate ion reduction to manganate.

1. Write down the ionic reaction equation for formate titration with permanganate in an aqueous solution containing ~0.5 M NaOH.

$2\text{MnO}_4^- + \text{HCOO}^- + 3\text{OH}^- = 2\text{MnO}_4^{2-} + \text{CO}_3^{2-} + 2\text{H}_2\text{O}$	Total:	2 p
	If unbalanced	2 p
		1 p

Titration with permanganate in alkaline medium is often supplemented by addition of a barium salt, which leads to precipitation of manganate as BaMnO_4 .

2. Which side redox processes involving manganate is suppressed by the barium salt? Write down an example of equation of the corresponding reaction.

$\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- = \text{MnO}_2 + 4\text{OH}^-$		
OR		
$3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} = \text{MnO}_2 + 2\text{MnO}_4^- + 4\text{OH}^-$		2 p
	Total:	2 p
	If unbalanced	1 p

10.00 mL (V_{Mn}) of 0.0400 M (c_{Mn}) KMnO_4 solution was placed in each of flasks **A**, **B**, and **C** and different reactions were conducted in each flask.

3. To flask **A**, a sample solution containing crotonic acid (CA) $\text{CH}_3\text{--CH=CH--COOH}$, an alkali and barium nitrate (both in an excess) were added, and the reaction mixture was incubated for 45 min. It is known that crotonic acid loses 10 electrons under the experiment conditions.

a) Write down the total ionic reaction equation.

$\text{C}_4\text{H}_5\text{O}_2^- + 10\text{MnO}_4^- + 14\text{OH}^- + 12\text{Ba}^{2+} = 10\text{BaMnO}_4 + \text{CH}_3\text{COO}^- + 2\text{BaCO}_3 + 8\text{H}_2\text{O}$		
		4 p
	If unbalanced	3 p
	If CO_2 is evolved	3p

8.00 mL (V_{CN}) of 0.0100 M (c_{CN}) potassium cyanide solution was further added to the incubated mixture. This resulted in completion of the following reaction:



BaMnO_4 precipitate was then filtered off, and the excess of cyanide in the filtrate was titrated with 0.0050 M (c_{Ag}) AgNO_3 solution till detectable precipitation was observed. Note that both CN^- and CNO^- are analogs of halide ions, but CNO^- affords soluble silver salt.

b) Give the formula for the complex formed when Ag^+ ions were initially added to the cyanide solution (until the precipitate was formed).

b) (before the endpoint was attained): $[\text{Ag}(\text{CN})_2]^-$	2 p
--	-----

c) Give the formula of the precipitate formed.

(after the endpoint): $\text{Ag}^+ + \text{Ag}(\text{CN})_2^- = \text{Ag}[\text{Ag}(\text{CN})_2] \downarrow$, or $\text{Ag}^+ + \text{CN}^- = \text{AgCN} \downarrow$ So, AgCN or Ag[Ag(CN) ₂] is the answer.	2 p
---	-----

d) Derive the formula for calculating the amount of crotonic acid in the sample solution. Calculate the mass of crotonic acid (in mg) if 5.40 mL (V_{Ag}) of the silver salt solution was consumed for the titration to the endpoint.

