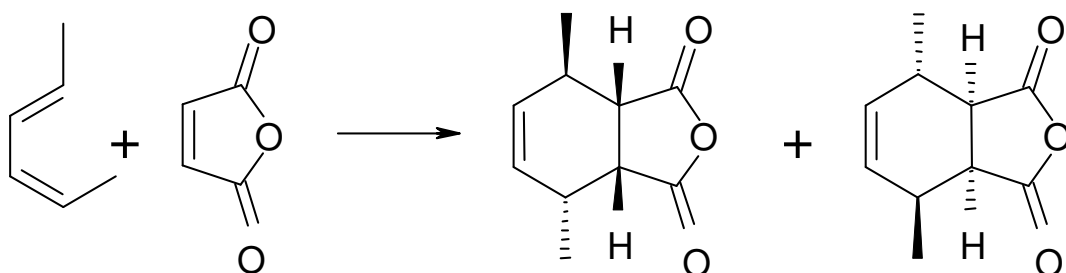
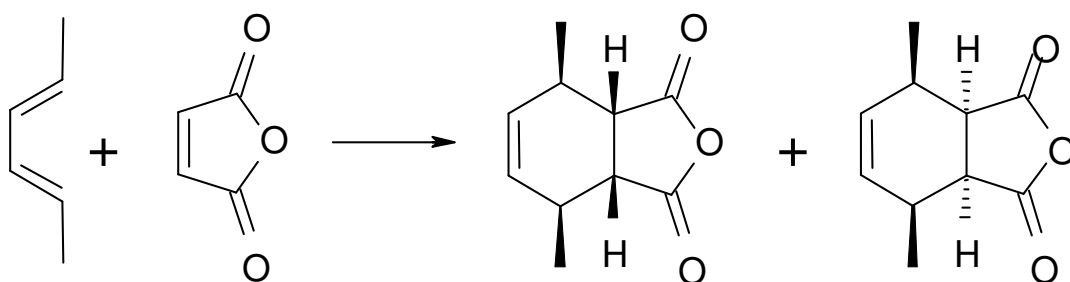


The 40th Ukrainian Chemistry Olympiad

Tasks and Answers



**Ternopol
March 2003**

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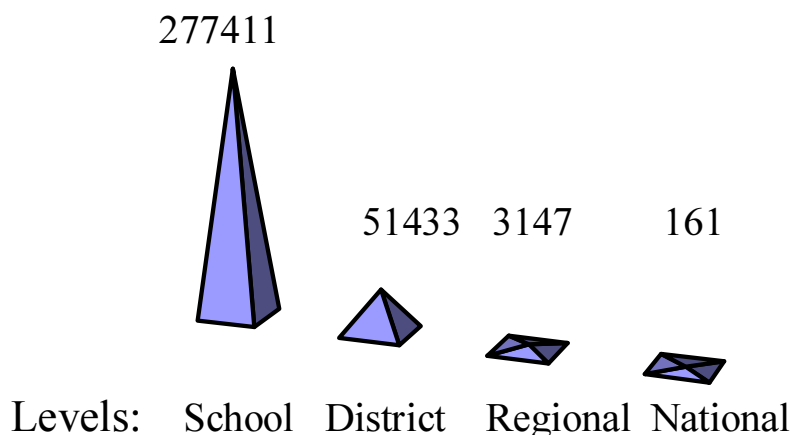
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General Information

The Ukrainian Chemistry Olympiad is held at four stages and includes the competitions at the school, district, regional and national levels. The Olympiad is organized by the Ministry of Education and Science. This year about 300 000 higher school students took part in the Olympiad.



Participants of the Chemistry Olympiad in academic year 2002/2003

The All-Ukrainian chemistry olympiad is the gathering of the best students from all over the country. The competitors are divided into four age groups from 14 to 17 years old. The winners of the olympiad are defined separately in each group, and approximately one half of the participants is awarded. The olympiad consists of three rounds: two theoretical and experimental. Tasks of the first theoretical round must be in the strict agreement with the basic chemistry program for the secondary school, while tasks of the second theoretical round are fairly complicated.

This booklet presents several tasks proposed to the participants belonging to the elder age group (students of the 11 class).

Task 1. A hydrogen-like ion consists of a nucleus with the nuclear charge $+Z$, $Z > 1$, and one electron (for instance, He^+ , Li^{2+} , Be^{3+} and so on). The Bohr theory of hydrogen-like ions gives the following expression for the electron energy at the Bohr orbit

$$E_n = -k \frac{Z^2}{n^2},$$

where k is the ionization energy of the ground state of the hydrogen atom, n is the quantum number, $n = 1, 2, 3, \dots$. Also, the radius of the Bohr orbit may be found:

$$r_n = a_0 \frac{n^2}{Z},$$

where a_0 is the radius of the first Bohr orbit, $a_0 = 0,0529$ nm.

1. Calculate the value of k (kJ/mol), if it is known that the convergence limit of the Lyman series of the atomic hydrogen corresponds to the frequency $3,287 \cdot 10^{15}$ Hertz. This series appears due to the electron transfer to the energy level with $n = 1$.

2. Calculate the wave-length of the electromagnetic radiation necessary to ionize the ground state of the hydrogen atom.

3. Write down the expressions for the 2nd ionization energy of the helium atom and the 3rd ionization energy of the lithium atom. Calculate these energies in kJ/mol.

4. Draw the diagrams of the energy levels for Li^{2+} and Be^{3+} . Compare them with the energy diagram of the hydrogen atom.

5. Write down the expressions for the radii of the Bohr orbits ($n = 1; 2$) for He^+ and Li^{2+} ions. Calculate these radii and compare them with the corresponding values for the hydrogen atom.

