

# Theoretical tour 1

## Solutions

### Problem 1 (author Gulevich D. G.)

1. Calculation the value of Henry's constant at 278 K:  $\ln \left[ \frac{k(T_2)}{k(T_1)} \right] = \frac{-\Delta H^\circ(T_1 - T_2)}{RT_1 T_2}$ .

By substituting numerical values, we obtain that  $k_H(278 \text{ K}) = 0.059 \text{ M}\cdot\text{atm}^{-1}$ . Then at 278 K in 500 mL of water at the indicated pressure dissolves  $0.059 \times 2.0 \times 0.5 = 0.059 \text{ mol CO}_2$ , which corresponds to 0.52 mass%. Therefore, the water obtained under the above conditions is highly carbonated. Determination of  $k_H(278 \text{ K})$  1.5 points, calculation of  $n(\text{CO}_2)$  in mol. and mass.% by 0.5 points, **total 2.5 points.**

2. In area I, the value  $P(\text{CO}_2)$  is described by the ideal gas equation:  $P(\text{CO}_2) V_{\text{gas}} = n_{\text{gas}} RT$ . In area II:  $C(\text{CO}_2) = n_{\text{liq}} / V_{\text{liq}} = k_H \cdot P(\text{CO}_2)$ . It is also known from the text of the problem that  $n_{\Sigma}(\text{CO}_2) = n_{\text{gas}} + n_{\text{liq}}$ . Solving this system of equations, we find an expression for the pressure of carbon dioxide in the closed bottle:

$$P_{\text{CO}_2} = \frac{n_{\Sigma} RT}{V_{\text{gas}} + k_H V_{\text{liq}} RT} \quad \mathbf{2.5 \text{ points}}$$

3. The volume occupied by the gas phase can be calculated as the volume of the bottle neck cylinder:  $V_{\text{gas}} = \pi r^2 h = 3.14 \times (0.014)^2 \times 0.04 = 2.5 \cdot 10^{-5} \text{ m}^3$ . Converting Henry's constant into  $\text{mol}\cdot\text{m}^{-3}\cdot\text{Pa}^{-1}$ , we calculate of  $P(\text{CO}_2)$ :

$$P_{\text{CO}_2} = \frac{0.045 \cdot 8.314 \cdot 298}{2.5 \cdot 10^{-5} + 3.3 \cdot 10^{-2} : 10^{-3} : 101325 \cdot 5 \cdot 10^{-4} \cdot 8.314 \cdot 298} = 2.6 \cdot 10^5 \text{ Pa. } \mathbf{1 \text{ point}}$$

4. Taking into account the indicated assumptions and the given constants, we obtain  $k_{a1} = [\text{H}^+]^2 / k_H P_{\text{CO}_2}$ . Therefore,  $\text{pH} = 5.7$  **2 points.**

5. At a constant temperature  $P_1 V_1 = P_{\text{atm}} V_{\text{surf}}$ . Pressure at the bottom of the source  $P_1$

$$= P_{\text{atm}} + \rho_{\text{H}_2\text{O}} gh. \text{ Then } (P_{\text{atm}} + \rho_{\text{H}_2\text{O}} gh) V_1 = P_{\text{atm}} V_{\text{surf}} \text{ and } \frac{V_{\text{surf}}}{V_1} = \frac{R_{\text{surf}}^3}{R_1^3} = \frac{1 + \rho gh}{P_{\text{atm}}}$$

