International Olympiad of Kazan Federal University in Chemistry

The final stage
2024-2025 academic year

Solutions and scoring

Task 1. Guessing game 1

Solution

1. The solution to the problem must begin with determining the substances $\mathbf{X_1}$ and $\mathbf{X_5}$. $\mathbf{X_1}$ is a nitrate, since it is formed in a reaction with nitric acid. Then $\mathbf{X_5}$ is some kind of oxide of element **X**. The further description of the reaction of $\mathbf{X_5}$ with nitric acid (namely the formation of two **X**-containing products) indicates that this is a mixed oxide. Let's try to determine **X**, assuming that $\mathbf{X_5}$ has the composition $\mathbf{X_3O_4}$. Let's write the equation of ***reaction 1*** in general form:

$$6\mathbf{X}(NO_3)_n = 2X_3O_4 + 6nNO_2 + (3n-4)O_2$$

The mass loss was 31.0%. Then:

$$2M(\mathbf{X}_3O_4) : 6M(\mathbf{X}(NO_3)_n) = 1 - 0.31$$

Let us denote the mass of element **X** as x, then:

$$(6x + 16\cdot8) : (6x + 372n) = 0.69$$

Hence $x = 138n - 68.84$. Going through the oxidation state of **X** in nitrate (n), we get x. At $n = 2$ $x = 207.2$, which corresponds to lead. Therefore, **X** – Pb, $\mathbf{X_1}$ – $Pb(NO_3)_2$, $\mathbf{X_5}$ – Pb_3O_4, $\mathbf{X_6}$ – PbO_2.

Gas **G** causes lime water to become cloudy, and enters into redox reaction with PbO_2, which means **G** is SO_2, $\mathbf{X_3}$ is $PbSO_4$. Returning to the second paragraph: ***reactions 4*** and ***5*** produce Pb and SO_2, and in the case of the fifth reaction the amount of sulfur dioxide is twice as large. This makes it clear that $\mathbf{X_2}$ is PbS, $\mathbf{X_4}$ is PbO.

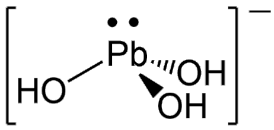
The last paragraph describes the amphoteric properties of lead, meaning $\mathbf{X_7}$ – $Pb(OH)_2$, which dissolves in excess alkali to form $\mathbf{X_8}$ – $Na[Pb(OH)_3]$.

2. Reaction equations:

$$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$
$$Pb(NO_3)_2 + 2NaCl \rightarrow PbCl_2\downarrow + 2NaNO_3$$
$$Pb(NO_3)_2 + 2NaI \rightarrow PbI_2\downarrow + 2NaNO_3$$

$PbS + PbSO_4 = 2Pb + 2SO_2$
$2PbO + PbS = 3Pb + SO_2$
$SO_2 + Ca(OH)_2 = CaSO_3 + H_2O$
$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$
$3Pb(NO_3)_2 = Pb_3O_4 + 6NO_2 + O_2$
$2Pb_3O_4 = 6PbO + O_2$
$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O$
$PbO_2 + SO_2 = PbSO_4$
$Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 + 2NaNO_3$
$Pb(OH)_2 + NaOH = Na[Pb(OH)_3]$

3. In the $[Pb(OH)_3]^-$ anion, lead has three substituents and one unshared electron pair (type AX_3E according to the Gillespie method), therefore, it has a pyramidal geometry:



Scoring:
1. Substances **X**, **X_1-X_8**, **G** – **1 point each**. Total **10 points**.
2. ***Reactions 1-13*** – **1 point each**. Total **13 points**.
3. Geometry of the $[Pb(OH)_3]^-$ ion – **2 points**.

Task 2. Guessing game 2

Solution

1. The color of the flame indicates that all compounds contain sodium.

2. In solution **A** the environment is alkaline, in solution **C** it is acidic.

3. Solution **C** behaves as an acid in many reactions: it reacts with iron and chalk, releasing gases; gases are also released when **C** interacts with **A** and **B**. Most likely, **C** is an acidic salt. Since **C** forms a precipitate with chalk, this acidic salt can be either hydrogen sulfate or dihydrogen phosphate.