6. It was reported in 1976 that the first atoms of the super heavy element with the atomic number 126 were obtained. Estimate the radius of the Bohr orbit for the electrons nearest to the nucleus in this atom. Discuss the stability of this atom.

The Planck constant $h = 6,63 \cdot 10^{-34}$ J·s; the Avogadro constant

$N_A = 6,02 \cdot 10^{23}$ mol⁻¹; the velocity of light $c = 3 \cdot 10^8$ m·s⁻¹; $c = \lambda \nu$.

Answers

1. The value of k is equal to the ionization energy of the ground state of the hydrogen atom. The convergence limit of the Lyman series corresponds to this state. The frequency of radiation ν_{limit} is connected with the ionization energy of atom (I) through the following expression

$$I = h\nu_{\text{limit}}.$$

Hence,

$$I = 6,63 \cdot 10^{-34} \text{ J} \cdot \text{s} \times 3,287 \cdot 10^{15} \text{ s}^{-1} = 21,79 \cdot 10^{-19} \text{ J}.$$

For 1 mol of atoms

$$I' = I \cdot N_A = 21,79 \cdot 10^{-19} \text{ J} \times 6,02 \cdot 10^{23} \text{ mol}^{-1} = 1,312 \cdot 10^6 \text{ J} \cdot \text{mol}^{-1} = 1312 \text{ kJ} \cdot \text{mol}^{-1}.$$

At $Z = 1$ and $n = 1$ one obtains: $k = I = 1312 \text{ kJ} \cdot \text{mol}^{-1}$.

$$2. \lambda = c / \nu = 3 \cdot 10^8 \text{ M} \cdot \text{c}^{-1} / 3,287 \cdot 10^{15} \text{ c}^{-1} \approx 91 \cdot 10^9 \text{ M} = 91 \text{ nm}.$$

$$3. \quad I = kZ^2,$$

$$I_2(\text{He}) = 4 \cdot 1312 \text{ kJ} \cdot \text{mol}^{-1} = 5248 \text{ kJ} \cdot \text{mol}^{-1},$$

$$I_3(\text{Li}) = 9 \cdot 1312 \text{ kJ} \cdot \text{mol}^{-1} = 11808 \text{ kJ} \cdot \text{mol}^{-1}.$$

4. For the hydrogen atom

$$E_1 = -\frac{k}{1}, \quad E_2 = -\frac{k}{4}, \quad E_3 = -\frac{k}{9}.$$

for the Li^{2+} ion

$$E_1 = -\frac{9k}{1}, \quad E_2 = -\frac{9k}{4}, \quad E_3 = -\frac{9k}{9}.$$

for the Be^{3+} ion

$$E_1 = -\frac{16k}{1}, \quad E_2 = -\frac{16k}{4}, \quad E_3 = -\frac{16k}{9}.$$

$$5. \text{He}^+: r_1 = a_0 / 2, r_2 = a_0 \frac{2^2}{2}; \text{Li}^{2+}: r_1 = a_0 \frac{1^2}{3}, r_2 = a_0 \frac{2^2}{3}.$$

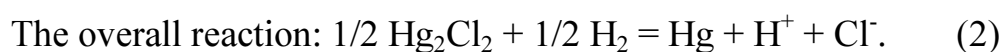
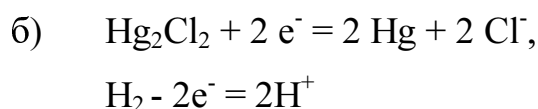
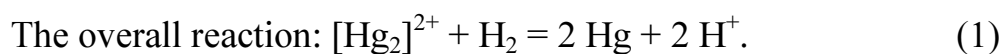
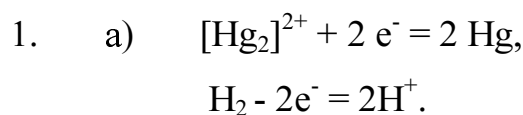
$$6. r_1 = a_0 \frac{1}{126} = 0,0529 \text{ nm} / 126 = 4,2 \cdot 10^{-4} \text{ nm}.$$

Task 2. The following reference data are known: $E_1^0([\text{Hg}_2]^{2+}/\text{Hg}) = 0,789 \text{ V}$; $E_2^0(\text{Hg}/\text{Hg}_2\text{Cl}_2, \text{solid}/\text{Cl}^-) = 0,268 \text{ V}$.

- Write down the corresponding galvanic cells, give the balanced equations of reactions that occur at the electrodes. Write the equation for the overall reaction.
- Calculate the solubility of Hg_2Cl_2 in water at 25°C :

The Faraday constant $F = 96500 \text{ Coulomb}\cdot\text{mol}^{-1}$; $R = 8,314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

Answer



2. The solubility (S) of Hg_2Cl_2 is determined by reaction:



$$S = [\text{Hg}_2^{2+}] = (1/2)\cdot[\text{Cl}^-].$$

Hence, the solubility product $K_{s0} = S\cdot(2S)^2 = 4S^3$,

$$\log S = \{\log K_{s0} - \log 4\} / 3.$$

Let us consider the linear combination of reactions:

$$(3) = (2) - (1).$$

It is evident that $\Delta G_3^0 = \Delta G_2^0 - \Delta G_1^0$.