Permanganate left after the reaction with crotonic acid: $c_{\text{Mn}}V_{\text{Mn}} - 10n_{\text{CA}}$ mmol.	1 p
Cyanide consumed for the residual permanganate: $\frac{1}{2}(c_{\text{Mn}}V_{\text{Mn}} - 10n_{\text{CA}})$ mmol.	1 p
Cyanide excess: $c_{\text{CN}}V_{\text{CN}} - \frac{1}{2}(c_{\text{Mn}}V_{\text{Mn}} - 10n_{\text{CA}})$	1 p
<i>For the correct silver-cyanide stoichiometry (1:2):</i>	
$2c_{\text{Ag}}V_{\text{Ag}} = c_{\text{CN}}V_{\text{CN}} - \frac{1}{2}(c_{\text{Mn}}V_{\text{Mn}} - 10n_{\text{CA}})$.	1 p
Thus, $n_{\text{CA}} = (2c_{\text{Ag}}V_{\text{Ag}} - c_{\text{CN}}V_{\text{CN}} + \frac{1}{2}c_{\text{Mn}}V_{\text{Mn}})/5$	1 p
$n_{\text{CA}} = (2 \times 0.005 \times 5.40 - 0.0100 \times 8.00 + 0.5 \times 0.0400 \times 10.00)/5 = 0.0348$ mmol, so	
$m_{\text{CA}} = 0.0348 \times 86.09 = 3.00$ mg ($M_{\text{CA}} = 86.09$ g/mol).	1 p
<i>For the wrong silver-cyanide stoichiometry (1:1):</i>	
$c_{\text{Ag}}V_{\text{Ag}} = c_{\text{CN}}V_{\text{CN}} - \frac{1}{2}(c_{\text{Mn}}V_{\text{Mn}} - 10n_{\text{CA}})$	(1p)
$n_{\text{CA}} = (c_{\text{Ag}}V_{\text{Ag}} - c_{\text{CN}}V_{\text{CN}} + \frac{1}{2}c_{\text{Mn}}V_{\text{Mn}})/5$	(1p)
$n_{\text{CA}} = (0.005 \times 5.40 - 0.0100 \times 8.00 + 0.5 \times 0.0400 \times 10.00)/5 = 0.0290$ mmol, so	
$m_{\text{CA}} = 0.0290 \times 86.09 = 2.49$ mg	(1p)
Total for both cases	(6p)

4. Another sample of crotonic acid and alkali (in an excess) were added to flask **B**, this mixture lacking barium salt. An excess of KI (instead of cyanide) was added as a reducing agent. The mixture was further acidified, and the iodine evolved was titrated with 0.1000 M (c_{S}) thiosulfate solution. 4.90 mL (V_{S1}) of the titrant was used to reach the endpoint.

Derive the formula for calculating the amount of crotonic acid in this experiment. Calculate the mass of crotonic acid (in mg).

schematically	
$10\text{MnO}_4^- + 1\text{Crotonate} \rightarrow 10\text{MnO}_4^{2-} + \text{products}$	0 p
Permanganate left after the reaction with crotonic acid $c_{\text{Mn}}V_{\text{Mn}} - 10n_{\text{CA}}$ mmol	0 p
Manganate formed: $10n_{\text{CA}}$ mmol	1 p
Reactions occurred after iodide addition:	
$2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}$ and	1 p
$\text{MnO}_4^{2-} + 4\text{I}^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 2\text{I}_2 + 4\text{H}_2\text{O}$	1 p
Amount of the iodine evolved (mmol I_2):	
$2.5n_{\text{KMnO}_4 \text{ left}} + 2n_{\text{K}_2\text{MnO}_4} = 2.5(c_{\text{Mn}}V_{\text{Mn}} - 10n_{\text{CA}}) + 2 \cdot 10n_{\text{CA}}$.	1 p
$2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$	
$n_{\text{Na}_2\text{S}_2\text{O}_3} = 2n_{\text{I}_2} = 5(c_{\text{Mn}}V_{\text{Mn}} - 10n_{\text{CA}}) + 40n_{\text{CA}}$	1 p
Thus, $5(c_{\text{Mn}}V_{\text{Mn}} - 10n_{\text{CA}}) + 40n_{\text{CA}} = c_{\text{S}}V_{\text{S1}}$,	
And $n_{\text{CA}} = \frac{1}{2}c_{\text{Mn}}V_{\text{Mn}} - 0.1c_{\text{S}}V_{\text{S1}}$	1 p
$n_{\text{CA}} = 0.5 \times 0.0400 \times 10.00 - 0.1 \times 0.1000 \times 4.90 = 0.151$ mmol,	
$m_{\text{CA}} = n_{\text{CA}}M_{\text{CA}} = 13.00$ mg.	1 p
Total:	7 p

5. A sample containing tin(II) was added to flask C, and the medium was adjusted to weak alkaline. Tin(II) was quantitatively oxidized to Sn(OH)_6^{2-} , whereas a precipitate formed as a result of permanganate reduction. The precipitate was isolated, washed off, dried at 250°C , weighed (the mass of the water-free precipitate (m_{prec}), representing a binary compound, was of 28.6 mg), and dissolved in H_2SO_4 in the presence of an excess of potassium iodide. The evolved iodine was titrated with 0.1000 M thiosulfate solution. 2.5 mL (V_{S_2}) of the latter was consumed to attain the endpoint.

a) Write down the reaction of precipitation. Confirm it with calculations.

