

Grade 9

Problem 9-1

Benzyl chloride is prepared commercially by chlorination of toluene. A 0.255 g sample of commercial-grade benzyl chloride taken for a purity analysis was mixed with 25 mL of 4 N NaOH in a 100 mL round-bottom flask. The reaction mixture was refluxed for one hour, chilled to room temperature, and treated first with 50 mL of 20% HNO₃ and then with 25.00 mL of 0.100 N AgNO₃. The excess of silver nitrate was titrated with 0.100 N NH₄SCN using ferrous ammonium sulfate as an indicator.

- Write chemical equations that describe this analysis.
- Calculate the mass fraction of benzyl chloride in the analyzed sample assuming that the titration required 6.75 mL of the NH₄SCN solution.
- What impurities can be present in benzyl chloride prepared by the commercial method? Which of these impurities can affect results of the purity analysis?
- Is the above procedure suitable for a purity analysis of chlorobenzene? Give your reasoning.

Problem 9-2

The chemical composition of a thermally unstable sodium salt (compound **A**) was determined by a thermal gravimetric analysis of three samples prepared by mixing **A** with an inert filler. The samples were heated at 400 °C and their mass loss was recorded. The results are summarized in the following table:

Mass percent of A in the sample, %	20	50	70
Sample mass loss, %	7.4	18.5	25.8

- Based on the data provided, identify compound **A**. Show your calculations.
- What is the commercial production method for compound **A**? Write the chemical equations that describe this process.
- A solution of **A** was mixed with an equal mass of aqueous HCl. The mass of the mixture was found to be 10% less than the sum of the masses of the initial solutions. Calculate the mass percent of the product in the resulting solution.

Problem 9-3

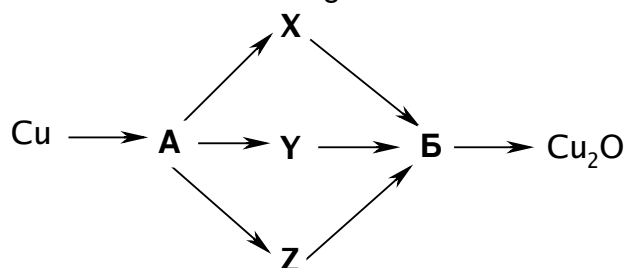
A collection of organic syntheses published in 1922 contained the following procedure for the preparation of a certain organic compound **X**. A two-neck round-bottom 500 mL Pyrex flask is loaded with 150 g of potassium hydroxide. One neck is fitted with a dropping funnel containing 100 g of 1-bromo-2-phenylethene. The other neck is fitted with a distillation condenser. The flask is heated on an oil bath and when the temperature reaches 200 °C, 1-bromo-2-phenylethene is added dropwise a rate of about one drop per second. As the reaction proceeds and the temperature rises to about 215-220 °C, volatile products boil off and condense in the receiver as a colorless

liquid which separates spontaneously into two immiscible layers. The upper layer is isolated, dried with KOH, and distilled at 142-144 °C. The procedure yields 37 g of compound **X** which is 94.08% carbon by mass.

- Draw the structural formulas of 1-bromo-2-phenylethene and all of its isomers that contain a benzene ring.
- Draw the structural formula of compound **X**. What is the systematic name of **X**?
- Write the chemical reaction for the synthesis of **X** and calculate the actual percent yield of the product.
- What compound forms the lower layer of the distillate?
- Suggest an alternative synthesis of compound **X**.

Problem 9-4

Each chemical reaction in the following scheme can be carried out in one step:



- Identify compounds **A**, **B**, **X**, **Y**, and **Z**.
- Write chemical equations that describe the above transformations and specify the appropriate reaction conditions.

Problem 9-5

One of the common corrosion prevention techniques consists in coating the corrosion-prone surface with a thin layer of another metal. Consider the process of applying a 300 μm layer of Ni metal over the surface of a metallic cylinder with a radius of 17 mm and a height of 0.260 m by the method of electrodeposition. The electrochemical cell constructed for this purpose contains 4.20 kg of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and 6.80 L of water. The current passed through the cell is 2.1 A.

- Write balanced equations for the half-reactions occurring at each electrode and for the overall chemical reaction occurring in the cell.
- Calculate the mass percent of nickel sulfate in the electrolyte solution at the beginning and at the end of the process.
- How many hours does the coating take assuming that the cell operates at 88% efficiency? The density of nickel metal is 8.90 g/cm^3 .

Hints: The volume of a cylinder is $\pi r^2 h$; Faraday's law: $m = \frac{M \cdot I \cdot t}{z \cdot F}$, where $F = 96500$ C/mol)

Grade 10

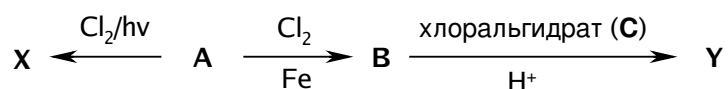
Problem 10-1

Solvent extraction is an important chemical separation technique based on the unequal distribution of a solute between two immiscible liquids. A series of experiments is conducted to study the distribution of a certain monoprotic organic acid **X** between water (w) and benzene (b). Under the conditions of the experiment, the distribution constant of **X** is $K_d = [\text{X}]_b/[\text{X}]_w = 1.00$. In the aqueous phase, **X** dissociates weakly according to the equation $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ and has $K_a = 1,00 \times 10^{-4}$. In the organic phase, **X** undergoes partial dimerization, $2\text{HA} \rightleftharpoons (\text{HA})_2$.

- Separation of the two phases followed by evaporation of the solvents showed that 1.00 L of the aqueous phase contains 3.05 mmol of compound **X**, while 1.00 L of the benzene layer contains 3.96 mmol of **X**. Calculate the concentrations of all species in the aqueous phase and predict its pH value.
- Calculate the dimerization constant of compound **X** in benzene.
- Sketch a graph showing the mole fractions of each form of compound **X** (monomer, dimer, and anion) as functions of pH.
- Propose a structural formula for **X** given that the molecule of this compound contains a benzene ring and that 1 g of **X** contains 3.85×10^{21} molecules.
- Explain why **X** dimerizes in benzene and propose a structure for the dimer.

Problem 10-2

Lindane (compound **X**) and DDT (compound **Y**) are two examples of chlorine-based insecticides that have been banned because of their toxicity to humans. Lindane is 73.1% chlorine by mass, while DDT is 50.0% chlorine. Both **X** and **Y** can be prepared starting from a certain compound **A** that begins the arene homologous series. The corresponding reaction sequences are as follows:



- Draw the structural formulas of compounds **A**, **B**, **C**, **X** and **Y**.
- DDT is an acronym for a full chemical name of compound **Y**. What is this name?
- How many stereoisomeric forms does each of compounds **X** and **Y** have? Draw the structural formulas for all possible stereoisomers of **X** and **Y**.
- A 0.300 g sample of a mixture of lindane and DDT was burned in an excess of oxygen gas. The volatile reaction products were bubbled through aqueous NaHCO_3 and the resulting solution was acidified with excess HNO_3 . Treatment of this solution with an excess of 0.1 M AgNO_3 yielded 0.750 g of a precipitate. Calculate the mass percent composition of the analyzed sample.