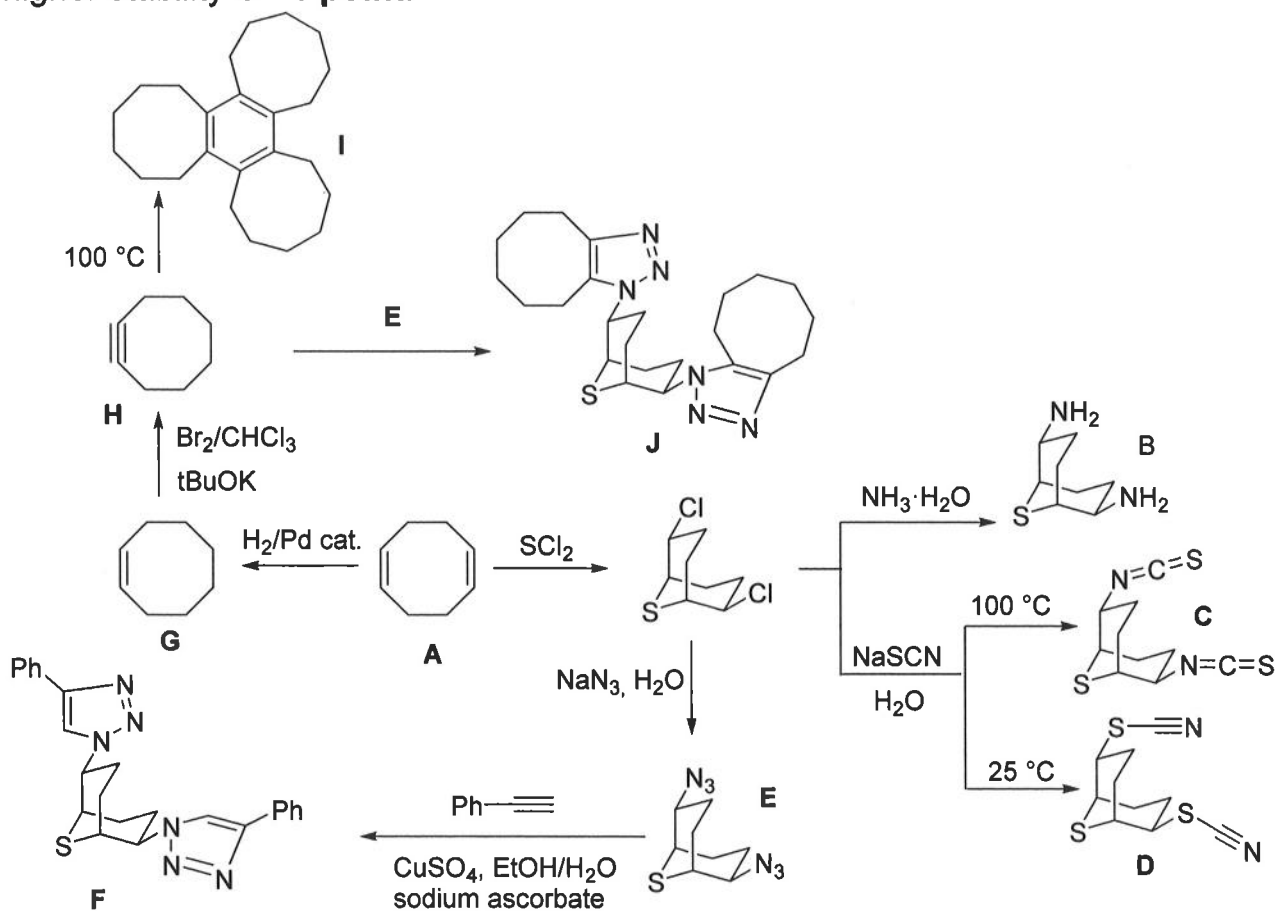
Consequently, the radius of the bubble when it reaches the surface will be

$$0.4 \cdot 10^{-3} \left( 1 + \frac{1000 \cdot 9.8 \cdot 30}{101325} \right)^{1/3} = 0.63 \text{ mm, i. e. will increase by 0.23 mm. } \mathbf{2 \text{ points.}}$$

### Problem 2

1. The reaction of **A** and **X** leads to the formation of a bicyclic adduct, from its structure it is clear that **A** is cyclooctadiene-1,5, and **X** is  $\text{SCl}_2$ . The reaction is of **A** and **X** an example of electrophilic addition. Subsequent reactions with ammonia, sodium thiocyanate and sodium azide are examples of nucleophilic substitution. **B** is the corresponding diamine, **C** is isothiocyanate, and **D** is thiocyanate. Rhodanide is an ambident anion that has two nucleophilic centers – the nitrogen and the sulfur. At room temperature, **D** is formed (kinetic control), in some cases thiocyanates can be converted to isothiocyanates, which are more stable products (thermodynamic control). The reaction with sodium azide leads to the formation of bis-azide **E**. The 2022 Nobel Prize was awarded for the reactions of organic azides with acetylenes. There are two major versions: the catalytic version, for example CuAAC (copper catalyzed cycloaddition of azides and alkynes), as well as with strained acetylenes

(SPAAC - strain-promoted cycloaddition azides and alkynes). The reaction of **E** and phenylacetylene is CuAAC leading to the regioselective formation of 1,4-substituted 1,2,3-triazoles. The transformation of **A** into **G** is the partial hydrogenation of one double bond. Exhaustive hydrogenation can be excluded taking into account the high reactivity of **G** and **H**. Bromination of **G** and subsequent action of potassium *tert*-butoxide yields strained cyclooctyne, which can enter into SPAAC with **E** to give cycloadduct **J**. When cyclooctyne is heated, it trimerizes to form the corresponding benzene **I**. Structures **B**, **E**, **C**, **D** 0.5 points each, other structures 1 point each, higher stability **C** - 1 point.