Tin(II) reduction with permanganate in weak alkaline medium led to an insoluble binary manganese compound. Drying conditions suggest it is either one of manganese oxides or their mixture.	
The amount of equivalent is just the same for thiosulfate, iodine and the precipitate.	1p
$n_{\text{eq}} = V_{\text{S}_2} c_{\text{S}} = 0.1000 \times 2.5 = 0.25 \text{ mmol}$	
$M_{\text{eq}} = 28.6 \text{ mg} / 0.25 \text{ mmol} = 114.4 \text{ g/mol}$. This is the so called molar mass of the equivalent of the precipitate.	1p
Let us consider possible cases.	
If MnO_2 was formed (scheme: $2\text{MnO}_4^- + 3\text{Sn(II)} \rightarrow 2\text{MnO}_2\downarrow + 3\text{Sn(IV)}$, $\text{MnO}_2 + 4\text{H}^+ + 2\text{I}^- \rightarrow \text{I}_2 + \text{Mn}^{2+} + 2\text{H}_2\text{O}$, $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$), the molar mass of its equivalent in the reaction with iodide would be: $86.94 / 2 = 43.47 \text{ g/mol}$.	1p
If Mn_2O_3 was formed ($\text{Mn}_2\text{O}_3 + 2\text{I}^- + 6\text{H}^+ \rightarrow \text{I}_2 + 2\text{Mn}^{2+} + 3\text{H}_2\text{O}$), the molar mass of its equivalent in the reaction with iodide would be: $157.88/4 = 78.9 \text{ g/mol}$.	1p
In the experiment, the molar mass of the equivalent is even higher, thus manganese compounds, not oxidizing iodide, can be present in the precipitate (i.e. manganese (II). The only possible variant is manganese(II, III) oxide ($\text{Mn}_3\text{O}_4 + 2\text{I}^- + 8\text{H}^+ \rightarrow \text{I}_2 + 3\text{Mn}^{2+} + 4\text{H}_2\text{O}$). The molar mass of the latter: $228.9/2 = 114.4 \text{ g/mol}$.	2p
Reaction: $6\text{MnO}_4^- + 13\text{Sn(OH)}_4^{2-} + 16\text{H}_2\text{O} = 2\text{Mn}_3\text{O}_4\downarrow + 13\text{Sn(OH)}_6^{2-} + 6\text{OH}^-$	1p
Total for 5a	7p

b) Calculate the mass of tin in the sample (in mg) referred to the metal.

Tin amount equals 13/2 of that of Mn_3O_4 , or $n_{\text{Sn}} = 28.6 / 228.9 \times 13/2 = 0.812 \text{ mmol}$ $m_{\text{Sn}} = 96.4 \text{ mg}$.	1p
--	----

Problem 8. Unique life of archaea (9 points)

Question	1	2	3	4	5	6	7	8	9a	9b	Total
Marks	2	7	3	8	4	4	5	4	3	4	44

Archaea (or archaeobacteria) are single-celled microorganisms. They significantly differ from bacteria and eukaryotes at the molecular level.

Enzymatic reaction of methylamine with water is the major energy source for some archaea. In a particular experiment, an archaea strain was cultivated at pH 7 under anaerobic (oxygen free) conditions with the nutrient medium containing $^{13}\text{CH}_3\text{NH}_2$ as the only energy source. After a certain incubation period, the gas over the archaea culture was sampled and analyzed. It was found that the gas contains two substances **A** and **B** in the molar ratio of 1.00:3.00 correspondingly (the sample density rel. H_2 is of 12.0).

1. Calculate the volume fractions (in %) of **A** and **B** in the mixture.

Volume ratio of gases A and B is equal to their molar ratio (1:3).	1 p
Volume fractions of A and B are 25 and 75%, respectively.	1 p
Total:	2 p