Problem 10-3

In a combustion analysis of a sample of compound **A** it was found that 736 mL (S.T.P.) of CO_2 and 296 mg of H_2O are produced. Compound **A** is 63.2% carbon by mass. Hydrolysis of **A** in the presence of an acid produces a certain bifunctional compound **B** and a neutral compound **C**. Compound **B** is poorly soluble in water and has a lower boiling temperature than its isomers differing from **B** by the position of the two functional groups. Reaction of **B** with acetic anhydride yields compound **D**. Compounds **A** and **D** are used as non-steroidal anti-inflammatory agents.

- Deduce the structural formulas of compounds **A** through **D**. Give your reasoning.
- Write chemical equations for the reactions that occur in this analysis.
- Determine the mass of the initial sample of **A**.
- What causes compound **B** to have a lower boiling temperature than its isomers?

Problem 10-4

Given below is a laboratory method for the preparation of a certain tellurium compound. A mixture of 100 g of tellurium powder and 200 g of crystalline KOH is ground thoroughly in a mortar, transferred to a ceramic crucible, and calcined at $430\text{ }^\circ\text{C}$ for 1 hour. After cooling, the reaction mixture is treated with a hot ($80\text{--}90\text{ }^\circ\text{C}$) solution of 90 g KOH in 900 mL of water and then filtered. The filtrate is heated to $100\text{ }^\circ\text{C}$ and treated with 10-20 mL portions of nitric acid (25-30%) until the pH value reaches 3.5 and remains steady for at least 20 min. The resulting precipitate is filtered off and washed on filter paper with distilled water to remove the nitrate ions. The washed crystals are heated at $170\text{ }^\circ\text{C}$ for 3 hours to give 120 g of the target compound.

- Synthesis of what tellurium compound is described above?
- Write chemical equations for the reactions that occur in this synthesis.
- Calculate the practical yield of the target compound.
- Propose an alternative method for the preparation of the target compound using the same reagents as in the above method. Write chemical equations that describe this synthesis and specify the appropriate reaction conditions.

Problem 10-5

See Problem 9-5.

Grade 11

Problem 11-1

A certain compound **A** is a colorless liquid. When heated, it turns into a brown gas **B** whose density is 1.59 times greater than that of air. Reaction of **B** with metal **C** produces salt **D**. When heated, salt **D** decomposes to give an oxide **E**. Treatment of **E** with concentrated hydrochloric acid produces salt **F** and a suffocating gas **G**.

- Identify compounds **A** through **G**, given that the mass percent of the metal in salt **D** is 32.22%, and the fact that the pink salt **F** turns blue when heated.
- Write chemical equations for the reactions that occur in this experiment.
- When a mixture of salt **F**, NH_4Cl and $\text{NH}_3 \cdot \text{H}_2\text{O}$ is heated slightly in air, a reddish-brown compound **X** is formed. If the temperature is increased, the starting salt **F** can be recovered. Write chemical equations describing these reactions and propose a possible structural formula for salt **X**.
- Calculate the concentration of free C^{n+} cations of metal **C** in a solution prepared by dissolving 0.010 mol of CCl_n in 1.00 L of 0.100 M aqueous NH_3 , given that $\log \beta_1 = 7.3$, $\log \beta_2 = 14.0$, $\log \beta_3 = 20.1$, $\log \beta_4 = 25.7$, $\log \beta_5 = 30.8$, $\log \beta_6 = 33.7$, where
$$\beta_i = \frac{[\text{C}(\text{NH}_3)_i]^{n+}}{[\text{C}^{n+}] \cdot [\text{NH}_3]^i}$$

Problem 11-2

Spectrophotometry is a standard technique for studying chemical equilibria involving colored substances. The technique is based on Beer's law which states that the absorbance is proportional to the light path l (the distance traveled by the light through the material) and to the molar concentration of the absorbing species.

Consider the reaction $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$. Note that NO_2 gas is brown, while N_2O_4 is colorless. Suppose we have two cells containing $\text{NO}_2/\text{N}_2\text{O}_4$ mixtures characterized by light paths l_1 and l_2 and suppose that we can adjust the total pressures p_1 and p_2 in the cells so that both mixtures have the same absorbance. Then it is possible to deduce the equilibrium constant for the reaction.

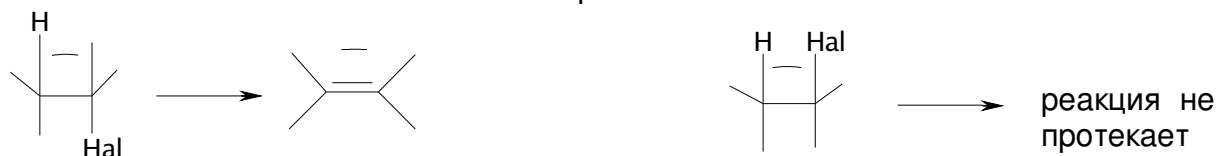
- Derive the expression for the equilibrium constant K_p in terms of p_1 , p_2 and the ratio $r=l_1/l_2$.
- In a certain experimental setup, $l_1=250$ mm and $l_2=50$ mm. Using the experimental data summarized in the following table, calculate the equilibrium constant K_p at the temperature of the experiment.

Experiment	Absorbance	p_1 , mm Hg	p_2 , mm Hg
I	A_I	2.00	11.0
II	A_{II}	4.00	23.5

- Which way will the equilibrium shift if the temperature is increased?
- Calculate the absorbance ratio A_I/A_{II} .

Problem 11-3

Dehydrohalogenation usually proceeds as *anti*- β -elimination. This fact is crucial for predicting the outcome of dehydrohalogenation of cyclic molecules where free rotation about carbon-carbon bonds is impossible:



A certain optically active compound **A** is a monochloro derivative of hydrocarbon **X**. When treated with a strong base, **A** gives another hydrocarbon **B**, which is also optically active. Reaction of **B** with an acidified KMnO_4 solution yields only one product, acid **C**. The complete neutralization of a 1.00 g sample of **C** requires 4.94 mL of 10.0% NaOH solution with a density of 1.11 g/cm^3 . Reaction of **C** with P_2O_5 produces compound **D** which is 37.5% oxygen by mass.

- Deduce the molecular formula of compound **C** and draw all possible structures for compounds **B** and **C**.
- Determine the unambiguous structure of compound **B**, given that not all products of addition of HCl to **B** are optically active. Give your reasoning.
- Draw the absolute configurations of compounds **A**, **D**, and **X** and give their systematic names using the R,S-nomenclature rules.
- Write the chemical equation for each reaction.

Problem 11-4

While strolling near an abandoned military base, a young chemist stumbled upon a metal barrel labeled "HL-CHM". The barrel had rusted through so that a white powder could be seen inside. The young chemist took a sample of the powder for a chemical analysis. A senior colleague later told him that the substance from the barrel is manufactured by bubbling chlorine gas through an excess of milk of lime, cooling the reaction mixture, separating the resulting precipitate, and drying the crystals in air.

- What is milk of lime?
- Write the reaction for the preparation of HL-CHM. What is a possible qualitative composition of this substance?
- To determine the quantitative composition of the powder, the chemist carried out a series of experiments. When he combined 1.000 g of the powder with 100 mL of water, he found that the resulting mixture had a pH of 12.78. Treatment of this mixture with an excess of aqueous Na_2CO_3 produced a white precipitate with a mass of 828 mg. Reaction of the powder with an excess of hydrochloric acid gave a mixture of gases with density of 3.128 g/L at STP. By measuring the amount of Cl_2 in this mixture, the chemist estimated the mass content of chlorine in the powder at 64.0%. Deduce the quantitative composition of the powder.
- What does HL-CHM stand for? How is this substance used by the military?