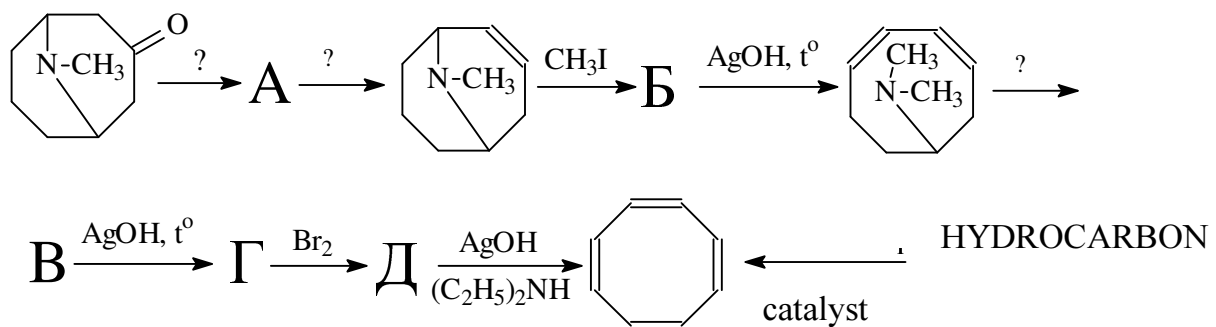
Taking into account that $\Delta G_2^0 = -2F\cdot E_2^0$, $\Delta G_1^0 = -2F\cdot E_1^0$, one obtains:

$$\Delta G_3^0 = -2F\cdot(E_2^0 - E_1^0) = -2\cdot 96500\cdot(0,268-0,789) = 100500 \text{ (J}\cdot\text{mol}^{-1}\text{)}.$$

$$\Delta G_3^0 = -2,3\cdot RT\cdot \log K_{s0}, \log K_{s0} = 100500/(2,3\cdot 8,314\cdot 298) = -17,63,$$

$$\log S = (-17,63 - \log 4) / 3 = -6,08; S = 8,3\cdot 10^{-7} \text{ (mol}\cdot\text{l}^{-1}\text{)}.$$

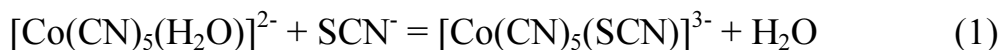
Task 3. For the first time, cyclooctotetraene was synthesized in many stages. This compound was obtained from alkaloid pseudopelterin present in the pomegranate rind:



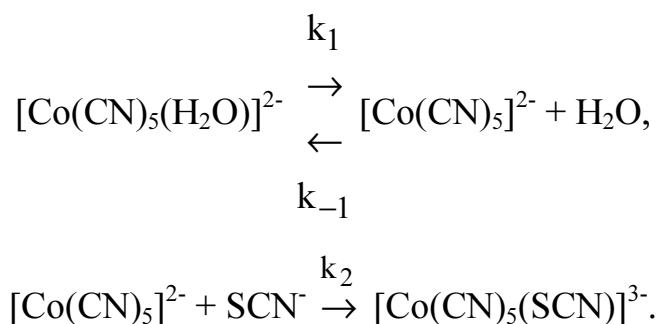
Nowadays cyclooctotetraene is prepared in one stage over a catalyst from the simple unsaturated hydrocarbon.

1. Add the formulas of reagents and structures of intermediate compound to the scheme.
2. Is cyclooctotetraene the aromatic substance? Prove your opinion.

Task 4. It was found that in aqueous solutions reaction



occurs in accordance to the dissociative mechanism



1. On the base of this mechanism derive the equation for the overall reaction rate $r = \frac{d[\text{Co}(\text{CN})_5(\text{SCN})]^{3-}}{dt}$ (apply the principle of quasi-stationary concentrations for intermediate). Write the dimensionalities of the rate constants, the reaction orders with respect to each reagent and the overall order.

2. The reaction rate was measured at 40 °C at the constant concentration of complex $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ $1,00 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}$ and different concentrations of ion SCN^- . Calculate the rate constants for the separate stages (or, if it is impossible, their combinations). Use the data from the table.

№	$C_{\text{SCN}^-}, \text{ mol} \cdot \text{l}^{-1}$	$r, 10^{-6} \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$
1	0,05	0,15
2	0,10	0,31
3	0,40	1,15
4	0,70	2,00
5	1,00	2,62

Answers

1. According to the principle of quasi-stationary concentrations,

$$0 = \frac{dC_{[\text{Co}(\text{CN})_5]^{2-}}}{dt} =$$

$$= k_1 \cdot C_{[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}} - k_{-1} \cdot C_{[\text{Co}(\text{CN})_5]^{2-}} - k_2 \cdot C_{\text{SCN}^-} \cdot C_{[\text{Co}(\text{CN})_5]^{2-}},$$

whence it follows that $C_{[\text{Co}(\text{CN})_5]^{2-}} = \frac{k_1 \cdot C_{[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}}}{k_2 \cdot C_{\text{SCN}^-} + k_{-1}},$

$$r = \frac{k_1 \cdot C_{[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}}}{k_2 \cdot C_{\text{SCN}^-} + k_{-1}} \times k_2 \cdot C_{\text{SCN}^-} =$$

$$= k_1 \times \frac{C_{\text{SCN}^-}}{C_{\text{SCN}^-} + k_{-1}/k_2} \times C_{[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}}$$

The dimensionality of the rate constants k_1, k_{-1} is s^{-1} while the dimensionality of k_2 is $\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.

The orders of reaction are as follows:

with respect to $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ — 1,

with respect to SCN^- – varying (from 1 at $C_{\text{SCN}^-} \ll k_{-1}/k_2$ to 0 at high SCN^- concentrations).

The overall order is from 1 to 2.