2. Determine **A** and **B** if there is no nitrogen atoms in gas collected.

Your work:			
Molecular mass of the A and B mixture equals $12.0 \cdot 2.0 = 24.0$ g/mol.			1 p
The variant of two gases, both with molecular masses of 24.0 g/mol is impossible. Thus, one of the gases is lighter, whereas the other is heavier.			1 p
Reaction of ^{13}C -methylamine with water under anaerobic conditions can theoretically lead to two nitrogen-free gases with the molecular mass lower than 24.0 g/mol: H_2 , NH_3 or $^{13}\text{CH}_4$. Further considerations are summed up in the table.			
Light gas	Volume fraction of the light gas, %	Molecular mass of the heavy gas, g/mol	
H_2	25	31.3	
	75	90.0	
NH_3	25	27.7	
	75	49.0	
$^{13}\text{CH}_4$	25	26.3	
	75	45.0	
At neutral pH values typical of living cells, ammonia exists in the form of ammonium ion and does not transfer into gaseous phase. Thus, the only possible variant is: $^{13}\text{C}^{16}\text{O}_2$ (A) and $^{13}\text{C}^1\text{H}_4$ (B).			5 p
Total:			7 p

3. Write down the equation of enzymatic reaction of methylamine with water described in the above experiment using predominant form of each species.

$4\ ^{13}\text{CH}_3\text{NH}_3^+ + 2\text{H}_2\text{O} \rightarrow 3\ ^{13}\text{CH}_4 + ^{13}\text{CO}_2 + 4\text{NH}_4^+$	Total:	3 p
The correct reaction products (even in case of non-protonated)		1 p

Methylamine and/or ammonia protonated	1 p
Right coefficients:	1 p

Enzymes containing the residue of α -amino acid **X** are found in many archaea capable of methylamine utilization. It is known that **X**:

- is composed of atoms of 4 elements;
- is 18.8 % oxygen by mass;
- possesses the single individual tRNA and is incorporated into proteins of archaea during translation.

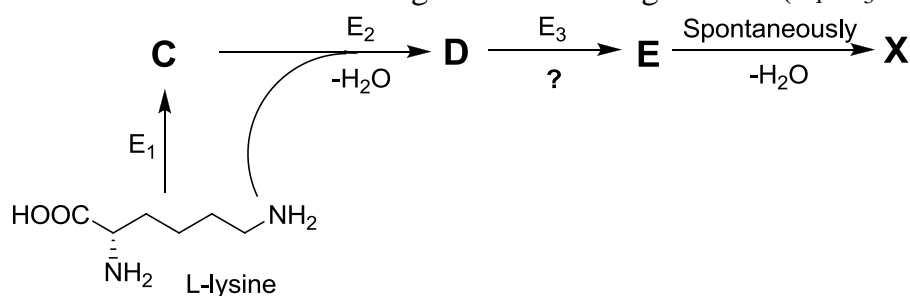
Amino acid *L*-lysine (see the structure in scheme below) was identified as the **X** precursor in archaea. All carbon and nitrogen atoms found in **X** originate from two starting lysine molecules. Different isotope-labeled *L*-lysines were introduced into a model system to clarify the biosynthetic pathways of **X**. The results are summarized in the table.

Isotope composition of <i>L</i> -lysine	Molecular mass (rounded to integer) of the X residue [RCH(NH ₂)CO], bound to tRNA, g/mol
Normal	238
All carbons ¹³ C, all nitrogens ¹⁵ N	253
ϵ -Amino group with ¹⁵ N	239

4. Determine the molecular formula of **X**.

Calculations:	
The molecular mass of X : $238 + 17$ (OH-group) = 255 g/mol.	1 p
The number of oxygens in X : $\frac{255 \cdot 0.188}{16.00} = 3$	1 p
Two lysines contain 12 carbons and 4 nitrogens, 16 in total.	1 p
From comparison of lines 1 and 2 of the table: 15 of 16 carbons and nitrogens are found in X .	1 p
From comparison of lines 1 and 3 of the table: 1 of 2 ϵ -amino nitrogens is lost during X biosynthesis.	1 p
X contains 12 carbons and 3 nitrogens.	1 p
The rest of the molecular mass: $255 - 12 \cdot 12 - 3 \cdot 14 - 3 \cdot 16 = 21$ g/mol is due to hydrogen (21 atoms).	
Thus, C ₁₂ H ₂₁ N ₃ O ₃	2 p
Total:	8 p

X is biosynthesized in archaea according to the following scheme (E₁–E₃ – enzymes):



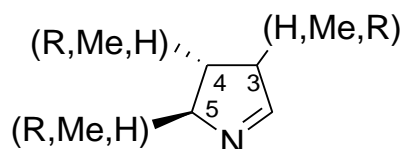
At the first step, lysine is transformed into its structural isomer of lysine (α -amino acid,

C), whereas **D** contains a peptide bond, and **E** a formyl group $\left[\begin{array}{c} \text{O} \\ \parallel \\ -\text{C} \\ | \\ \text{H} \end{array} \right]$. All reaction coefficients in the above scheme equal 1.