### Problem 3 (author Karpushkin E. A.)

1. The particle surface area is the total area of two square in-plane edges  $a^2$  and four rectangular (side) edges  $ad$ :  $S = 2a^2 + 4ad$ . The particle volume is  $V = a^2d$ . Hence, the dispersity is  $D = \frac{S}{V} = \frac{2}{d} + \frac{4}{a}$ . The particle mass is  $m = V\rho = a^2d\rho$ , then its specific surface area is  $S_{sp} = \frac{2}{d\rho} + \frac{4}{a\rho}$  (2 points).

2. From the accurate expression for the dispersity  $D = \frac{S}{V} = \frac{2}{d} + \frac{4}{a}$  it is clear that if  $a \gg d$ , the second term is negligibly small in comparison with the first one (this is what the independence of  $D$  on  $a$  means). The dispersity neglecting  $a$  is  $D' = \frac{2}{d}$ . The condition on the difference between the true and approximate dispersity  $D - D' \leq 0.01D$  or  $1 - \frac{D'}{D} \leq 0.01 \Leftrightarrow 1 - \frac{2/d}{2/d + 4/a} \leq 0.01$  is held at  $\frac{a}{d} \geq 198$  (1 point).

3. Let us calculate the mass of a  $1 \text{ m}^2$  graphene layer. From graphite structure, each right hexagon with the side length equal to the C-C bond contains  $6 \cdot 1/3 = 2$  carbon

atoms (each carbon atom in graphite belongs to three adjacent hexagons). Area of the right hexagon with the side length  $r_{C-C}$  equals  $\frac{3\sqrt{3}}{2} r_{C-C}^2 = 5.24 \cdot 10^{-20} \text{ m}^2$ , and mass of two carbon atoms is  $\frac{2 \cdot 12.01}{6.02 \cdot 10^{23}} = 3.99 \cdot 10^{-23} \text{ g}$ , i. e. mass of the graphene is  $d_s = 7.61 \cdot 10^{-4} \text{ g} \cdot \text{m}^{-2}$ . Specific surface area of a graphite layer equals  $2/d_s = 2628 \text{ m}^2 \cdot \text{g}^{-1}$  (since graphene layer has two surfaces) **(2 points)**.

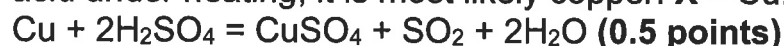
4. Under condition of complete coverage with the adsorbate monolayer, 1 g of graphene can hold  $2628 \text{ m}^2 / 0.025 \text{ nm}^2 = 1.05 \cdot 10^{23}$  molecules, i. e. 0.175 mol of the adsorbate **(1 point)**.

5. Evidently, surface area of the  $n$ -layered graphite particle is  $n$  times smaller than that of a single-layer graphene of the same mass (since we neglect the adsorption at the side edges and intercalation between the graphite layers). Then, maximum amount of the adsorbate at the graphite particle with mass of 1 g is  $\frac{0.175}{n}$  mol. Since it is given that this value is 0.001 mol, number of layers in the considered particle is  $\frac{0.175}{0.001} = 175$  **(2 points)**.

6. The interlayer spacing in graphite is required to recalculate the number of layers into the particle thickness. Let us consider a graphite cube with 1 m edges. Its mass (from the density given in the task) is  $2.15 \cdot 10^6 \text{ g}$ , whereas the mass of  $1 \text{ m}^2$  of the single layer (cf. i. 3) equals  $7.61 \cdot 10^{-4} \text{ g}$ ; therefore, this cube consists of  $2.15 \cdot 10^6 / 7.61 \cdot 10^{-4} = 2.83 \cdot 10^9$  layers, and the interlayer spacing is  $1 / 2.83 \cdot 10^9 = 3.54 \cdot 10^{-10} \text{ m}$  (0.354 nm). Hence, thickness of the graphite particle consisting of 175 layers is  $174 \cdot 3.54 \cdot 10^{-10} = 6.16 \cdot 10^{-8} \text{ m}$  (61.6 nm) **(2 points)**.

#### Problem 4 (author M.S. Likhanov)

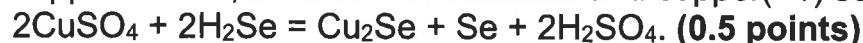
1. **X** and **Y** – are red-orange simple substances. These can be metallic copper, red phosphorus, red selenium, bromine. Since **X** dissolves in concentrated sulfuric acid under heating, it is most likely copper. **X** – Cu.



