International Olympiad of Kazan Federal University in Chemistry

The final stage
2024-2025 academic year

Recommendations

The maximum score for each task is 25.

When solving computational problems, it is desirable to use numerical values with an accuracy of up to four significant digits. This is especially true for relative **atomic masses**, which are recommended to be used with an **accuracy of up to hundredths**.

Task 1. Guessing game 1

Simple substance **X** dissolves in concentrated nitric acid to form $\mathbf{X_1}$ (***reaction 1***), one of the few water-soluble substances of element **X**. When sodium chloride and iodide are added to a solution of $\mathbf{X_1}$, white and yellow precipitates are observed, respectively (***reactions 2*** and ***3***).

Stoichiometric mixtures of substances $\mathbf{X_2}$ with $\mathbf{X_3}$ and $\mathbf{X_2}$ with $\mathbf{X_4}$, when heated to a temperature of 900°C, react to form the same two products (but in different quantities): simple substance **X** and gas **G** (***reactions 4*** and ***5***). If in two experiments we take identical weighed portions of $\mathbf{X_2}$ and corresponding portions of $\mathbf{X_3}$ (in the first experiment) and $\mathbf{X_4}$ (in the second), and after heating and the reactions, gas **G** is quantitatively absorbed by a solution of $Ca(OH)_2$ (***reaction 6***), then the masses of the white precipitates that fall will be related as 2:1. $\mathbf{X_3}$ can be obtained from $\mathbf{X_2}$ by the action of a concentrated solution of peroxide (***reaction 7***).

When calcined at certain temperatures, $\mathbf{X_1}$ is converted into substance $\mathbf{X_5}$ with a mass loss of 31.0% (***reaction 8***), which, in turn, decreases in mass by another 1.024 times upon further heating (***reaction 9***). The reaction of $\mathbf{X_5}$ with HNO_3 leads to the formation of $\mathbf{X_1}$ and $\mathbf{X_6}$ (***reaction 10***). $\mathbf{X_6}$ is capable of absorbing gas **G** with the formation of $\mathbf{X_3}$ (***reaction 11***).

The interaction of $\mathbf{X_4}$ with a NaOH solution leads to the precipitation of $\mathbf{X_7}$ (***reaction 12***), which is soluble in excess NaOH to form $\mathbf{X_8}$ (***reaction 13***), in which the coordination number of the central atom is 3.

?1. Determine the formulas of substances $\mathbf{X_1}$–$\mathbf{X_8}$, element **X**. Justify your answer with calculations.

?2. Write down the equations of ***reactions 1–13***.

?3. What is the anion shape in $\mathbf{X_8}$?

Task 2. Guessing game 2

Three unknown solutions of individual substances – **A**, **B** and **C** – were discovered in the laboratory. A series of experiments were carried out to determine their composition.

First, to identify the cation, samples of the solutions were introduced into the flame of a gas burner: in all three cases, the flame turned bright yellow.

Then indicator papers were dipped into solutions **A** and **C**. In solution **A** the universal indicator paper turned blue, and in **C** it turned red. Merging some of the solutions with each other led to the release of colorless gas **X**, which entered a glass of distilled water through a gas outlet tube. It turned out that **X** is quite soluble in water.

Solution **B** was added to solution **C**, in which case a colorless gas **Y** was released. Through the gas outlet tube it entered a glass of water, in which **X** had previously been dissolved. Gradually, the water in the glass became cloudy, and a light sediment formed at the bottom.

After this, a piece of chalk was placed in solution **C**. Bubbles of colorless gas **Z** emerged from the solution, but the solution became cloudy and a white sediment remained at the bottom. Then a pre-cleaned iron nail was placed in solution **C**: it gradually became covered with bubbles of colorless gas, which slowly emerged from the solution.

Then bromine water was added to all three solutions. In **A** the red color disappeared and a light precipitate formed, in **B** the color disappeared but no precipitate formed, and in **C** even the red color of the "water" did not disappear.