Problem 11-5

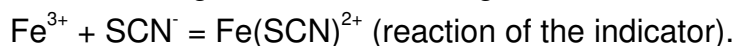
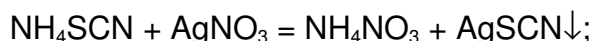
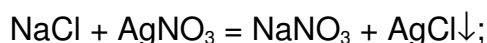
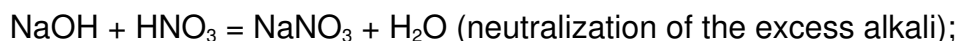
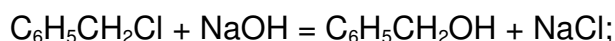
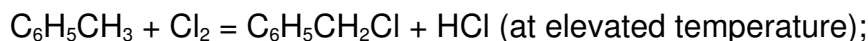
Polyelectrolytes are polymers that ionize in water and have many industrial applications (e.g., as ingredients of soaps, shampoos, and laundry detergents). Polyacrylic acid (PAA), a polymer of acrylic (2-propenoic) acid, is a typical polyelectrolyte. In the following questions, assume that each PAA molecule contains 100 monomer units.

- a) Draw the structural formulas of acrylic acid and PAA.
- b) Calculate the molar mass of PAA.
- c) The dissociation constant of a carboxylic group in the PAA molecule is $K_a = 1.32 \times 10^{-5}$. Calculate the pH of a 500 mL solution containing 10 g of PAA.
- d) At what pH value does the degree of dissociation of all carboxylic groups in a PAA solution become exactly 50%?

Solutions

Problem 9-1

- a) The reactions are as follows:



- b) The number of moles of benzyl chloride in the sample is equal to the difference between the number of moles of Ag^+ in the AgNO_3 solution and the number of moles of NH_4SCN required for the titration:

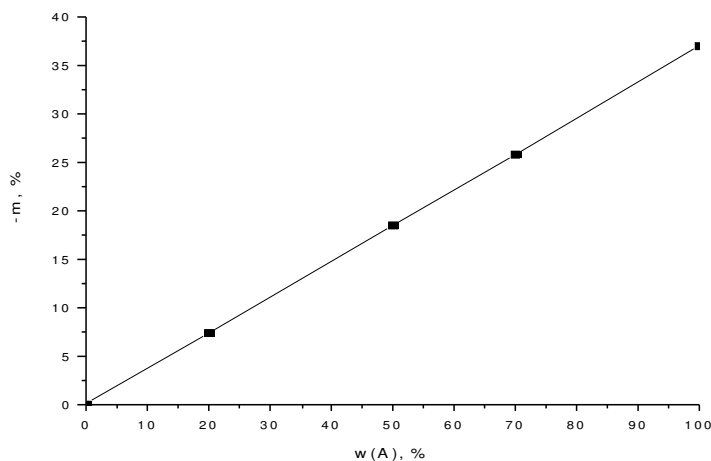
$$M(\text{C}_6\text{H}_5\text{CH}_2\text{Cl}) = 126.6 \text{ g/mol.}$$

Then $m(\text{C}_6\text{H}_5\text{CH}_2\text{Cl}) = 126.6 \times (0.100 \times (25.00 - 6.75)) = 231 \text{ mg}$. Therefore, the mass fraction of benzyl chloride in the sample is $\frac{231}{255} = 0.906$, or 90.6 %.

- c) The sample may be contaminated with the reactants ($\text{C}_6\text{H}_5\text{CH}_3$, Cl_2 , HCl) as well as di- and trisubstituted chlorination products ($\text{C}_6\text{H}_5\text{CHCl}_2$, $\text{C}_6\text{H}_5\text{CCl}_3$). All of these compounds except toluene contain Cl atoms and hence can affect the results of the analysis.
- d) The procedure is not suitable for the analysis of chlorobenzene because this compound reacts with aqueous alkali only under very harsh conditions. Under the specified conditions, hydrolysis of chlorobenzene is not quantitative.

Problem 9-2

- a) A quick data check (e.g., by plotting) reveals a linear correlation between the mass loss and the mass fraction of the compound:

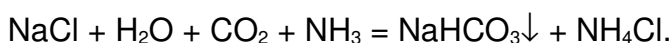


This means that thermal decomposition of compound **A** is not complicated by bulk effects. (The purpose of using the inert filler is precisely to avoid them).

For the pure salt, the mass loss would have been $7.4 \cdot \frac{100}{20} = 37\%$.

The description of chemical properties of compound **A** (thermal instability, reaction with aqueous HCl to produce a gas) suggests that it is a salt of a weak volatile acid. A numerical check rules out the reaction of a hydrate $\text{NaX} \cdot n\text{H}_2\text{O} \rightarrow \text{NaX}$. Another possibility is a hydrogen salt decomposing by the equation: $2\text{NaHA} \rightarrow \text{Na}_2\text{A} + \text{H}_2\text{A}$. The mass loss data are consistent with the identification **A** = NaHCO_3 (sodium bicarbonate). The equation for the decomposition of salt **A** is $2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$.

- b) Sodium bicarbonate is prepared commercially by the Solvay process, in which an equimolar mixture of ammonia and carbon dioxide is passed through a cold saturated aqueous solution of sodium chloride (brine). Because of its relatively low solubility at cold temperatures, sodium bicarbonate precipitates from the reaction mixture. The overall reaction is



- c) Note the scarcity of numerical data. Nevertheless, the information we have is sufficient to solve the problem. The overall reaction is



The mass loss is due entirely to the formation of CO_2 . The number of moles of NaCl is equal to the number of moles of CO_2 . $M(\text{CO}_2) = 44.0 \text{ g/mol}$, $M(\text{NaCl}) = 58.5 \text{ g/mol}$. Let the mass of each solution be $m \text{ g}$. Then the amount of CO_2 gas is

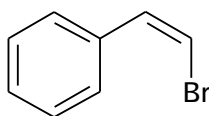
$$0.10(m + m) = 0.20m \text{ g or } \frac{0.20 \cdot m}{44.0} \text{ mol. Thus, } (2m - 0.20m) = 1.80m \text{ g of the final}$$

reaction mixture contains $58.5 \cdot \frac{0.20 \cdot m}{44.0} = 0.266m \text{ g of NaCl}$.

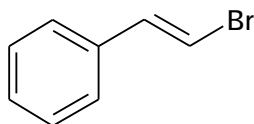
The mass fraction of NaCl in the resulting solution is $\frac{0.266 \cdot m}{1.80 \cdot m} = 0.148$ or 14.8 %.