5. Give the chemical formula of C, D and E. From the reaction types given hereunder, choose (tick) **only one** corresponding to the enzyme E_3 catalyzed reaction.

<p>Calculations.</p> <p>C is an isomer of lysine, thus $2 \cdot \text{C}_6\text{H}_{14}\text{N}_2\text{O}_2 = \text{C}_{12}\text{H}_{28}\text{N}_4\text{O}_4$ enter the reaction of D synthesis.</p> <p>One molecule of water is formed at each of the steps [C + lysine \rightarrow D ($\text{C}_{12}\text{H}_{28}\text{N}_4\text{O}_4 - \text{H}_2\text{O} = \text{C}_{12}\text{H}_{26}\text{N}_4\text{O}_3$)] and [E \rightarrow X ($\text{C}_{12}\text{H}_{21}\text{N}_3\text{O}_3 + \text{H}_2\text{O} = \text{C}_{12}\text{H}_{23}\text{N}_3\text{O}_4$)].</p> <p>Thus, loss/gain of atoms at D\rightarrowE step: $\text{C}_{12}\text{H}_{24}\text{N}_4\text{O}_3 - \text{C}_{12}\text{H}_{21}\text{N}_3\text{O}_4$, minus NH_3, plus O. Thus, it is oxidative deamination:</p> <p>$\text{R-CH}_2\text{-NH}_2 + [\text{O}] \rightarrow \text{R-CH=O} + \text{NH}_3$ (schematically).</p> <p style="text-align: right;">Total:</p>			Each C – E 1 p
<p>C</p> <p>$\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$</p>	<p>D</p> <p>$\text{C}_{12}\text{H}_{26}\text{N}_4\text{O}_3$</p>	<p>E</p> <p>$\text{C}_{12}\text{H}_{23}\text{N}_3\text{O}_4$</p>	4 p
<p><input checked="" type="checkbox"/> Oxidative deamination;</p> <p><input type="checkbox"/> Decarboxylation;</p> <p><input type="checkbox"/> Intermolecular deamination;</p> <p><input type="checkbox"/> Hydroxylation;</p> <p><input type="checkbox"/> Peptide bond hydrolysis.</p>			1 p

X contains the following fragment:



R is a massive substituent ($M > 100$ g/mol). The 3rd carbon atom is non-asymmetric, 4th and 5th carbon atoms are stereogenic centers. All carbon atoms in the cycle are bound with at least one hydrogen atom. Each substituent (H, Me and R) is found only once.

6. Determine the positions of substituents H, Me, and R.

Your work:

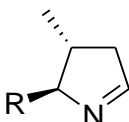
H atom bound to the 4th or 5th C atom would mean the loss of chirality, thus it is unambiguously attributed to the 3rd C atom. 1 p

It is needed to decide about the amino group forerunning the heterocyclic nitrogen to attribute the positions of the other two substituents.

Nitrogen is included in the cycle due to the reaction of an amino and formyl groups, the latter appearing as a result of the oxidative deamination. 1 p

The size of the cycle suggests it was the α -amino group, thus:

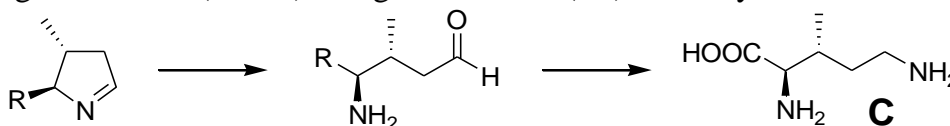
the 3rd position – H; the 4th position – Me; the 5th position – R. 1+1 p



Total: 4 p

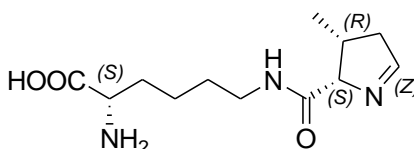
7. Draw structural formulae of **C** and **X** with stereochemical details. Mark every stereocenter of **X** with either *R* or *S*.