2. The reaction rate

$$r = Y \times C_{[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}},$$

where $Y = k_1 \times \frac{C_{\text{SCN}^-}}{C_{\text{SCN}^-} + k_{-1}/k_2}$. It is possible to determine k_1 and parameter

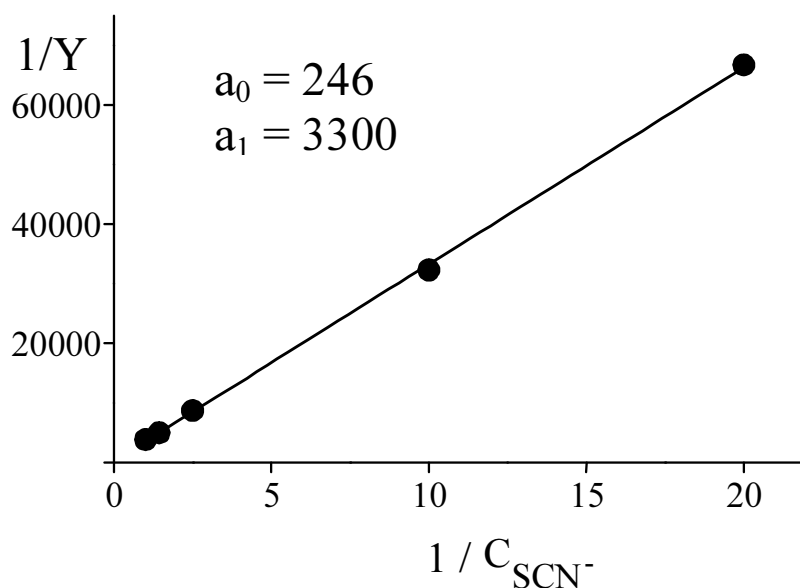
$\beta = k_{-1} / k_2$ from the dependence of r on C_{SCN^-} . This equation may be transformed

into another one:

$$\frac{1}{Y} = \frac{1}{k_1} + \frac{\beta}{k_1} \cdot \frac{1}{C_{\text{SCN}^-}} = a_0 + a_1 \cdot \frac{1}{C_{\text{SCN}^-}}.$$

It is easy to find coefficients a_0 and a_1 from the linear plot of $1/Y$ vs. $1/C_{\text{SCN}^-}$ and to calculate $k_1 = 1/a_0$ and $\beta = a_1 / a_0$.

№	C_{SCN^-} , $\text{l}\cdot\text{mol}^{-1}$	r , 10^{-6} $\text{mol}/(\text{l}\cdot\text{s})^{-1}$	$1/C_{\text{SCN}^-}$, $\text{l}\cdot\text{mol}^{-1}$	Y , 10^{-4} $\text{mol}/(\text{l}\cdot\text{s})^{-1}$	$1/Y$
1	0,05	0,15	20	0,15	$6,67 \cdot 10^4$
2	0,10	0,31	10	0,31	$3,23 \cdot 10^4$
3	0,40	1,15	2,5	1,15	$8,70 \cdot 10^3$
4	0,70	2,00	1,43	2,00	$5 \cdot 10^3$
5	1,00	2,62	1	2,62	$3,83 \cdot 10^3$



$$k_1 = 1 / 246 = 4 \cdot 10^{-3} \text{ (s}^{-1}\text{)}, \beta = 3300 / 246 = 13 \text{ (mol} \cdot \text{l}^{-1}\text{)}.$$

Task 5. Compound **A** is the monochlorine derivative of saturated hydrocarbon (mass fraction of carbon 38,38%). When **A** is treated with potassium *tert*-butylate in DMSO, three isomeric gaseous hydrocarbons **B**, **C** and **D** are formed. If the solution of these three gases is treated with reagent **Y** (mass fraction of chlorine 45,81%), it is possible to isolate compounds **E** (does not contain chlorine) and **F** (mass fraction of chlorine 33,33%). The NMR ^1H spectrum of **F** contains quartet (1H), singlet (3H) and doublet (3H), while the signals of four types of protons are present in the NMR ^1H spectrum of compound **E**.

1. Determine substances **A–F** and write down the equations of reactions.
2. Determine reagent **Y**, if it is known that
 - a) there are two chlorine atoms in its molecule;
 - б) 4 mol of NaOH are necessary to neutralize the orange solution obtained at interaction of 1 mol of **Y** with water.
3. Write the possible mechanism of transformations **B** \rightarrow **E** and **D** \rightarrow **F**.

Answers

A: 2- chlorobutane; **B:** butene-1; **C:** *cis*-butene-2; **D:** *trans*-butene-2;
F: CH₃-CO-CHCl-CH₃; **E:** CH₂=CH-CO-CH₃; **Y:** CrO₂Cl₂.

Task 6. The boiling point of substance **A** is 7 °C. At standing, **A** turns into compound **B**, which is sublimated at 135 °C. At heating, substance **B** is decomposed to solid **C** (melting point 160 °C), liquid **D** (boiling point 67 °C) and gas **E**. At standing, compound **D** is transformed into solid substance **F** with melting point 175 °C (this is the first-order reaction with the half-decomposition time 35 hours).

The mass and molar fractions of elements in the compounds are given below.

Compound	X		Y		Z	
	%, mass	%, molar	%, mass	%, molar	%, mass	%, molar
A, B	19,49	16,67	44,63	33,33	35,88	50,00
C	14,87	16,67	85,13	83,33	–	–
D	16,15	16,67	73,94	66,67	9,91	16,67
E	24,58	16,67	–	–	75,41	83,33
F	16,15	16,67	73,94	66,67	9,91	16,67

1. Determine compounds **A–F** if it is known that **X** and **Y** are the elements of the 3rd period of the Periodic Table.
2. Draw the space structures of all compounds.
3. Write down the balanced equations of the reactions mentioned.
4. What time is necessary for substance **D** to be decomposed for 66%?
5. The chemical equilibrium



takes place at high temperatures. At 227 °C the equilibrium constant is equal to $3,38 \cdot 10^4$ Pa. Calculate the reaction progress (%) at this temperature 227 °C and $1,01 \cdot 10^5$ Pa.