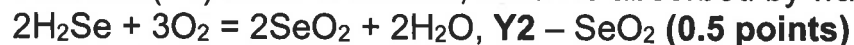
In addition, it is known that the  $\omega(\text{O}) = 1/4\omega(\text{X})$  in one of the **X** oxides. Thus,  $\omega(\text{O}) = 0.2$  and  $\omega(\text{X}) = 0.8$ . For the **XO** formula of oxide, we obtain  $M(\text{X}) = 64 \text{ g/mol}$ , which confirms the initial assumption. (0.5 points for calculation)

Since **X** and **Y** are in the same period of the Periodic Table, we conclude that **Y** is selenium or bromine. Binary compound of **Y** with aluminum is subject to hydrolysis. Aluminum bromide is highly soluble in water therefore **Y** cannot be bromine, then **Y** is Se. During the hydrolysis of aluminum selenide, a poisonous gas, hydrogen selenide, is emitted.  $\text{Al}_2\text{Se}_3 + 6\text{H}_2\text{O} = 3\text{H}_2\text{Se} + 2\text{Al}(\text{OH})_3$ , **Y1** –  $\text{H}_2\text{Se}$

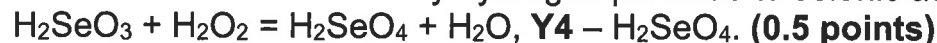
$\text{H}_2\text{Se}$  really exhibits reducing properties, when it is passed through a solution of copper sulfate, a mixture of selenium and copper(+1) selenide precipitates:



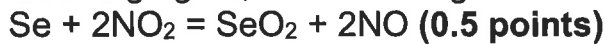
Since **X1** has a qualitative composition similar to **X3** (a binary compound between Cu and Se), then **X1** is  $\text{Cu}_2\text{Se}$ . When  $\text{H}_2\text{Se}$  is burned in excess of oxygen, selenium(+4) oxide is formed, which is absorbed by water to form selenous acid.



Selenous acid is oxidized by hydrogen peroxide to selenic acid:



Let's consider how else oxides of selenium(+4) can be obtained. Gas **G** is an oxidizing agent, with  $M = 46 \text{ g/mol}$  – it can be  $\text{NO}_2$ . (0.5 points for calculation).



This reaction proceeds energetically and is self-sustaining, as  $\text{NO}$  oxidizes in air to form again a  $\text{NO}_2$ , which again oxidizes selenium.

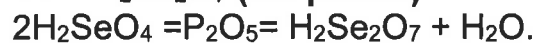
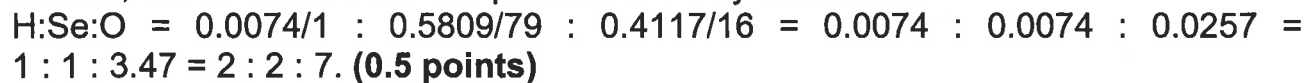
Earlier, we established the composition of one of the copper oxides –  $\text{CuO}$  – when it is fused with  $\text{SeO}_2$ , copper(+2) selenite is formed:



The reduction of  $\text{CuSeO}_3$  with ammonia leads to the formation of copper(+2) selenide:  $\text{CuSeO}_3 + 2\text{NH}_3 = \text{CuSe} + \text{N}_2 + 3\text{H}_2\text{O}$ , **X3** –  $\text{CuSe}$ . (0.5 points)

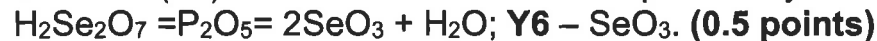
**(0.3 points for each unknown compound, 3 point in total. 1 point for calculations in total. 0.5 points for each selected reactions, 3 points in total)**

2. Obviously, several water molecules are lost under the gradual dehydration of selenic acid, but at first complete dehydration does not occur and pyroselenic acid is formed; Let us confirm the composition of **Y5** by calculation:

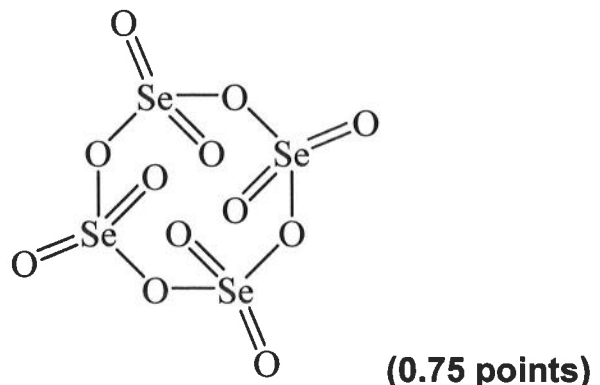
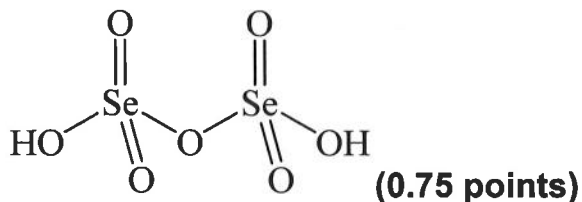