Moving backwards (**X**→**D**) one gets that **C** is (3*R*)-3-methyl-*D*-ornithine: 2.5 p



Stereochemistry of **C** is derived from that of the above cyclic fragment with an account that no isomerization occurs on the way from **C** to **X**.

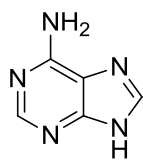
Both amino groups of lysine can form the peptide bond with the carboxylic group of **C**. Still, involvement of only the ϵ -amino group will provide **X** as α -amino acid. **X** is pyrrolysine, the 22nd amino acid of the genetic code: 2.5 p



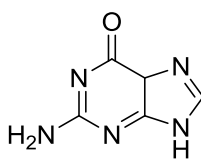
Total: 5 p

Penalty for each wrong or no decision about the stereocenter (*R* or *S*) -0.5 p

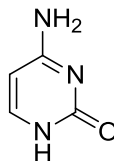
Only one codon is responsible for the incorporation of **X** residues into proteins in archaea. The nitrogen bases forming this codon contain two exocyclic amino groups and three exocyclic oxygen atoms in total.



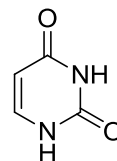
adenine



guanine



cytosine



uracil

8. Determine the nucleotide composition of the codon by filling in the hereunder table. Write down the number of each nitrogen base in the codon encoding **X**. Tick only one box in each line.

Nitrogen base	The number of bases in the codon				
	1	2	3	0 or 1	1 or 2
A	<input checked="" type="checkbox"/>				
C				<input checked="" type="checkbox"/>	
G				<input checked="" type="checkbox"/>	
U	<input checked="" type="checkbox"/>				
A has 1 amino group and 0 oxygen atoms					
C has 1 amino group and 1 oxygen atom					
G has 1 amino group and 1 oxygen atom					
U has 0 amino groups and 2 oxygen atoms					
2 amino groups per 3 bases suggest one U.					1 p
There are 2 amino groups and 1 oxygen atom per two bases left. A is one of these.					1 p
Either G or C is the last one.					2 p
Total:					4 p
In case of more than one box ticked in one line:					0 p

The fragment of mRNA coding sequence given below contains the codons encoding **X** residue incorporation into an archaea enzyme:

5'...AAUAGAAUAGCGGAACAGAGGGUGAC...3'

9a. Using the table of the genetic code, decide how many amino acid residues are incorporated into the enzyme chain due to this fragment translation.

9b. Write down the amino acid sequence translated from this fragment. Note that more than one **X** residue is found in the fragment.

a. The fragment contains only four U, which can be used as the starting point to determine the reading frame. There should be only one A in the triplet. UGA and UAG are the options, the latter met twice. Both are STOP codons in the table. But the fragment of mRNA represents coding sequence! Within definite nucleotide motives, the STOP codons can be responsible for amino acid incorporation into proteins. Therefore, 8 amino acids encoded in the fragment (if UGA is STOP codone, then 7 amino acids residues:

...AA|UAG|AAU|UAG|CGG|AAC|AGA|GGG|UGA|C...

Number of amino acids = 8

3 p

b. Fill in the boxes with the amino acid abbreviations (from N- to C-terminus). Note that the number of boxes is excessive. If there is more than one possibility, write all separated by “/”. If the translation is stopped in a particular position, write “STOP” and leave all the boxes to the right empty.

Your work:

Since only one codon is responsible for the incorporation of **X** residues into proteins in archaea, it is UGA or UAG. There are more than one **X** residue in the polypeptide fragment, thus it is UAG (met twice), while UGA encodes Sec. (No penalty if STOP instead of Sec).

X	Asn	X	Arg	Asn	Arg	Gly	Ses		
---	-----	---	-----	-----	-----	-----	-----	--	--

4 p

7 p

Total:

(a) RNA Codons for the Twenty Amino Acids

		Second base					
First base		U	C	A	G		Amino-acid abbreviations
	U	Phe Phe Leu Leu	Ser Ser Ser Ser	Tyr Tyr STOP STOP	Cys Cys STOP Trp	U C A G	Ala = Alanine Arg = Arginine Asp = Aspartic acid Asn = Asparagine Cys = Cysteine Glu = Glutamic acid Gln = Glutamine Gly = Glycine His = Histidine Ile = Isoleucine Leu = Leucine Lys = Lysine Met = Methionine Phe = Phenylalanine Pro = Proline Ser = Serine Thr = Threonine Trp = Tryptophan Tyr = Tyrosine Val = Valine
	C	Leu Leu Leu Leu	Pro Pro Pro Pro	His His Gln Gln	Arg Arg Arg Arg	U C A G	
	A	Ile Ile Ile Met (start)	Thr Thr Thr Thr	Asn Asn Lys Lys	Ser Ser Arg Arg	U C A G	
Third base	G	Val Val Val Val	Ala Ala Ala Ala	Asp Asp Glu Glu	Gly Gly Gly Gly	U C A G	

IUPAC Periodic Table of the Elements																	2
1																	18
H hydrogen [1.007; 1.009]	2											13	14	15	16	17	He helium 4.003
3	4											5	6	7	8	9	10
Li lithium [6.938; 6.997]	Be beryllium 9.012											B boron [10.80; 10.83]	C carbon [12.00; 12.02]	N nitrogen [14.00; 14.01]	O oxygen [15.99; 16.00]	F fluorine 19.00	Ne neon 20.18
11	12											13	14	15	16	17	18
Na sodium 22.99	Mg magnesium 24.31											Al aluminium 26.98	Si silicon [28.08; 28.09]	P phosphorus 30.97	S sulfur [32.05; 32.08]	Cl chlorine [35.44; 35.46]	Ar argon 39.95
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K potassium 39.10	Ca calcium 40.08	Sc scandium 44.96	Ti titanium 47.87	V vanadium 50.94	Cr chromium 52.00	Mn manganese 54.94	Fe iron 55.85	Co cobalt 58.93	Ni nickel 58.69	Cu copper 63.55	Zn zinc 65.38(2)	Ga gallium 69.72	Ge germanium 72.63	As arsenic 74.92	Se selenium 78.96(3)	Br bromine 79.90	Kr krypton 83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb rubidium 85.47	Sr strontium 87.62	Y yttrium 88.91	Zr zirconium 91.22	Nb niobium 92.91	Mo molybdenum 95.96(2)	Tc technetium	Ru ruthenium 101.1	Rh rhodium 102.9	Pd palladium 106.4	Ag silver 107.9	Cd cadmium 112.4	In indium 114.8	Sn tin 118.7	Sb antimony 121.8	Te tellurium 127.6	I iodine 126.9	Xe xenon 131.3
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs caesium 132.9	Ba barium 137.3	lanthanoids	Hf hafnium 178.5	Ta tantalum 180.9	W tungsten 183.8	Re rhenium 186.2	Os osmium 190.2	Ir iridium 192.2	Pt platinum 195.1	Au gold 197.0	Hg mercury 200.6	Tl thallium [204.3; 204.4]	Pb lead 207.2	Bi bismuth 209.0	Po polonium	At astatine	Rn radon
87	88	89-103	104	105	106	107	108	109	110	111	112		114		116		
Fr francium	Ra radium	actinoids	Rf rutherfordium	Db dubnium	Sg seaborgium	Bh bohrium	Hs hassium	Mt meitnerium	Ds darmstadtium	Rg roentgenium	Cn copernicium		Fl flerovium		Lv livermorium		

Key:
 atomic number
Symbol
 name
 standard atomic weight

Notes

- IUPAC 2009 Standard atomic weights abridged to four significant digits (Table 4 published in *Pure Appl. Chem.* 83, 359-396 [2011]; doi: 10.1351/PAC-REP-10-09-14). The uncertainty in the last digit of the standard atomic weight value is listed in parentheses following the value. In the absence of parentheses, the uncertainty is one in that last digit. An interval in square brackets provides the lower and upper bounds of the standard atomic weight for that element. No values are listed for elements which lack isotopes with a characteristic isotopic abundance in natural terrestrial samples. See PAC for more details.

- "Aluminum" and "caesium" are commonly used alternative spellings for "aluminium" and "caesium."

- Claims for the discovery of all the remaining elements in the last row of the Table, namely elements with atomic numbers 113, 115, 117 and 118, and for which no assignments have yet been made, are being considered by a IUPAC and IUPAP Joint Working Party.

For updates to this table, see iupac.org/reports/periodic_table/. This version is dated 1 June 2012.

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