Answer

1. Let us determine the empirical formulas of the compounds:

A and B ($X_xY_yZ_z$):

$$x : y : z = 16,67 : 33,33 : 50,00 = 1 : 2 : 3 \quad (XY_2Z_3).$$

C (X_xY_y):

$$x : y = 16,67 : 83,33 = 1 : 5 \quad (XY_5).$$

E (X_xZ_z):

$$x : z = 16,67 : 83,33 = 1 : 5 \quad (XZ_5).$$

D and F ($X_xY_yZ_z$):

$$x : y : z = 16,67 : 66,67 : 16,67 = 1 : 4 : 1 \quad (XY_4Z).$$

On the other hand, equations may be written

for **C**

$$A_r(X) : 5A_r(Y) = 14,87 : 85,13,$$

$$A_r(X) : A_r(Y) = 14,87 : 17,03 = 0,873,$$

for **E**

$$A_r(X) : 5A_r(Z) = 24,58 : 75,41,$$

$$A_r(X) : A_r(Z) = 24,58 : 15,08 = 1,630.$$

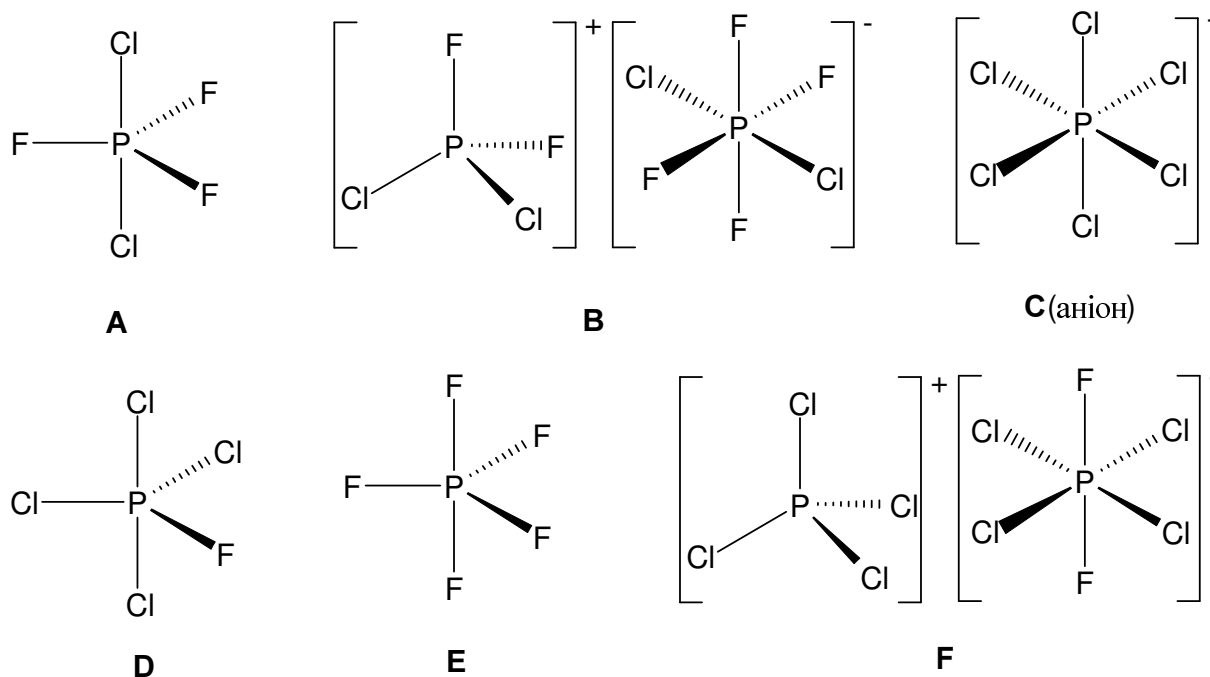
Taking into account that **X** and **Y** belong to the 3rd period and $A_r(X) = 0,873A_r(Y)$, it is possible to determine them.

Y	Al	Si	P	S	Cl	Ar
$A_r(X)$	23,5	24,4	27	28	31	35
X	–	(Mg)	(Al)	(Si)	P	–

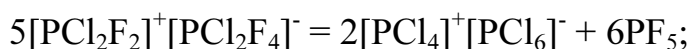
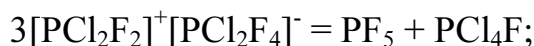
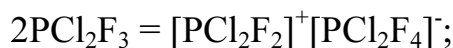
So, **X** = P, **Y** = Cl and $A_r(Z) = 31/1,63 = 19$, that corresponds to fluorine.

Compound **A** and **D** have the molecular structure. Hence, $\mathbf{A} = \text{PCl}_2\text{F}_3$ and $\mathbf{D} = \text{PCl}_4\text{F}$. On the contrary, **B** and **F** should be the ionic substances. In accordance with the electronegativity of elements it may be concluded that $\mathbf{B} = [\text{PCl}_2\text{F}_2]^+[\text{PCl}_2\text{F}_4]^-$, $\mathbf{F} = [\text{PCl}_4]^+[\text{PCl}_4\text{F}_2]^-$, $\mathbf{C} = [\text{PCl}_4]^+[\text{PCl}_6]^-$, $\mathbf{E} = \text{PF}_5$.

2.



3.



4.

$$\ln(N/N_0) = -k \cdot \tau = -\ln 2 \cdot \tau / \tau_{1/2},$$

$$\tau = -\tau_{1/2} \times \ln(N/N_0) / \ln 2.$$

$$\tau_{66\%} = -35 \text{ h} \times \ln 0.33 / \ln 2 = 56 \text{ h}.$$

5.