The structure of pyroselenic acid is similar to pyrosulfuric acid - two  $\text{SeO}_4$  tetrahedra connected through a common vertex:

Selenium(+6) oxide is formed under complete dehydration:



$\text{SeO}_3$  possesses a molecular structure. Let us calculate the composition of its structure unit. The molar mass of  $\text{SeO}_3$  lies in the range of 400-520 g/mol - this corresponds to 4  $M(\text{SeO}_3)$ ,  $M((\text{SeO}_3)_4) = 508 \text{ g/mol}$ . We can assume the structure of  $\text{SeO}_3$  -  $\text{SeO}_4$  tetrahedra are connected in a cycle through common vertices.



### Problem 5 (Khvalyuk V.N.)

When stored in air, lime can absorb water and carbon dioxide. During drying, water is removed, therefore, the sample consists of hydroxide and calcium carbonate (impurity). Reactions take place:  $\text{Ca(OH)}_2 + 2\text{HNO}_3 = \text{Ca(NO}_3)_2 + 2\text{H}_2\text{O}$ ;  $\text{CaCO}_3 + 2\text{HNO}_3 = \text{Ca(NO}_3)_2 + \text{H}_2\text{O} + \text{CO}_2$  **(0.5 points per reaction, 1 point in total)**

During cooling, either calcium nitrate itself or its crystalline hydrate could precipitate of the solution.  $\text{Ca(NO}_3)_2 \cdot x\text{H}_2\text{O}$ . Theoretically, when the deposited precipitate was heated, different solid products could be formed:



The low temperature (220 °C) refers in favor to the latter process, at which the mass

decreases by 30.50% (removal of crystallization water). This means that the mass fraction of water of crystallization in A is 30.50%.

$$M_r(\text{Ca}(\text{NO}_3)_2) = 164.1 \quad M_r(\text{H}_2\text{O}) = 18.0; \quad 0.3050 = \frac{x \cdot 18.0}{164.1 + x \cdot 18.0}$$

Solving this equation, we get  $x = 4$ . Substance **A** –  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , **B** –  $\text{Ca}(\text{NO}_3)_2$ . The final solid residue of the subsequent thermolysis of  $\text{Ca}(\text{NO}_3)_2$  will be calcium oxide. Substance **C** –  $\text{CaO}$ . **(1 point per each substance, 3 points in total)**

The mass of the reactants is  $(34.85 + 85.00 \cdot 1.138) = 131.58$  g. The mass of the resulting solution is  $2 \cdot (24.98 + 40.02) = 130.00$  g. The difference between these values is the mass of  $\text{CO}_2$  released.  $M_r(\text{CO}_2) = 44.0$   $M_r(\text{CaCO}_3) = 100$

It is formed  $(131.58 - 130.00) = 1.58$  g or  $\frac{1.58}{44.0} = 0.036$  mol  $\text{CO}_2$ . It means that the initial sample contained 0.036 mol or  $0.036 \cdot 100 = 3.60$  g of  $\text{CaCO}_3$ . Its mass fraction in the initial sample is equal to  $\frac{3.60}{34.85} = 0.103 = 10.3\%$ . **(2 points)**

1. During the thermolysis of  $\text{Ca}(\text{NO}_3)_2$ , a redox reaction occurs. The oxidizing agent is N(+5), the reducing agent is O(-2). The oxidation product will be oxygen  $\text{O}_2$ , but not everything is so simple with the reduction product. In school chemistry textbooks, this product is N(+4) (in the form of  $\text{NO}_2$ ). However, like everything related to nitric acid (remember its reaction with metals) and nitrates (thermolysis), this is not so obvious. The composition of the products largely depends on the conditions of the process. Products may include N(+2) (as  $\text{NO}$ ). It can also be assumed that the products will also contain a mixture of different states of nitrogen, for example, N(+4) and N(+2), as is the case (in reality) when nitric acid reacts with metals. Let us determine the molar ratio of the initial salt and the evolved gases.

$$M_r(\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}) = 236.1$$

Total received  $(24.98 + 26.64) = 51.62$  g or  $\frac{51.62}{236.1} = 0.2186$  mol of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ .

In each of the experiments for thermolysis, we used  $\frac{0.2186}{2} = 0.1093$  mol of  $\text{Ca}(\text{NO}_3)_2$ .

At 580 °C it is evolved  $\frac{102.3 \cdot 26.52}{8.314 \cdot (580 + 273)} = 0.3826$  mol of gases. It is in  $\frac{0.3826}{0.1093} = 3.50$  times more than quantity of decomposed  $\text{Ca}(\text{NO}_3)_2$ .

At 600 °C it is evolved  $\frac{103.5 \cdot 22.99}{8.314 \cdot (600 + 273)} = 0.3278$  mol of gases. It is in  $\frac{0.3278}{0.1093} = 3.00$  times more than quantity of decomposed  $\text{Ca}(\text{NO}_3)_2$ .

Let us write the reaction equations for different decomposition options:



It can be concluded that at 580 °C decomposition proceeds according to reaction 2, and at 600 °C - according to reaction 3. It is clear that when the gas mixture is cooled to room temperature, the reaction between  $\text{NO}$  and  $\text{O}_2$  will proceed and the total equation will become the same as in the school chemistry textbook (reaction 1). **(2 points for each equation, 4 points in total)**

### Problem 6 (authors Karpushkin E.A., Berkovich A.K.)

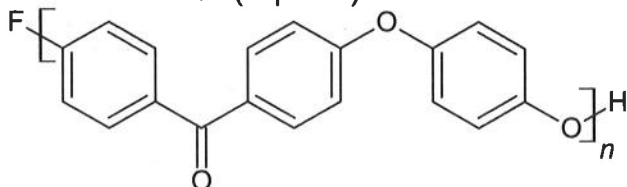
1. Equivalent weight of the polymer can be calculated directly from the definition:  $M_{\text{eq}} = [x \cdot M(\text{C}_2\text{F}_4) + y \cdot M(\text{C}_2\text{F}_3) + y \cdot z \cdot M(\text{C}_3\text{F}_6\text{O}) + y \cdot M(\text{C}_2\text{F}_4\text{O}_4\text{SH})] / y = (100 \cdot 100.02 + 50 \cdot 81.02 + 50 \cdot 3 \cdot 166.03 + 50 \cdot 221.115) / 50 = 1000$  g/mol (1 point).

2. If  $z = 1$ , the above expression for the equivalent weight is re-written as:  $M_{eq} = [x \cdot 100.02 + y \cdot 81.02 + y \cdot z \cdot 166.03 + y \cdot 221.115] / y = x \cdot 100.02 / y + 81.02 + 166.03 + 221.115$ . Since  $M_{eq} = 1100$ ,  $x/y = 6.32$ . The value of  $y$  is the number of the ionic groups in the molecule (55), then  $x = 347.6$ . The polymerization degree of the backbone is  $x + y = 402.6$ . (2 points; 402 and 403 accepted if in line with rounding of the intermediate values).

3. The volume of the membrane specimen equals  $21.0 \times 29.7 \times 120 \cdot 10^{-4} = 7.48 \text{ cm}^3$ , and the polymer mass in it is  $7.48 \cdot 1.45 \cdot (1 - 0.3) = 7.59 \text{ g}$ . This mass of the polymer is dissolved in  $7.59 \cdot 0.15 = 50.6 \text{ g}$  or  $50.6 / 1.1 = 46.01 \text{ mL}$  of the alcoholic solution (1 point).

4.  $10^{-6} \cdot 300 \cdot 78.5 = 0.024 \text{ mol}$  of NaCl or  $0.024 / (4 \cdot 0.1) = 6\%$  of the initial salt is transferred in  $60 \cdot 5 = 300 \text{ s}$  across the membrane with the area of  $3.14 \cdot (10/2)^2 = 78.5 \text{ cm}^2$  (1 point).

5. Since the water flux (and thus changes of the solution volumes) is neglected, the salt is distributed between the starting solution and water in the ratio equal to that of the volumes (1:10).  $10/11 = 90.9\%$  of the salt is removed from the mixture at each dialysis cycle, and  $(1/11)^3 = 0.075\%$  of the starting salt remains in the mixture with the protein after three cycles. The mass of the protein in the final solution equal to its initial mass ( $14300 \times 0.1 \times 1 \cdot 10^{-3} = 1.43 \text{ g}$ ), whereas the mass of the residual salt is  $58.44 \times 0.1 \times 4 \times 7.5 \cdot 10^{-4} = 0.0175 \text{ g}$ . The mass fraction of the salt in the dried protein specimen is  $1.21\%$  (2 point).