From **A** and **B**, when reacting with the "acid" (**C**), colorless gases are released (these can be sulfites, carbonates, sulfides, cyanides, etc.), which form a light precipitate when passed into one solution. Of the listed anions that release gases with acids, only sulfite and sulfide are suitable, since hydrogen sulfide and sulfur dioxide easily react with the release of sulfur: $2H_2S + SO_2 \rightarrow 3S\downarrow + 2H_2O$. This also satisfies the condition that the three substances contain 3 common elements: one of them is sodium, and the other is sulfur. Then substance **C** is sodium hydrosulfate, $NaHSO_4$.

To distinguish solutions **A** and **B**, let us consider the last experiments. Sulfite will be oxidized by bromine water without forming a precipitate (solution **B**), and sulfide will be oxidized with the release of $S\downarrow$ (solution **A**).

However, all substances also contain a third common element. Oxygen cannot be contained in the substance from solution **A**, which behaves in all reactions as sodium sulfide. However, all three salts can be acidic, and then the third common element is hydrogen. Therefore, **A** is NaHS, sodium hydrosulfide, and **B** is $NaHSO_3$, sodium hydrosulfite.

Gas **X** is released from **A**, this is hydrogen sulfide, H_2S. **Y** is released from **B**, this is SO_2. **Z** is released from chalk, this is carbon dioxide, CO_2.

4. Reaction equations:

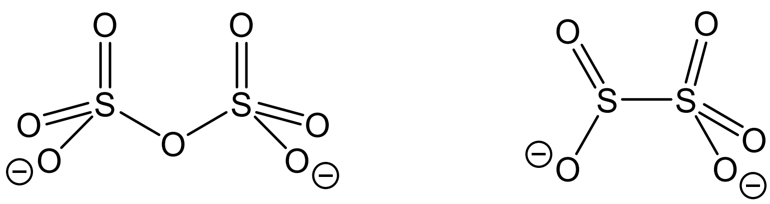
$NaHSO_4 + NaHS \rightarrow Na_2SO_4 + H_2S\uparrow$
$NaHSO_4 + NaHSO_3 \rightarrow Na_2SO_4 + H_2O + SO_2\uparrow$
$2H_2S + SO_2 \rightarrow 3S\downarrow + 2H_2O$
$CaCO_3 + 2NaHSO_4 \rightarrow CaSO_4\downarrow + Na_2SO_4 + H_2O + CO_2\uparrow$
$Fe + 2NaHSO_4 \rightarrow FeSO_4 + Na_2SO_4 + H_2\uparrow$
$Br_2 + NaHS \rightarrow S\downarrow + NaBr + HBr$
$Br_2 + NaHSO_3 + H_2O \rightarrow NaHSO_4 + 2HBr$

5. Alkali can convert hydrosulfide to sodium sulfide. Since $\mathbf{A_1}$ is qualitatively identical to $NaHSO_3$, it may be sodium sulfide crystal hydrate, $Na_2S\cdot nH_2O$. From the equation $16n : (78 + 18n) = 0.5995$ we find $n = 9$, that is, $\mathbf{A_1}$ is $Na_2S\cdot 9H_2O$.

Since the qualitative composition changes during crystallization of the $NaHSO_3$ solution, dehydration may occur, and $\mathbf{B_1}$ does not contain hydrogen. If the oxidation state of sulfur has not changed, then the formula can be represented as $Na_{2x}S_yO_{x+2y}$ (based on the oxidation states of the elements). Then from the equation $16(x + 2y) : (62x + 64y) = 0.4208$, we find the ratio $y = 2x$, that is, the formula of the compound is $Na_{2x}S_{2x}O_{5x}$, that is, $\mathbf{B_1}$ is $Na_2S_2O_5$ (sodium pyrosulfite).