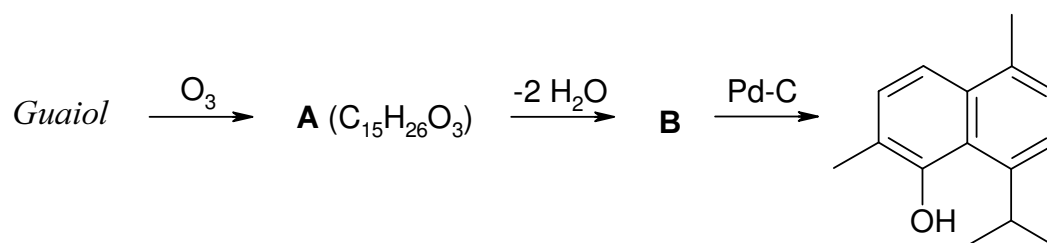
$$p(\text{PCl}_3) = p(\text{Cl}_2),$$

$$p(\text{Cl}_2) + p(\text{PCl}_3) + p(\text{PCl}_5) = p,$$

$$K_p = p(\text{PCl}_3) \times p(\text{Cl}_2) / p(\text{PCl}_5).$$

$$\begin{aligned}
 p(\text{PCl}_5) &= p - 2 \times p(\text{PCl}_3), \\
 K_p &= p(\text{PCl}_3)^2 / (p - 2 \times p(\text{PCl}_3)), \\
 p(\text{PCl}_3)^2 + 2 K_p \times p(\text{PCl}_3) - K_p \times p &= 0, \\
 p(\text{PCl}_3) &= -K_p + (K_p^2 + K_p \times p)^{1/2} = 3,37 \cdot 10^{-4} \text{ (Pa)}, \\
 p(\text{PCl}_5) &= 3,36 \cdot 10^{-4} \text{ (Pa)}, \\
 \alpha &= p(\text{PCl}_3) / (p(\text{PCl}_3) + p(\text{PCl}_5)) = 0,50 \text{ (50\%)}.
 \end{aligned}$$

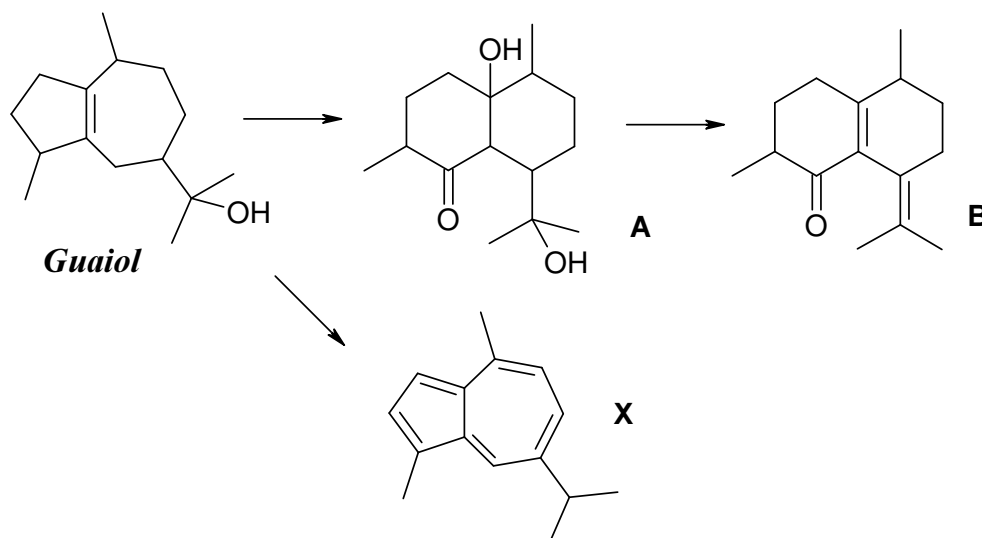
Task 7. The crystalline alcohol *guaiol* ($\text{C}_{15}\text{H}_{26}\text{O}$) is the terpenic substance. It was isolated from the oil of *Bulnesia sarmienyi* wood. When *guaiol* is dehydrated consequently with sulfur, the non-benzenoid aromatic blue hydrocarbon **X** ($\text{C}_{15}\text{H}_{18}$) is obtained. When this hydrocarbon is dissolved in concentrated sulfuric acid, the intensive blue color disappear. After mixing of this solution with water, **X** is restored in the initial form. It is very difficult to hydrogenate *guaiol* catalytically. As a result of the following transformations the naphthalene derivative **A** may be obtained (substance **A** is the only product of the ozonolysis reaction).



- 1 Determine the structures of *guaiol* and compound **X** if it is known that *guaiol* has the hydroxyl group at the tertiary exocyclic carbon atom.
- 2 Explain why **X** has the blue color. Explain the behavior of **X** in acidic solutions.
- 3 Decipher the above scheme of transformations and explain the formation of **A**.
- 4 How many isoprene fragments are in the molecule of **X**?

- 5 Ascribe the signals in the ^1H NMR spectra of hydrocarbon **X** ^1H : 0,98 (6H, d), 1,56 (3H, s), 1,84 (3H, s), 2,28 (1H, hept), 6,10 (1H, d), 6,21 (1H, d), 6,47 (1H, d), 6,85 (1H, d), 7,55 (1H, d).