Problem 9-3

- a) 1-bromo-2-phenylethene exists as *cis*- and *trans*-isomers :

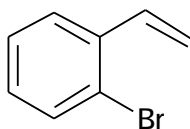


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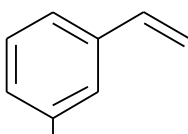


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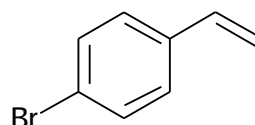
There are three isomers of this compound that contain a benzene ring:



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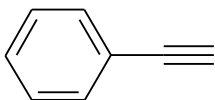


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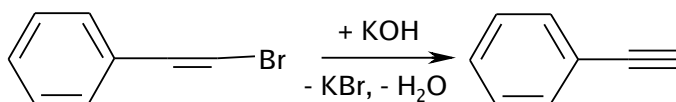
- b) The high carbon content of **X** suggests that it is a hydrocarbon. The ratio of carbon and hydrogen atoms in the molecule of **X** is

$$\text{C} : \text{H} = \frac{94,08}{12,01} : \frac{100 - 94,08}{1,01} = 7.83 : 5.86 = 4 : 3.$$

The number of hydrogen atoms in a hydrocarbon is always even, so the molecular formula is C_8H_6 . Hence, **X** is ethynylbenzene (phenylacetylene):



- c) The reaction is:



$$M(\text{C}_8\text{H}_7\text{Br}) = 183 \text{ g/mol}$$

$$M(\text{KOH}) = 56 \text{ g/mol}$$

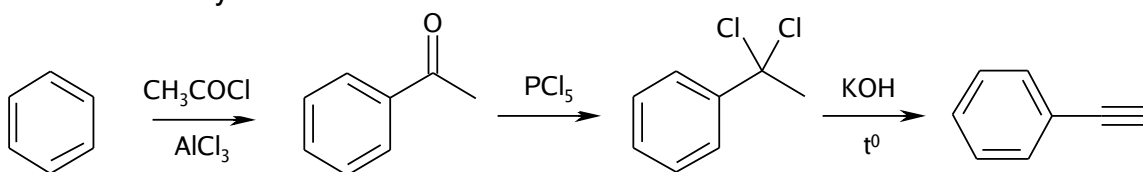
$$M(\text{C}_8\text{H}_6) = 102 \text{ g/mol}$$

The amount of 1-bromo-2-phenylethene is $\frac{100}{183} = 0.546 \text{ mol}$, while the amount of

KOH is $\frac{150}{56} = 2.68 \text{ mol}$. The organic halide is the limiting reagent. The reaction yields $0.546 \times 102 = 55.7 \text{ g}$ of phenylacetylene.

The actual yield is $\frac{37}{55,7} = 0.664$ or 66.4 %.

- d) The liquid in the receiver is a mixture of phenylacetylene and water. Hydrocarbons do not dissolve in water and have a lower density than water. Therefore, the lower layer is H_2O (containing a trace amount of phenylacetylene).
- e) An alternative synthesis:



Problem 9-4

- a) The problem has more than one solution. One possible solution is:

$$\mathbf{A} = \text{CuO};$$

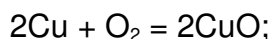
$$\mathbf{B} = \text{Cu}(\text{OH})_2;$$

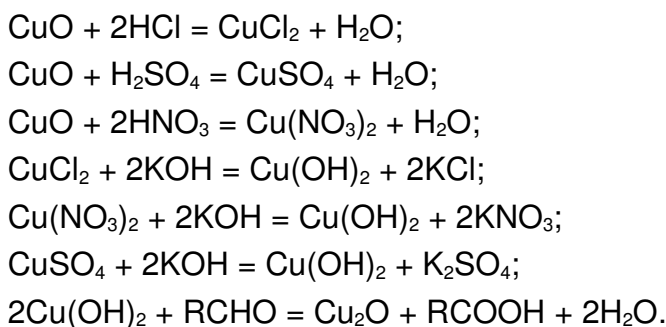
$$\mathbf{X} = \text{CuCl}_2;$$

$$\mathbf{Y} = \text{CuSO}_4;$$

$$\mathbf{Z} = \text{Cu}(\text{NO}_3)_2.$$

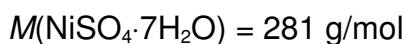
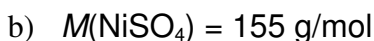
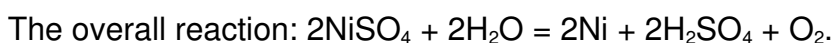
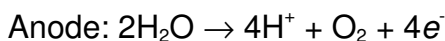
- b) The chemical reactions corresponding to the above solution are:





The first reaction requires a high temperature; the next three reactions require a hot acid; the reactions with KOH occur in solution; the last reaction occurs when copper hydroxide is heated with an aldehyde in the presence of tartaric acid.

Problem 9-5



4.20 kg of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ is $\frac{4,20 \cdot 10^3}{281} = 14.95 \text{ mol}$, which corresponds to

$14.95 \times 155 \times 10^{-3} = 2.32 \text{ kg}$ of NiSO_4 .

The initial mass of the electrolyte solution is $4.20 + 6.80 = 11.00 \text{ kg}$.

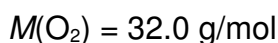
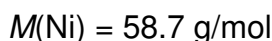
Thus, the mass fraction of NiSO_4 in the initial solution is $\frac{2,32}{11,00} = 0.211$ or 21.1 %.

The volume of the cylinder before coating: $V_0 = \pi \cdot r_0^2 \cdot h_0 = 236.06 \text{ cm}^3$.

The coated cylinder has a radius of $(1.70 + 0.03) = 1.73 \text{ cm}$, and a height of $(26.0 + 2 \times 0.03) = 26.06 \text{ cm}$. Thus, the volume of the coated cylinder is $V_1 = 245.03 \text{ cm}^3$.

The volume of the nickel metal layer is $V(\text{Ni}) = (245.03 - 236.06) = 8.97 \text{ cm}^3$.

The mass of Ni comprising the layer is $m = \rho V = 8.97 \times 8.90 = 79.8 \text{ g}$.



The number of moles of Ni in the coating layer is $\frac{79,8}{58,7} = 1.36 \text{ mol}$.

The mass of the O_2 gas is $\frac{1}{2} \cdot 1,36 \cdot 32 = 21.8 \text{ g}$

Therefore, the final mass of the solution is $11.00 - 10^{-3}(79.8 + 21.8) = 10.90 \text{ kg}$.

This solution contains $(14.95 - 1.36) = 13.59 \text{ mol}$ of NiSO_4 .

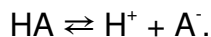
The mass fraction of NiSO_4 in the final solution is $\frac{155 \cdot 13,59 \cdot 10^{-3}}{10,90} = 0.193$ or 19.3 %.

c) Using Faraday's law we obtain

$$t = \frac{m(\text{Ni}) \cdot z \cdot F}{M(\text{Ni}) \cdot I \cdot \eta} = \frac{79,8 \cdot 2 \cdot 96500}{58,7 \cdot 2,1 \cdot 0,88} = 1,42 \times 10^5 \text{ s} = 39,4 \text{ h.}$$

Problem 10-1

a) A carboxylic acid is a monoprotic acid. In the aqueous phase, it dissociates according to the equation:



We know that $[\text{HA}] + [\text{A}^-] = 3,05 \times 10^{-3} \text{ M}$.

We also have the expression for the dissociation constant $\frac{[\text{H}^+] \cdot [\text{A}^-]}{[\text{HA}]} = 1,00 \cdot 10^{-4}$,

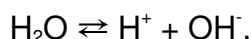
and the electrical neutrality condition: $[\text{H}^+] = [\text{A}^-]$.

By combining these three equations we obtain $\frac{[\text{H}^+] \cdot [\text{H}^+]}{3,05 \cdot 10^{-3} - [\text{H}^+]} = 1,00 \cdot 10^{-4}$

Hence $[\text{H}^+] = 5,05 \times 10^{-4} \text{ M}$.

But then $[\text{A}^-] = 5,05 \times 10^{-4} \text{ M}$, and so $[\text{HA}] = 2,55 \times 10^{-3} \text{ M}$.