Additionally, it is known that all three dissolved substances contain three common elements.

?1. What conclusion can be made from the first experiment?

?2. What is the environment in solutions **A** and **C**?

?3. Determine the formulas of gases **X**, **Y** and **Z** and substances in solutions **A**, **B** and **C**.

?4. Write the equations of all the reactions described (7 in total).

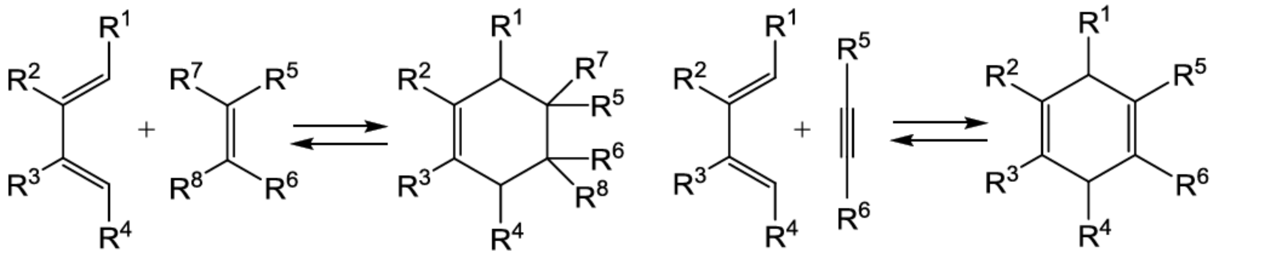
After all the experiments, it was decided not to pour out the remaining solutions. A certain amount of alkali was added to **A** and substance $\mathbf{A_1}$ with an oxygen mass fraction of 59.95% was crystallized, its qualitative composition coinciding with the substance from solution **B**. Solution **B** was evaporated and solid substance $\mathbf{B_1}$ with an oxygen mass fraction of 42.08% was obtained, its qualitative composition not coinciding with the substance initially contained in solution **B**. Solution **C** was evaporated and the residue was calcined. The resulting solid substance $\mathbf{C_1}$ contains 50.43% oxygen and its qualitative composition coincides with $\mathbf{B_1}$.

?5. Determine the formulas of $\mathbf{A_1}$, $\mathbf{B_1}$ and $\mathbf{C_1}$. Justify your answer with calculations.

?6. Draw the structural formulas of the anions contained in $\mathbf{B_1}$ and $\mathbf{C_1}$, if it is known that the anion $\mathbf{B_1}$ is asymmetrical.

Task 3. Strategic importance

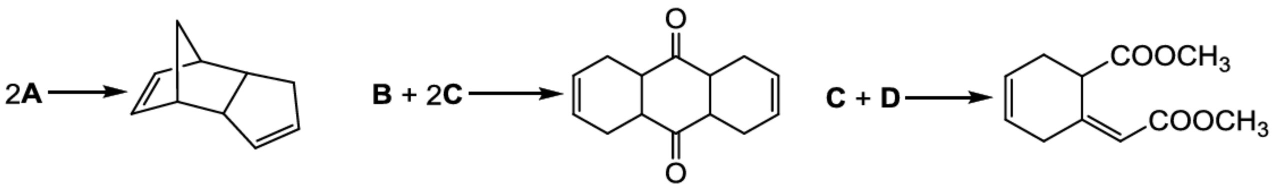
The Diels-Alder reaction is an incredibly important way to prepare six-membered rings from dienes and alkenes/alkynes (collectively referred to as dienophiles in this transformation) in organic synthesis. The general reaction scheme for the two cases mentioned is shown below:



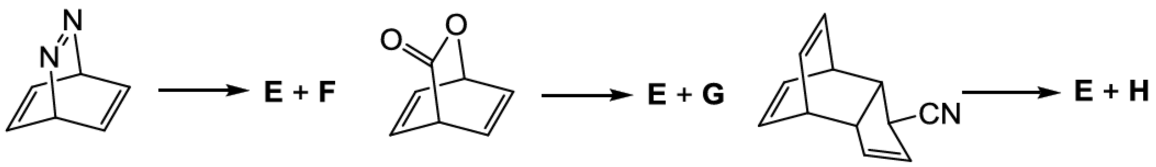
?1. In a mixture of 2,3-dimethylbutadiene-1,3 and tetrafluoroethylene, equilibrium is established, and among the products, two products of the Diels-Alder reaction can be found. Draw their structural formulas, indicate which of the reactants is a diene and which is a dienophile.

?2. How many Diels-Alder reaction products can be formed if a mixture of butadiene-1,3 and propene is used as the reaction mixture? Draw their structures (conformations are not taken into account).

?3. Provide the structural formulas of substances **A**, **B**, **C** and **D** that yield the following products in Diels-Alder reactions (the coefficients in the reactions are placed correctly):



An interesting way of using the Diels-Alder reaction in multi-step organic synthesis is its reversibility – this is the so-called retro-Diels-Alder reaction. Examples are given below:



For the given schemes of the retro-Diels-Alder reaction, there are two possible decay paths in which substance **E** is the same for all three reactions, while substance **E** is not the same for the two decay paths: in the first, substance **E** is a gas; in the second, it is a liquid (at room temperature), and the latter can be obtained from the gas formed in the first path.

?4. Determine the substances **E**, **F**, **G** and **H** for both of the above mentioned decay paths. Draw the structural formulas of the substances. How can we obtain liquid **E** of the second decay path from gas **E** of the first decay path?

Task 4. Silver pseudohalides

Salts of the anions SCN^- and CN^- are called pseudohalides due to their similarity to ordinary halides. Thus, silver thiocyanate is a water-insoluble substance with a solubility constant $K_s = [Ag^+][SCN^-] = 1.1\cdot10^{-12}$.

?1. What is the maximum possible concentration of cyanide ions in a solution containing $2.11\cdot10^{14}$ Ag^+ ions in one liter?

The equilibrium of AgSCN precipitate formation is complicated by the formation of the $[Ag(SCN)_2]^-$ complex. The equilibrium constant of its formation is called the stability constant (β):

$$Ag^+ + 2SCN^- \rightleftharpoons [Ag(SCN)_2]^- \qquad \beta = 3.7\cdot10^7$$

?2. Express β in terms of the equilibrium concentrations of ions in the solution.

?3. Obtain an expression for the solubility of silver cyanide s (mol/l), equal to the total concentration of particles containing silver in a solution with a known concentration of CN^- through K_s and β. Find the concentration of cyanide ions at which the solubility is minimal.

?4. At what maximum concentration of cyanide ions the solubility does not exceed 10^{-5} mol/l?

Another pseudohalide that will be discussed is silver cyanide. Solid silver cyanide can be considered an inorganic polymer in which each cyanide ion forms two bonds with silver atoms through lone electron pairs. The decomposition reaction of silver cyanide upon heating is used to produce gaseous cyanogen (C_2N_2). The enthalpies of formation of AgCN and C_2N_2 are −146 and 309 kJ/mol, respectively.

?5. Draw the structural formula of polymeric AgCN and C_2N_2 molecule. What is the coordination number of silver in AgCN?

?6. Calculate the enthalpy of the decomposition reaction (per 1 mole of cyanogen) using the given values.

?7. For precise calculations of the enthalpy of formation, it is customary to recalculate for the reaction temperature. Using the following dependence of the molar heat capacity of C_2N_2 (J/(mol·K)) on temperature, calculate the heat required to heat 1 mole of cyanogen from 298 K to 528 K (the decomposition temperature of AgCN), and the enthalpy of formation of C_2N_2 at this temperature:

$$c(C_2N_2) = 34.00 + 0.09645T$$