When sodium hydrogen sulfate is calcined, dehydration also occurs, forming $Na_2S_2O_7$, sodium pyrosulfate. By calculating the mass fraction, one can verify the correctness of this assumption, $\mathbf{C_1}$ – $Na_2S_2O_7$.

6. Structural formulas for $S_2O_7^{2-}$ and $S_2O_5^{2-}$:



Scoring:

1. Sodium indication – **1.5 points**.

2. Correctly determined environment of both solutions – **1.5 points**.

3. Formulas **A**, **B**, **C** – **1.5 points each**, formulas **X**, **Y**, **Z** – **1 point each**. Total **7.5 points**.

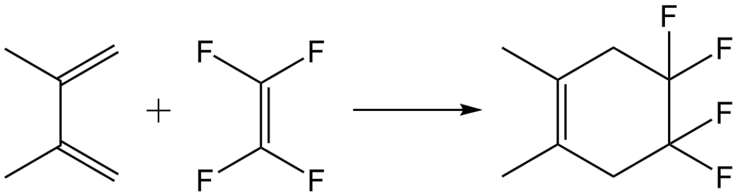
4. Equations of 7 reactions – **1 point each**. Total **7 points**.

5. Formulas of three compounds – **1.5 points each**. Total **4.5 points**.
6. Structural formulas of two anions – **1.5 points each**. Total **3 points**.

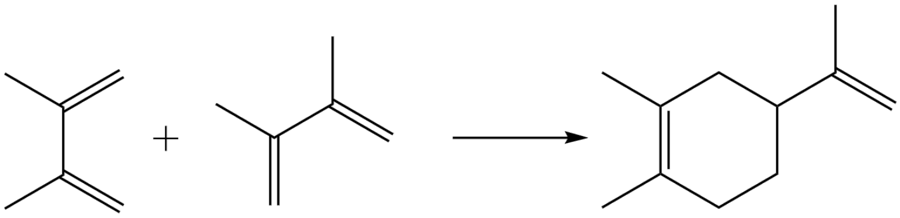
Task 3. Strategic importance

Solution

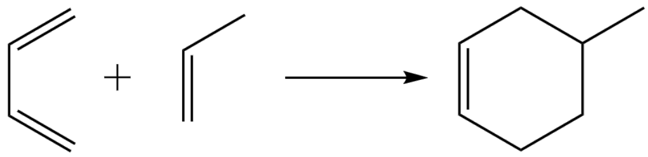
1. In the first case, 2,3-dimethylbutadiene-1,3 is a diene, and tetrafluoroethylene is a dienophile:

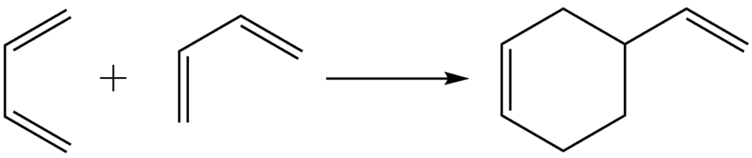


In the second case, 2,3-dimethylbutadiene-1,3 is both a diene and a dienophile:

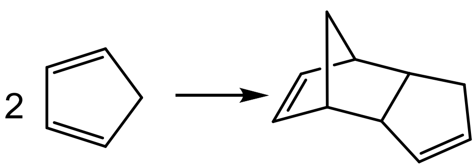


2. 2 products are formed:

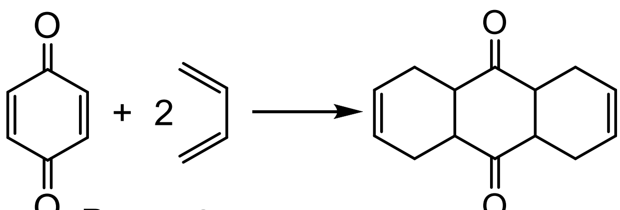




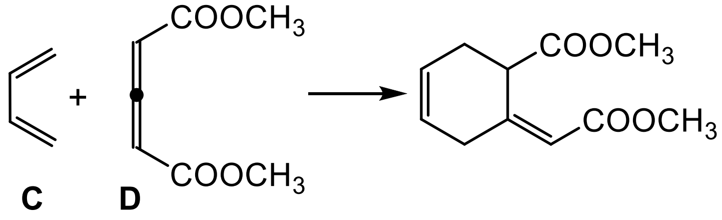
3. Compounds **A**–**D** undergo classical Diels–Alder reactions. In the second reaction, it occurs twice. In the third reaction, the dienophile is the allene fragment.:



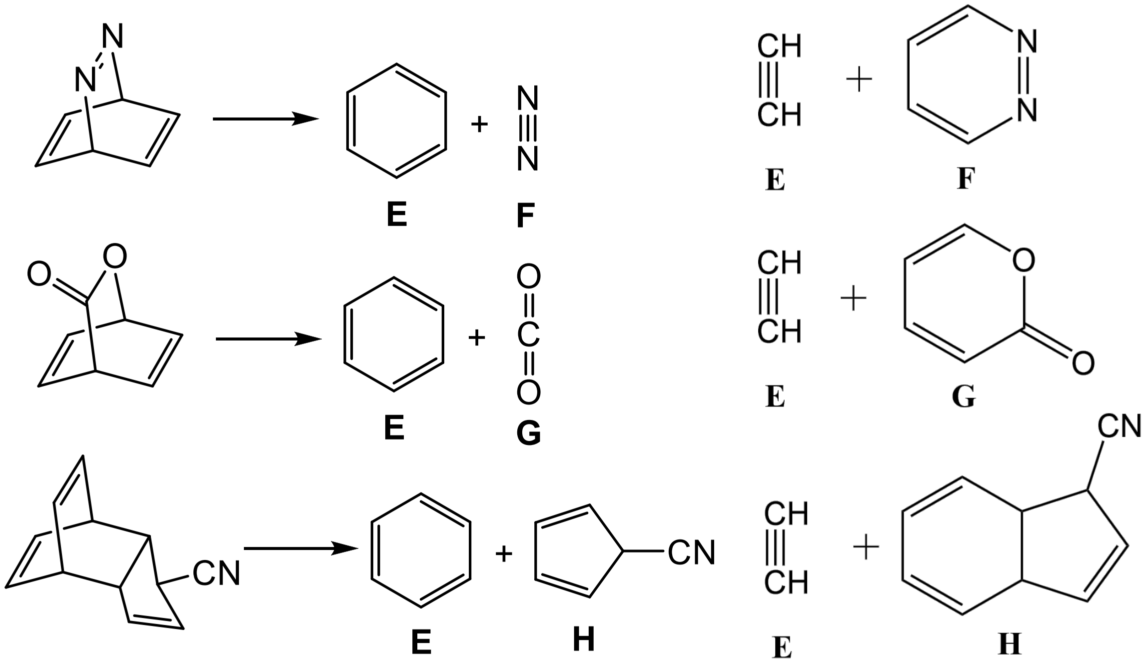
A



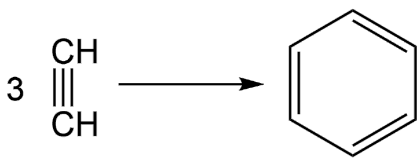
B **C**



4. The stable molecule formed from the substances described in the condition, according to the reaction reverse to the Diels-Alder reaction, can be benzene (liquid **E**) or acetylene (gas **E**). The decay paths with the formation of the mentioned compounds are shown in the diagram below with the formation of benzene (left) and the formation of acetylene (right):



Benzene can be obtained by catalytic trimerization of acetylene:



Scoring:

1. 2 product structures – **1 point each**, determination of dienes and dienophiles – **1 point** for **each** product. Total **4 points**.

2. 2 product structures – **1 point each**. Total **2 points**.

3. Structures of substances **A**, **B**, **C** and **D** – **1.5 points each**. Total **6 points**.

4. Structures of 8 substances – **1.5 points each**, obtaining benzene from acetylene – **1 point**. Total **13 points**.