We should also account for the autoionization of water:



$[\text{H}^+][\text{OH}^-] = 1,00 \times 10^{-14}$, which gives $[\text{OH}^-] = \frac{1,00 \cdot 10^{-14}}{5,05 \cdot 10^{-4}} = 1,98 \times 10^{-11}$.

$\text{pH} = -\log[\text{H}^+] = 3,30$.

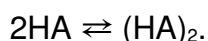
b) The benzene-water distribution constant is:

$$K_d = [\text{HA}]_b / [\text{HA}]_w = 1,00.$$

Hence, the equilibrium concentrations are $[\text{HA}]_w = [\text{HA}]_b = 2,55 \times 10^{-3} \text{ M}$.

The organic layer contains $3,96 \times 10^{-3} \text{ M}$ of **X**.

The dimerization reaction is:

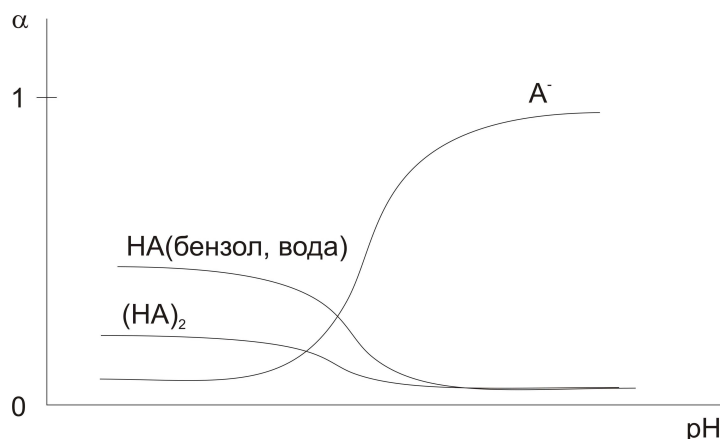


Therefore, $2[(\text{HA})_2] + [\text{HA}]_b = 3,96 \times 10^{-3} \text{ M}$, which gives $[(\text{HA})_2] = 7,05 \times 10^{-4} \text{ M}$.

The dimerization constant is:

$$K_{\text{dum}} = \frac{7,05 \cdot 10^{-4}}{(2,55 \cdot 10^{-3})^2} = 108.$$

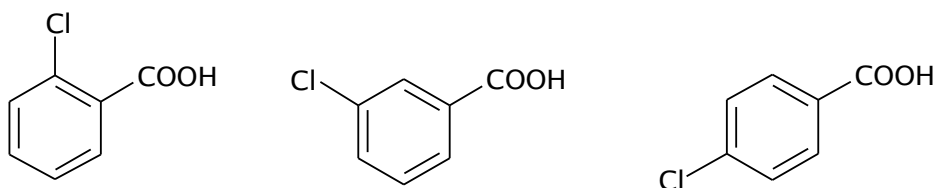
c) High pH shifts the equilibrium $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ to the right. As the pH value increases, the equilibrium mole fraction of the ionized acid $\alpha(\text{A}^-)$ in the two-layer system approaches 1, while the fractions of the molecular forms $\alpha(\text{HA})$ and $\alpha(\text{dimer})$ approach zero. At low pH, $\alpha(\text{A}^-)$ decreases to zero, while the sum $\alpha(\text{HA}) + \alpha(\text{dimer})$ approaches 1. The mole fraction of the dimer depends on pH indirectly through the fraction of the monomer in the organic layer where 50% of all the monomer molecules are. Thus, $\alpha(\text{dimer})$ is a fixed fraction of $\alpha(\text{HA})$ at any given pH. The dependence of the mole fractions of HA, $(\text{HA})_2$, and A^- on pH is sketched below:



- d) Given the number of molecules per 1 g of substance, the molecular mass of **X** is

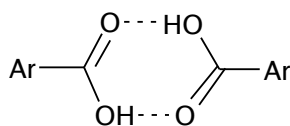
$$M = \frac{6,02 \cdot 10^{23}}{3,85 \cdot 10^{21}} = 156.5 \text{ g/mol}$$

The half-integer value suggests that **X** contains chlorine atoms. Given that **X** is a weak electrolyte, we identify **X** as chlorobenzoic acid. However, the information we have is insufficient to decide between *ortho*-, *meta*- and *para*-isomers



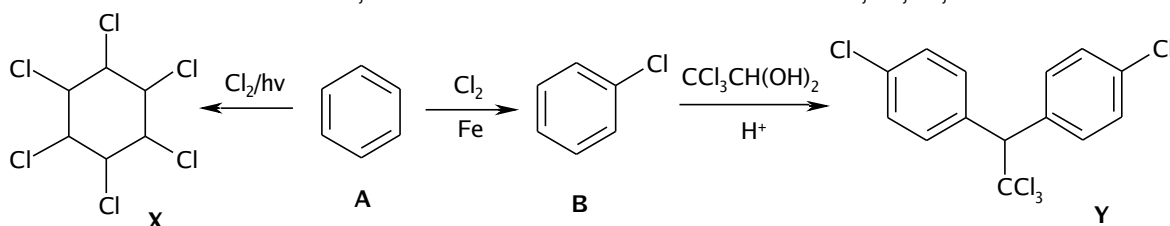
without knowing their K_a values. ($K_a = 1.00 \times 10^{-4}$ actually corresponds to the *para*-benzoic acid).

- e) Carboxylic acids dimerize in gas phase and in nonpolar solvents by forming strong hydrogen bonds. The structure with two hydrogen bonds shown below maximizes this intermolecular interaction and, therefore, will be more likely to occur:

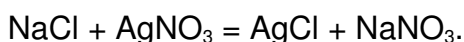
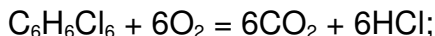


Problem 10-2

- a) The compound that begins the arene homologous series is benzene (**A**). The formula of chloral hydrate (compound **C**) is $\text{CCl}_3\text{CH}(\text{OH})_2$. Using this information and the chlorine content data, we can deduce the structures of **A**, **B**, **X**, and **Y**:



- b) Dichloro-diphenyl-trichloromethylmethane or dichloro-diphenyl-trichloroethane.
 c) DDT is optically inactive. 1,2,3,4,5,6-Hexachlorocyclohexane exists as 8 stereoisomers that differ from one another by the relative orientation of the C-Cl bonds (and, hence, by biological activity). Lindane is γ -hexachlorocyclohexane.
 d) The reactions are:



$$M(\text{C}_6\text{H}_6\text{Cl}_6) = 290.8 \text{ g/mol.}$$

$$M(\text{C}_{14}\text{H}_9\text{Cl}_5) = 354.5 \text{ g/mol.}$$

$$M(\text{AgCl}) = 143.3 \text{ g/mol.}$$

Suppose the sample contains x mol of hexachlorocyclohexane (HCH) and y mol of DDT. Then $290.8x + 354.5y = 0.300$

On the other hand,

$$143.3(6x + 5y) = 0.750.$$

Solving this system of equations we obtain

$$x = 5.28 \times 10^{-4}, y = 4.13 \times 10^{-4}.$$

Then the mass percent composition of the sample is

$$w(\text{DDT}) = \frac{354,5 \cdot 4,13 \cdot 10^{-4}}{0,3000} = 0.488 \text{ or } 48.8\%.$$

$$w(\text{HCH}) = (100 - 48.8) = 51.2\%.$$

Problem 10-3

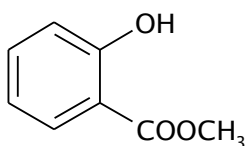
- a) The combustion produced $\frac{736}{22,4} = 32.8$ mmol of CO_2 and $\frac{296}{18,0} = 16.4$ mmol of H_2O .