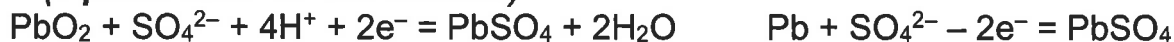


6. (1 point).

7. The gross formula of the repeat unit of **A** is  $C_{19}H_{12}O_3$ . Treatment with concentrated  $H_2SO_4$  leads to partial substitution of the H atoms by the sulfonic groups. The gross formula of **B** after substitution of  $x$  atoms of H in each unit is  $C_{19}H_{12}O_3(SO_3)_x$ .  $x$  can be calculated from the sulfur content as:  $0.0213 = \frac{x \cdot 32.065}{19 \cdot 12.01 + 12 \cdot 1.008 + (3 + 3x) \cdot 16.00 + x \cdot 32.065} \leftrightarrow x = 0.203$ . The mass per 0.203 ionic groups:  $19 \cdot 12.01 + 12 \cdot 1.008 + (3 + 3 \cdot 0.203) \cdot 16.00 + 0.203 \cdot 32.065 = 304.54$ , and the equivalent weight of **B** is  $304.54 / 0.203 = 1500 \text{ g/mol}$  (2 points).

### Problem (by L. Malinina)

1. (1 point total for this section)

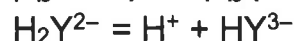
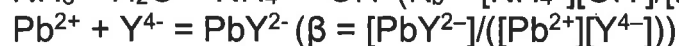
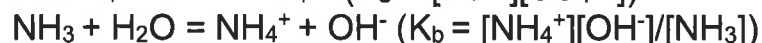
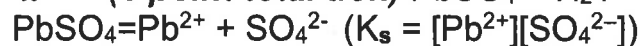


2. "Boiling" is associated with the electrolysis of water with the formation of gas bubbles:  $H_2O = H_2 + \frac{1}{2}O_2$  (0.5 points).

This process reduces the amount of water and results in a potentially explosive mixture of gases:  $2H_2 + O_2 = 2H_2O$  (explosion) (0.5 points).

3.  $PbSO_4 \downarrow$  (0.5 points).

4. (1 point total)  $PbSO_4 + H_2Y^{2-} + 2NH_3 = PbY^{2-} + 2NH_4^+ + SO_4^{2-}$





5. The pH value of the described desulfating solution can be estimated as follows (assuming that alkalinity is determined by the presence of ammonia):

$$c(\text{NH}_3) = \frac{45 \text{ mL} \cdot 0.907 \text{ g/mL} \cdot 0.25}{17 \text{ g/mol} \cdot 1 \text{ L}} = 0.6 \text{ M},$$

$$K_b = [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3] = [\text{OH}^-]^2 / (c(\text{NH}_3) - [\text{OH}^-]),$$

$$[\text{OH}^-] = (-K_b + \{K_b^2 + 4 K_b c(\text{NH}_3)\}^{1/2}) / 2 = 3.24 \cdot 10^{-3} \text{ M},$$

or by using a simplified formula:  $[\text{OH}^-] = (K_b \cdot c)^{1/2} = 3.25 \cdot 10^{-3} \text{ M}$ , pH = 11.5 (2 points).

The concentration of EDTA in the desulfating solution:  $c(\text{Na}_2\text{H}_2\text{Y}) = 20/336/1 = 0.060 \text{ M}$

Considering mole fraction of  $[\text{Y}^{4-}]$ :  $c(\text{Na}_2\text{H}_2\text{Y}) \alpha(\text{Y}^{4-}) = 0.060 \text{ M} \cdot 0.95 = 0.057 \text{ M}$ .

Solubility is the concentration of dissolved lead (equal to the concentration of sulfate ion, which results only from dissolution of lead sulfate) is the sum of its two forms:

$S(\text{Pb}) = c(\text{Pb}^{2+}) = [\text{SO}_4^{2-}] = [\text{Pb}^{2+}] + [\text{PbY}^{2-}]$ . Thus, for the solubility product and the complexation constant there is a the system of equations:

$$(1) \quad K_s = ([\text{Pb}^{2+}] + [\text{PbY}^{2-}])[\text{Pb}^{2+}],$$

$$(2) \quad \beta = [\text{PbY}^{2-}] / ([\text{Pb}^{2+}] \cdot \alpha(\text{Y}^{4-}) \cdot c(\text{Na}_2\text{H}_2\text{Y}))$$