Answer



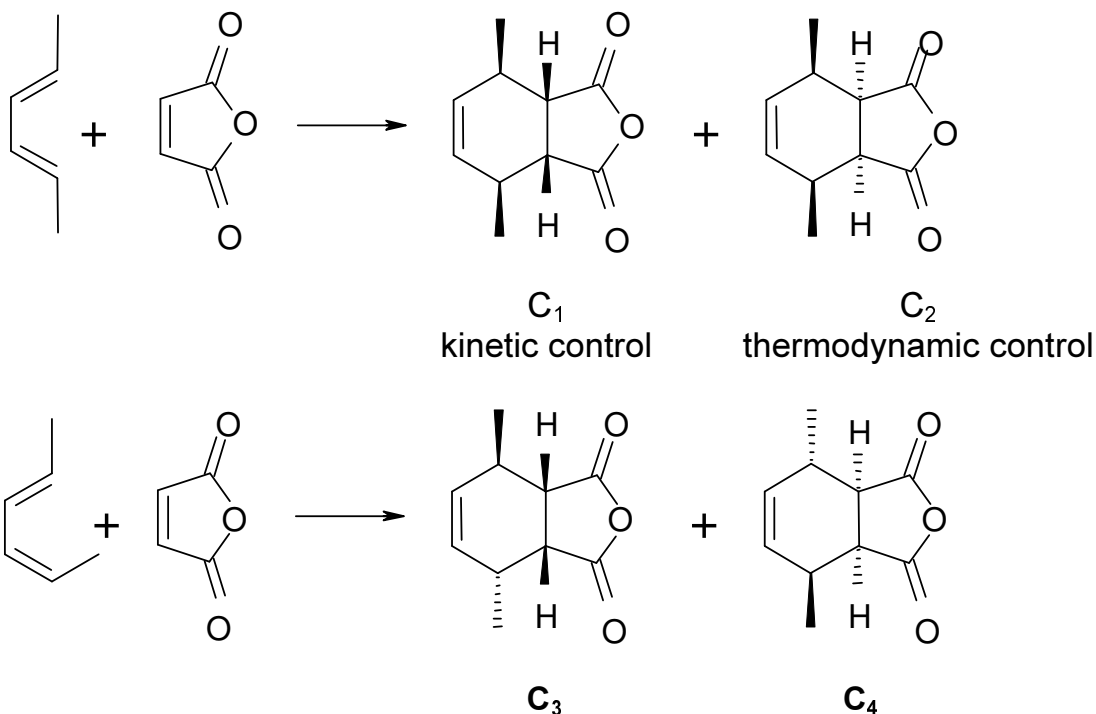
Task 8. The isomeric hydrocarbons **A** and **B** (C_6H_{10}) react with substance **X** in different ways. The mixture of two optically nonactive stereoisomers **C**₁ and **C**₂ is rather easily obtained from **A**. The reaction between **B** and **X** requires a long-continued heating. As a result, the mixture of enantiomers **C**₃ and **C**₄ is obtained with a small yield (**C**₃ and **C**₄ are the stereoisomers of **C**₁ and **C**₂). Only **C**₁ and **C**₂ are formed if the reaction is performed in the presence of I_2 . The acids **Y** and **D**_{*i*} are formed if substances **X** and **C**_{*i*} (*i* = 1, 2, 3, 4) are hydrolyzed (the equivalent molar masses of these acids in the neutralization reactions are equal to $58 \text{ g}\cdot\text{mol}^{-1}$ and $99 \text{ g}\cdot\text{mol}^{-1}$, respectively). Four signals with the ratio of the integral intensities 1 : 1 : 1 : 3 are present in the ^1H NMR spectra of substances **C**₁ and **C**₂. Two intensive bands at 1850 and 1790 cm^{-1} are present in the IR spectra of compounds **X** and **C**_{*i*} (these bands correspond to the symmetric and asymmetric vibrations of one group of atoms).

1. Determine all lettered substances.
2. Give the names of hydrocarbons **A** and **B** according to the *Z,E*-nomenclature.
3. Explain the different reactivity of **A** and **B** and the significance of iodine.
4. The formation of isomers **C**₁ and **C**₂ may be controlled kinetically or thermodynamically. What isomer is formed under the kinetic control and what isomer is resulted from the thermodynamic control?

Answer

X: maleic anhydride; **Y**: maleic acid; **A**: *E,E*-hexa-2,4-dien; **B**: *E,Z*-hexa-2,4-dien.

All substances **C**_{*i*} are drawn in the figure. Substances **D**_{*i*} are the corresponding dicarboxylic acids.



Task 9. NH_4HS is the unstable compound that is easily decomposed to NH_3 and H_2S .

1. Calculate $\Delta_r H_{298}^0$, $\Delta_r S_{298}^0$, $\Delta_r G_{298}^0$ for this reaction.
2. Calculate the standard equilibrium constants and constants K_p for this reaction at 25 and 35 °C.
3. 30,0 g NH_4HS were placed into the evacuated vessel (volume 10,0 L). The vessel was heated to 35 °C. Calculate the pressure in the vessel and the mass of solid at equilibrium.
4. Solution 2 was obtained when 11,48 g NH_4HS were placed at 25 °C in solution 1 obtained after dissolution of 61,50 g $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ in 500 ml of water. Calculate pH of solution 2.

The standard pressure $P_0 = 1,013 \cdot 10^5 \text{ Pa}$

Substance	$\Delta_f H_{298}^0$, $\text{kJ} \cdot \text{mol}^{-1}$	S_{298}^0 , $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$\text{NH}_4\text{HS, solid}$	-156,9	113,4
NH_3, gas	-45,9	192,6
$\text{H}_2\text{S, gas}$	-20,4	205,6

$$\log K_H(\text{NH}_3 + \text{H}^+ = \text{NH}_4^+) = 9,24;$$

$$\log \beta_1(\text{Cu}^{2+} + \text{NH}_3 = \text{CuNH}_3^{2+}) = 3,99; \quad \log \beta_2(\text{Cu}^{2+} + 2 \text{NH}_3 = \text{Cu}(\text{NH}_3)_2^{2+}) = 7,33;$$

$$\log \beta_3(\text{Cu}^{2+} + 3 \text{NH}_3 = \text{Cu}(\text{NH}_3)_3^{2+}) = 10,06; \quad \log \beta_4(\text{Cu}^{2+} + 4 \text{NH}_3 = \text{Cu}(\text{NH}_3)_4^{2+}) = 12,03;$$

The densities of all solutions are equal to 1,000 $\text{g} \cdot \text{ml}^{-1}$. The volume of solid NH_4HS in the vessel and the change of solution volumes at reactions are negligibly small.