This suggests that compound **A** consists of carbon, hydrogen, and oxygen (the mass percent of carbon is too low for a hydrocarbon). Furthermore, the ratio of carbon to hydrogen atoms is 1:1. Let us write the molecular formula of **A** as $\text{C}_x\text{H}_x\text{O}_y$.

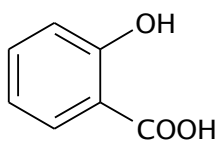
Then we have

$$0.632 = \frac{12,0 \cdot x}{12,0 \cdot x + 1,01 \cdot x + 16,0 \cdot y}, \text{ which can be simplified to } 3x = 8y.$$

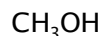
Thus, the empirical formula of compound **A** is $\text{C}_8\text{H}_8\text{O}_3$. The reference to its medicinal use suggests the following structures:



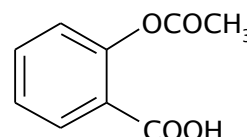
A



Б

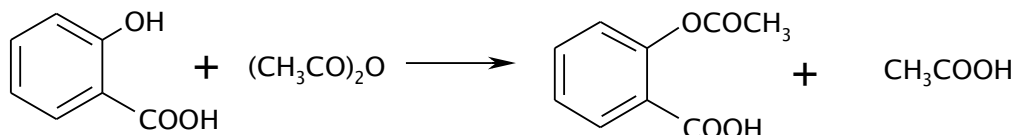
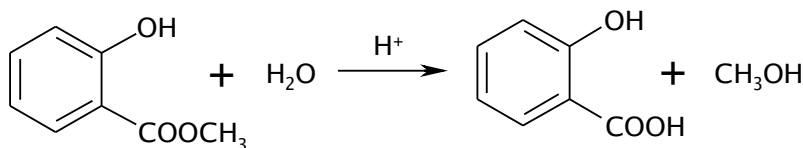
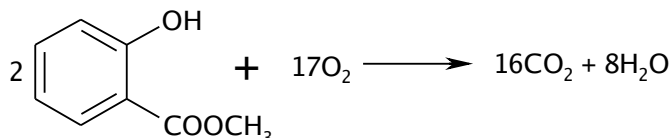


В



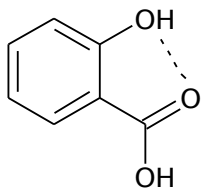
Г

b) The reactions are:



c) $M(\text{C}_8\text{H}_8\text{O}_3) = 152 \text{ g/mol}$. The number of moles of **A** is 1/8 of the number of moles of CO_2 . The mass of the sample is, therefore, $m(\mathbf{A}) = 152 \cdot \frac{32,8 \cdot 10^{-3}}{8} = 0.623 \text{ g}$.

d) Compound **B** is *ortho*-hydroxybenzoic (salicylic) acid. It has a lower boiling temperature than the *meta*- and *para*-isomers, because it forms intramolecular rather than intermolecular hydrogen bonds:



Problem 10-4

a) $M(\text{KNO}_3) = 101 \text{ g/mol}$.

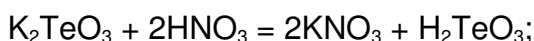
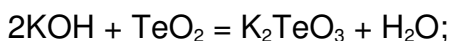
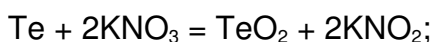
$M(\text{Te}) = 128 \text{ g/mol}$.

$M(\text{KOH}) = 56 \text{ g/mol}$.

$$n(\text{KNO}_3) = \frac{200}{101} = 1.98 \text{ mol}, \quad n(\text{Te}) = \frac{100}{128} = 0.78 \text{ mol}, \quad n(\text{KOH}) = 1.61 \text{ mol}$$

The ratio is approximately 5 : 2. When the reaction mixture is heated, the redox reaction produces tellurium oxide. The latter is converted into potassium tellurite by aqueous alkali. The addition of HNO_3 precipitates tellurous acid which decomposes into TeO_2 when heated. Thus, the final product is TeO_2 .

b) The reactions are:



- c) Based on the calculations carried out in part a), tellurium is the limiting reagent.
 $M(\text{TeO}_2) = 160 \text{ g/mol}$.
 The theoretical yield of TeO_2 is $160 \text{ g/mol} \times 0.78 \text{ mol} = 125 \text{ g}$.
 Thus, the practical yield is $\frac{120}{125} = 0.96$ or 96%.
- d) TeO_2 can be alternatively prepared by treating finely dispersed tellurium metal with hot nitric acid, evaporating the reaction mixture, and calcining the residue at $400 \text{ }^\circ\text{C}$.
 The overall reaction: $\text{Te} + 4\text{HNO}_3 = \text{TeO}_2 + 4\text{NO}_2 + 2\text{H}_2\text{O}$.

Problem 10-5

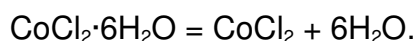
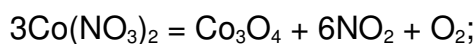
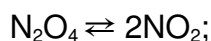
See Problem 9-5.

Problem 11-1

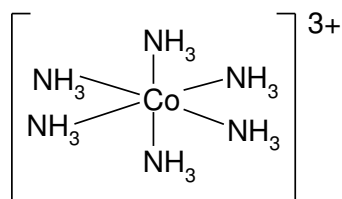
- a) The molar mass of gas **B** is $M(\mathbf{B}) = 1.59 \times 29.0 = 46.1 \text{ g/mol}$. The fact gas **B** is brown suggests that it is NO_2 . Then the colorless liquid **A** is N_2O_4 . Compound **D** must be the nitrate of metal **C**, since thermolysis of **D** produces an oxide. We have

$$M(\mathbf{D}) = \frac{62,01 \cdot n}{1 - 0,3222} = 91.49n \text{ g/mol}$$
, where n is the oxidation number of metal **C** in the nitrate. The atomic mass of **C** is therefore $29.48n$, which suggests $n=2$ and **C** = Co, so **D** is $\text{Co}(\text{NO}_3)_2$. The fact that the reaction of oxide **E** with HCl yields Cl_2 gas (compound **G**) suggests that **E** is Co_3O_4 while **F** is $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. (The hexahydrate has a pink color which disappears when salt **F** is heated).
 Thus, **A** = N_2O_4 ; **B** = NO_2 ; **C** = Co; **D** = $\text{Co}(\text{NO}_3)_2$; **E** = Co_3O_4 ; **F** = $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; **G** = Cl_2 .