When solving this system, we can obtain:

$$[\text{Pb}^{2+}] = (K_s / (\beta \cdot \alpha(\text{Y}^{4-}) \cdot c(\text{Na}_2\text{H}_2\text{Y}) + 1))^{0.5} = 6 \cdot 10^{-13},$$

$$S(\text{Pb}) = [\text{Pb}^{2+}] + [\text{PbY}^{2-}] = [\text{Pb}^{2+}] (1 + \alpha(\text{Y}^{4-}) \cdot c(\text{Na}_2\text{H}_2\text{Y}) \cdot \beta) = 3.5 \cdot 10^{-4} \text{ M} \quad (3 \text{ points})$$

Thus, taking into account the large value of the complexation constant, almost all lead will be bound to EDTA and its solubility will correspond to the concentration of EDTA ion, i.e., 0.057 M (1 point).

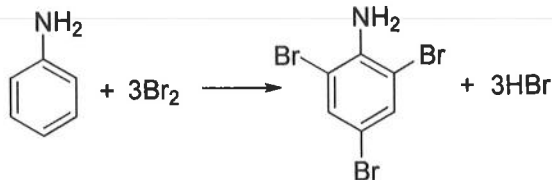
$$6. \quad m(\text{PbSO}_4) = 303 \text{ g/mol} \cdot 0.057 \text{ M} \cdot 1 \text{ L} = 17.3 \text{ g} \quad (0.5 \text{ points}).$$



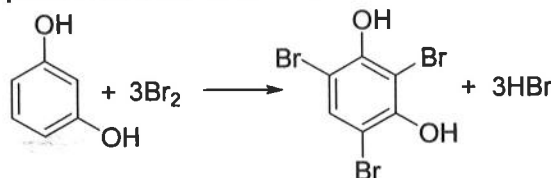


### Task 7 (author M.K. Beklemishev)

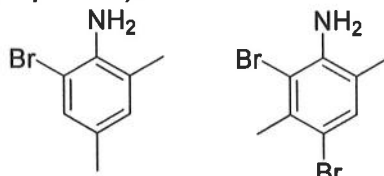
1. When titrating aniline, 3 mol of bromine is spent (1 point).



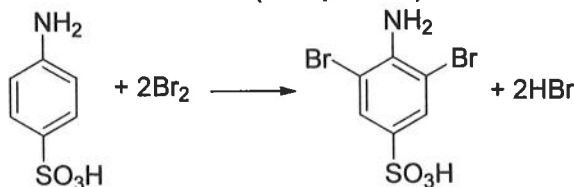
2. Stoichiometric bromination takes place in the case of resorcinol, in the structure of which two hydroxyl groups activate the corresponding positions. Hydroquinone is brominated in a complex manner and with less bromine consumption (2 points):



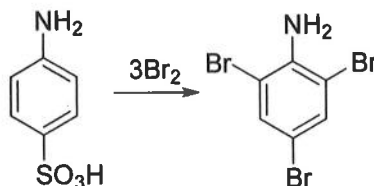
3. When interacting 1 mol of bromine is consumed with 2,4-dimethylaniline, and 2 mol for 2,5-dimethylaniline (2 points):



4. Bromination of sulfanilic acid at 0°C (0.5 points):

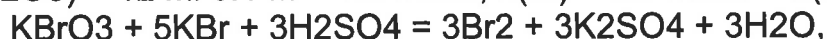


At 20–25°C (0.5 points):



5. From the amount of thiosulfate we find the amount of iodine (and an equal amount of bromine):  $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$

Then  $n(\text{Na}_2\text{S}_2\text{O}_3) = 12 \text{ ml } 0.1 \text{ M} = 1.2 \text{ mmol}$ ;  $n(\text{I}_2) = 0.6 \text{ mmol} = n(\text{Br}_2)$ .



Taking into account the stoichiometry,  $n(\text{KBrO}_3) = n(\text{Br}_2) / 3 = 0.2 \text{ mmol}$ , but this is 1/10 of the total amount, that is, the total bromate was 2 mmol, and this is unreacted bromate. The initial amount of bromate was  $5 \text{ ml} \cdot 1 \text{ M} = 5 \text{ mmol}$ , i.e., 3 mmol was used for analyte bromination. According to the condition, sulfapyridine behaves similarly to sulfanilic acid, i.e. at room temperature, the sulfo group is also replaced by bromine (point 4). Tribromaniline is formed (1 point).

For 1 mol of analyte, 3 mol of bromine or 1 mol of bromate will be consumed (see above). Then the amount of sulfapyridine is 3 mmol, or 0.747 g (3 points).