Answer

1. The decomposition of NH_4HS :



$$\Delta_r H_{298}^0 = -45,9 - 20,4 - (-156,9) = 90,6 \text{ (kJ} \cdot \text{mol}^{-1}\text{)},$$

$$\Delta_r S_{298}^0 = 192,6 + 205,6 - 113,4 = 284,8 \text{ (J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\text{)}.$$

$$\Delta_r G_{298}^0 = \Delta_r H_{298}^0 - T \cdot \Delta_r S_{298}^0 = 90600 - 298,15 \cdot 284,8 = 5687 \text{ (kJ} \cdot \text{mol}^{-1}\text{)}.$$

2. Let us denote K_a the standard equilibrium constants.

By definition,

$$\Delta_r G_{298}^0 = -RT \ln K_a = -2,3 \cdot RT \log K_a,$$

and for 25 °C

$$\log K_a = -\Delta_r G_{298}^0 / (2,3 \cdot RT) = -5687 / (2,3 \cdot 8,314 \cdot 298,15) = -1,00; \mathbf{K_a = 0,10}.$$

The dimensionless standard equilibrium constant

$$K_a = \prod_i \tilde{P}_i^{v_i} = \prod_i \left(\frac{P_i}{P_0} \right)^{v_i},$$

where P_i is the partial pressure of the i -s species, v_i is its stoichiometric coefficient.

Hence,

$$K_p = K_a \cdot (P_0)^{\Delta v}.$$

$$K_p = 10^{-1} \cdot (1,013 \cdot 10^5 \text{ Pa})^2 = \mathbf{1,03 \cdot 10^9 \text{ Pa}^2}.$$

Calculation of K_a and K_p for 35 °C. From equation

$$d \ln K_a = \frac{\Delta_r H^0}{RT^2},$$

assuming $\Delta_r H_{298}^0 = \text{const}$ one obtains:

$$\ln \left(\frac{K_a^{T_2}}{K_a^{T_1}} \right) = -\frac{\Delta_r H^0}{R} \times \left(\frac{1}{T_2} - \frac{1}{T_1} \right),$$

$$\log K_a^{T_2} = \log K_a^{T_1} - \frac{\Delta_r H^0 (T_1 - T_2)}{2,3 R T_1 T_2},$$

$$\log K_a^{308} = -1,00 - \frac{90600 \times (-10)}{2,3 \times 8,314 \times 298,15 \times 308,15} = -0,48; \mathbf{K_a^{308} = 0,33};$$

$$K_p^{308} = 0,33 \times (1,013 \cdot 10^5 \text{ Pa})^2 = \mathbf{3,34 \cdot 10^9 \text{ Pa}^2}.$$

3. The partial pressures of NH_3 and H_2S at 35 °C are equal to:

$$p(\text{NH}_3) = p(\text{H}_2\text{S}) = (K_p^{308})^{1/2} = (3,34 \cdot 10^9)^{1/2} = 5,78 \cdot 10^4 \text{ Pa}.$$

The total pressure $P_{\text{tot}} = 2 \times 5,78 \cdot 10^4 = \mathbf{1,16 \cdot 10^5 \text{ Pa}}$.

From the Mendeleev-Klapeiron equation

$$PV = n(\text{gas}) \cdot RT,$$

where $n(\text{gas}) = n(\text{NH}_3) = n(\text{H}_2\text{S})$ it is possible to calculate

$$n(\text{gas}) = 5,78 \cdot 10^4 \text{ Pa} \times 10 \cdot 10^{-3} \text{ m}^3 / (8,314 \frac{\text{J}}{\text{mol} \times \text{K}} \times 308 \text{ K}) = 0,23 \text{ mol}.$$

Before reaction

$$n^0(\text{NH}_4\text{HS}) = m^0(\text{NH}_4\text{HS}) / M(\text{NH}_4\text{HS}) = 30,0 \text{ g} / 51 \text{ g} \cdot \text{mol}^{-1} = 0,59 \text{ mol}.$$

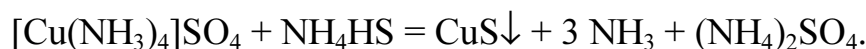
At equilibrium $n(\text{NH}_4\text{HS}_{,\text{solid}}) = 0,59 - 0,23 = 0,36 \text{ (mol)}$,

$$m(\text{NH}_4\text{HS}_{,\text{solid}}) = \mathbf{18,4 \text{ g}}.$$

$$4. n(\text{NH}_4\text{HS}) = 11,48 / 51 = 0,225 \text{ (mol)},$$

$$\begin{aligned} n([\text{Cu}(\text{NH}_3)_4]\text{SO}_4) &= m([\text{Cu}(\text{NH}_3)_4]\text{SO}_4) / M([\text{Cu}(\text{NH}_3)_4]\text{SO}_4) = \\ &= 57,00 / 228 = 0,250 \text{ (mol)}. \end{aligned}$$

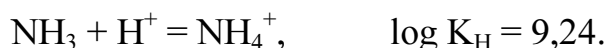
Hence, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ is in an abundance and practically all sulfur is precipitated as CuS :



So, the solution contains $(0,250 - 0,225) = 0,025 \text{ mol} [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$,

$3 \times 0,225 \text{ mol NH}_3$ and $0,225 \text{ mol} (\text{NH}_4)_2\text{SO}_4$.

Practically all Cu(II) exists in the form of $[\text{Cu}(\text{NH}_3)_4]^{2+}$, and pH value is determined by the equilibrium reaction



$$\mathbf{pH} = 9,24 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9,24 + \log \frac{3 \times 0,225}{2 \times 0,225} = 9,24 + \log 1,5 = \mathbf{9,42}.$$