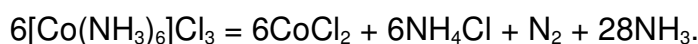
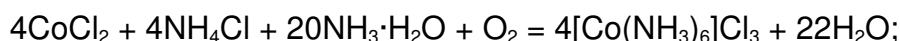
- b) The reactions are:



- c) Complex Co^{2+} ions are readily oxidized by atmospheric oxygen to Co^{3+} . This suggests that **X** is $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. Cations of **X** have the following structure



The reactions are:



- d) The total concentration of all forms of the Co^{3+} cation in the solution is:

$$c(\text{Co}^{3+}) = [\text{Co}^{3+}] + [\text{Co}(\text{NH}_3)^{3+}] + [\text{Co}(\text{NH}_3)_2^{3+}] + [\text{Co}(\text{NH}_3)_3^{3+}] + \\ + [\text{Co}(\text{NH}_3)_4^{3+}] + [\text{Co}(\text{NH}_3)_5^{3+}] + [\text{Co}(\text{NH}_3)_6^{3+}]$$

This can be rewritten in terms of β_i , $[\text{Co}^{3+}]$ and $[\text{NH}_3]$ as

$$c(\text{Co}^{3+}) = [\text{Co}^{3+}](1 + \beta_1[\text{NH}_3] + \beta_2[\text{NH}_3]^2 + \beta_3[\text{NH}_3]^3 + \beta_4[\text{NH}_3]^4 + \beta_5[\text{NH}_3]^5 + \beta_6[\text{NH}_3]^6).$$

Even if all Co^{3+} ions were hexacoordinated, the equilibrium concentration of ammonia in the solution would be no less than $(0.100 - 6 \times 0.010) = 0.04$ M. The actual numerical values of the complexation constants suggest that the equilibrium concentration of free Co^{3+} cations will be extremely small.

One can show that
$$\frac{\beta_{i+1}}{\beta_i} \cdot [\text{NH}_3] = \frac{[\text{Co}(\text{NH}_3)_{i+1}^{3+}]}{[\text{Co}(\text{NH}_3)_i^{3+}]}.$$

This means that the concentrations of all species except $[\text{Co}(\text{NH}_3)_5]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ are negligible. Then we can write

$$0,010 = [\text{Co}^{3+}](\beta_5[\text{NH}_3]^5 + \beta_6[\text{NH}_3]^6) = [\text{Co}(\text{NH}_3)_5^{3+}] + [\text{Co}(\text{NH}_3)_6^{3+}]$$

$$0,100 = [\text{NH}_3] + 5 \cdot [\text{Co}(\text{NH}_3)_5^{3+}] + 6 \cdot [\text{Co}(\text{NH}_3)_6^{3+}]$$

$$\frac{10^{33,7}}{10^{30,8}} \cdot [\text{NH}_3] = \frac{[\text{Co}(\text{NH}_3)_6^{3+}]}{[\text{Co}(\text{NH}_3)_5^{3+}]}$$

Solution of this system of three equations gives $[\text{NH}_3] = 0.0404$ M.

Using the first equation we obtain the final result $[\text{Co}^{3+}] = 4.45 \times 10^{-28}$ M.

Problem 11-2

- a) According to the ideal gas equation of state, concentration of a gas is proportional to its pressure:

$$C = \frac{n}{V} = \frac{P}{R \cdot T}.$$

Therefore, we can write Beer's law as $A = \varepsilon cl = kpl$, where A is the absorbance, and ε and k are proportionality constants.

The equilibrium constant for the reaction $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$

$$\text{is } K_p = \frac{p(\text{N}_2\text{O}_4)}{p^2(\text{NO}_2)} = \frac{1}{p} \cdot \frac{x(\text{N}_2\text{O}_4)}{x^2(\text{NO}_2)} = \frac{1}{p} \cdot \frac{(1-x(\text{NO}_2))}{x^2(\text{NO}_2)},$$

where p is the total pressure and x is the mole fraction of NO_2 .

Since the absorbances in both cells are equal, we can write

$$p_1(\text{NO}_2) \cdot l_1 = p_2(\text{NO}_2) \cdot l_2 \text{ (only } \text{NO}_2 \text{ gas absorbs light) which can be rewritten as}$$

$$(1) \quad p_1 \cdot x_1(\text{NO}_2) \cdot l_1 = p_2 \cdot x_2(\text{NO}_2) \cdot l_2.$$

The reaction quotients for the cells should be the same because each mixture is at equilibrium. Thus, we have two more equations

$$(2) \quad K_p = \frac{1}{p_1} \cdot \frac{(1-x_1(\text{NO}_2))}{x_1^2(\text{NO}_2)}$$

$$(3) \quad K_p = \frac{1}{p_2} \cdot \frac{(1-x_2(\text{NO}_2))}{x_2^2(\text{NO}_2)}$$

Using Eqs. (1)-(3) to express K_p in terms of p_1 , p_2 и $r = \frac{l_1}{l_2}$, we obtain

$$K_p = \frac{r \cdot (r-1) \cdot (p_2 - rp_1)}{(r^2 p_1 - p_2)^2}.$$

b) Substitution of the experimental values gives

$$\text{Experiment I: } K_p = 0.0131 \text{ (mm Hg)}^{-1}$$

$$\text{Experiment II: } K_p = 0.0120 \text{ (mm Hg)}^{-1}$$

We will take the average of these values as the true equilibrium constant. Thus, $K_p = 0.0126 \text{ (mm Hg)}^{-1}$.

c) The reaction $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ is exothermic. According to Le Châtelier's principle, if the temperature is increased, the equilibrium will shift to the left.

d) By Beer's law we have for each of the two cells ($i = 1, 2$):

$$A_i/A_{ii} = p_i^I(\text{NO}_2)/p_i^{II}(\text{NO}_2) = p_i^I x_i^I(\text{NO}_2)/p_i^{II} x_i^{II}(\text{NO}_2),$$

where p_i^I and p_i^{II} are the total pressures, and x_i^I and x_i^{II} are the mole fractions of NO_2 .

The mole fractions of NO_2 in each cell/experiment can be found from the expression for equilibrium constant $K_p = (1-x)/px^2$. Solution of this quadratic equation gives

$$x = [-1 + (1 + 4K_p p)^{1/2}] / 2K_p p.$$

For the first cell we obtain

$$A_i/A_{ii} = p_i^I x_i^I / p_i^{II} x_i^{II} = [-1 + (1 + 4K_p p_1^I)^{1/2}] / [-1 + (1 + 4K_p p_1^{II})^{1/2}] = 0.511$$

Similarly, for the second cell

$$A_i/A_{ii} = p_2^I x_2^I / p_2^{II} x_2^{II} = [-1 + (1 + 4K_p p_2^I)^{1/2}] / [-1 + (1 + 4K_p p_2^{II})^{1/2}] = 0.516$$

The average of these values is $A_i/A_{ii} = 0.514$

Problem 11-3

a) $M(\text{NaOH}) = 40.0 \text{ g/mol}$

The amount of NaOH required for the complete neutralization of acid **C** is

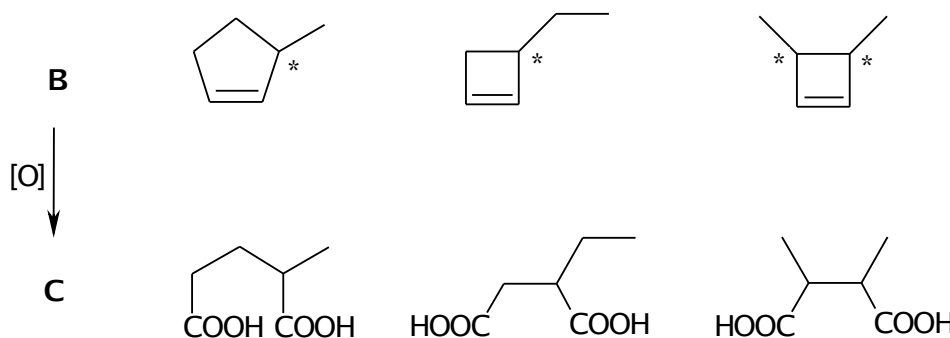
$$1.11 \times 4.94 \times 0.100 = 0.548 \text{ g or } \frac{0.548}{40.0} = 0.0137 \text{ mol}$$

Hence $M(\mathbf{C}) = \frac{1.00}{0.0137} \cdot n = 73.0n \text{ g/mol}$, where n is the number of protons.