Task 4. Silver pseudohalides

Solution

1. The amount of silver ions in 1 liter: $n = N/N_A = 3.5 \cdot 10^{-10}$ mol, means $[Ag^+] = 3.5 \cdot 10^{-10}$ M. $[SCN^-] = K_s / [Ag^+] = 3.1 \cdot 10^{-3}$ M.

2. The constant of complex formation can be expressed by the following equation in terms of the equilibrium concentrations of particles:

$$\beta = \frac{[Ag(SCN)_2^-]}{[Ag^+][SCN^-]^2}$$

3. Solubility is the sum of the concentrations of the complex and free silver in the solution: $s = [Ag^+] + [Ag(CN)_2^-]$, from where:

$$s = [Ag^+] + \beta[Ag^+][SCN^-]^2 = \frac{K_s}{[SCN^-]} + \beta\frac{K_s}{[SCN^-]}[SCN^-]^2 = \frac{K_s}{[SCN^-]} + \beta K_s[SCN^-]$$

To find the minimum, the derivative of solubility with respect to $[SCN^-]$ can be set to zero:

$$\frac{ds}{d[SCN^-]} = -\frac{K_s}{[SCN^-]} + \beta K_s = 0$$

$$[SCN^-] = \frac{1}{\sqrt{\beta}} = 1.64 \cdot 10^{-4}$$

4. The solubility goes through a minimum, so we need to choose the larger of the two roots of the equation:

$$10^{-5} = \frac{K_s}{[SCN^-]} + \beta K_s[SCN^-]$$

$$10^{-5} = \frac{1.1 \cdot 10^{-12}}{[SCN^-]} + 3.7 \cdot 10^{-3}[SCN^-]$$

$$10^{-5}[SCN^-] = 1.1 \cdot 10^{-12} + 3.7 \cdot 10^{-3}[SCN^-]^2$$

Roots of a quadratic equation are: $[SCN]_1 = 2.7 \cdot 10^{-3}$ M, $[SCN]_2 = 1.1 \cdot 10^{-7}$ M. We choose as the answer the root $[SCN]_1 = \mathbf{2.7 \cdot 10^{-3}}$ **M** as the larger of the two.

5. Structural formulas of the coordination polymer and dicyanogen:

The coordination number of silver in the coordination polymer is 2.

6. Decomposition reaction equation: $2AgCN \rightarrow 2Ag + C_2N_2$. From where:

$\Delta_r H = \Delta_f H(C_2N_2) - 2 \cdot \Delta_f H(AgCN) = 601$ kJ/mol.

7. Heat capacity is the amount of heat required to heat 1 mole of a substance per unit temperature. If it depends on temperature, heat capacity is the derivative of heat with respect to temperature.

$$c = \frac{dQ}{dT} = 34 + 0.09645T$$

$$dQ = (34 + 0.09645T)dT$$

$$Q = \int_{298}^{528} (34 + 0.09645T)dT = \left(34T + 0.09645\frac{T^2}{2}\right)\Bigg|_{298}^{528} =$$

$$\left(34 \cdot 528 + 0.09645 \cdot \frac{528^2}{2}\right) - \left(34 \cdot 298 + 0.09645 \cdot \frac{298^2}{2}\right) = 16982 \text{ Дж} \approx 17 \text{ кДж}$$

Heating means an increase in the enthalpy of a substance, which means:

$\Delta_f H_{528K} = \Delta_f H_{298K} + Q = 326$ kJ/mol.

Scoring:

1. The amount of Ag^+ ions and the concentration of SCN^- are **1 point each**. Total **2 points**.

2. Expression for β – **2 points**.

3. Expression for s, derivative of s, numerical value of concentration are **2 points each**. Total **6 points**.

4. Calculation of concentration – **3 points**.

5. 2 structural formulas and silver CN – **1 point each**. Total **3 points**.

6. Calculation of the enthalpy of reaction – **2 points**.

7. Writing the general form of the integral – **2 points**, calculating heat – **3 points**, calculating the enthalpy of formation – **2 points**. Total **7 points**.