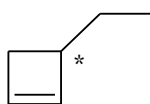
From the context, the molecular mass of **C** must be even, which implies $n=2$ and suggests that **C** is a dicarboxylic acid. Assuming the formula $\text{R}(\text{COOH})_2$ we deduce that $M(\mathbf{R}) = 56 \text{ g/mol}$ and, hence, $\mathbf{R} = \text{C}_4\text{H}_8$. Thus, $\mathbf{C} = \text{C}_6\text{H}_{10}\text{O}_4$.

Dehydration of the saturated dicarboxylic acid **C** with P_2O_5 can yield a cyclic anhydride with the molecular formula $\text{C}_6\text{H}_8\text{O}_3$ (compound **D**), an assumption which is supported by the oxygen content data. However, a cyclic anhydride is stable only when the two carboxylic groups are separated by at least 2 or 3 carbon atoms. This suggests that compound **B** is a four- or five-atom ring with a double carbon-carbon bond. Thus, **B** is a cycloalkene and **A** is a halogenated cycloalkane. We need to consider all possible chiral four- and five-atom cycloalkenes C_6H_{10} in which no double-bonded carbon atom is substituted (otherwise the oxidation with KMnO_4

would have yielded a diketone or a ketoacid). Only three cycloalkenes satisfy these requirements. The structures of these cycloalkenes and the structures of the corresponding oxidation products are shown below:



- b) Note that the elimination reaction which produces these cycloalkenes does not affect any of the marked chiral carbon atoms. Therefore, if compound **A** is a pure enantiomer, the **B** is also a pure enantiomer, not a racemic mixture. In the reaction of **B** with HCl, only 2-ethylcyclobutene can form an optically inactive product. Thus, compound **B** is



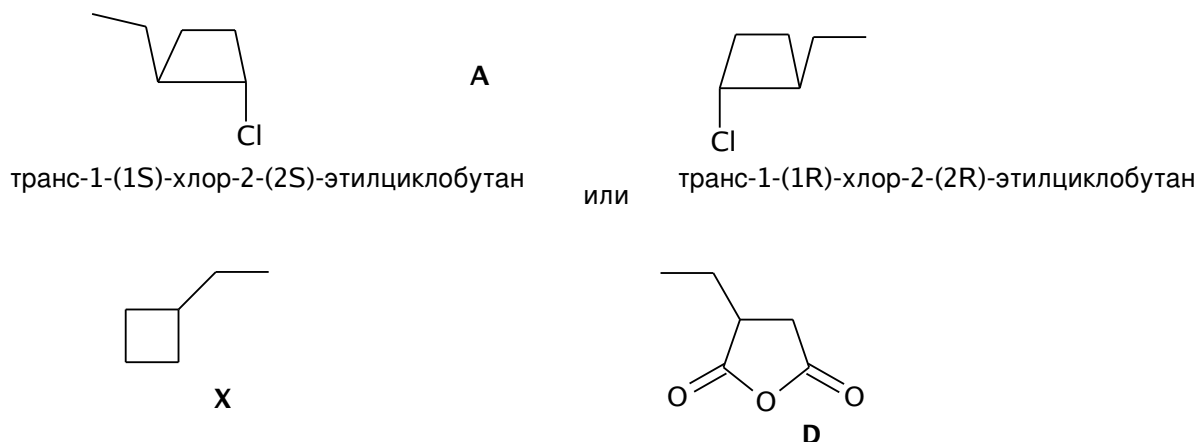
- c) The two possible structures of **A** are



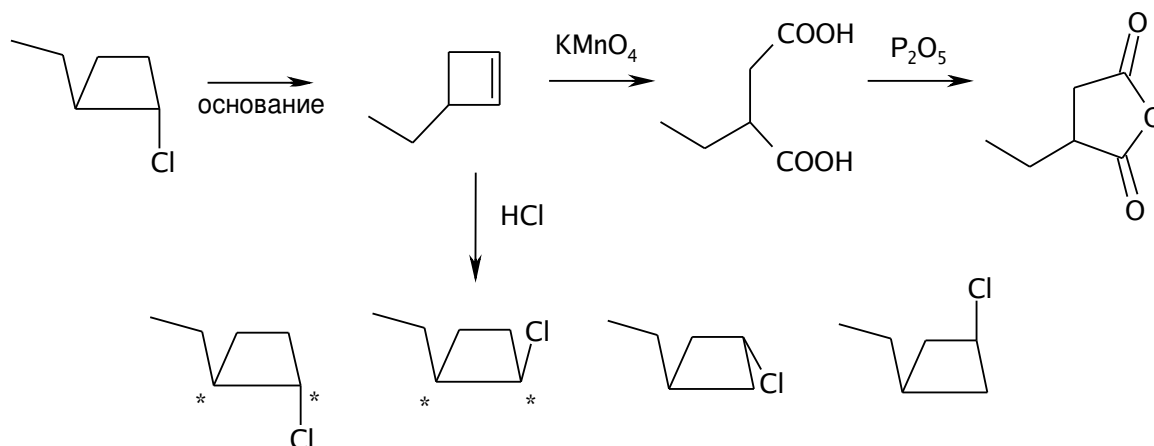
Only the second compound is optically active. Therefore, **A** is 1-chloro-2-ethylcyclobutane. Because dehydrohalogenation is *anti*- β -elimination, the Cl atom and the ethyl group of **A** must be in *trans*-positions. The information supplied in the problem statement is insufficient to decide which of the two enantiomers was actually used. We conclude that compound **A** is either

(*R,R*)-*trans*-1-chloro-2-ethylcyclobutane or (*S,S*)-*trans*-1-chloro-2-ethylcyclobutane.

The two possible structures of **A**, as well as the structures of **X** and **D** are as follows:



d) The reactions are:



Problem 11-4

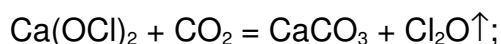
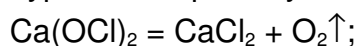
a) Milk of lime is a suspension of hydrated $\text{Ca}(\text{OH})_2$ in water.

b) Halogens undergo disproportionation in aqueous alkali:

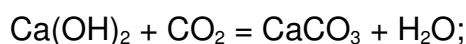


Therefore, the white powder may contain CaCl_2 , $\text{Ca}(\text{OCl})_2$, H_2O , excess $\text{Ca}(\text{OH})_2$, as well as the compounds produced by the reaction of the powder with atmospheric CO_2 (i.e., CaCO_3).

c) $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OCl})_2$ have a relatively low solubility in cold water and, therefore, their hydrates are the principal ingredients of the precipitate. Over time, calcium hypochlorite partially decomposes:



while calcium hydroxide can react with carbon dioxide:



Water content of the powder may also change over time.

At $\text{pH}=12.78$, hydrolysis of $\text{Ca}(\text{OCl})_2$ is suppressed. Therefore, the concentration of OH^- ion can be directly related to the concentration of $\text{Ca}(\text{OH})_2$

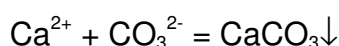
$$M(\text{Ca}(\text{OH})_2) = 74.1 \text{ g/mol}$$

$$[\text{OH}^-] = 10^{(\text{pH} - 14)} = 0.0603 \text{ M}.$$

Neglecting the volume-change effect we find that the amount of $\text{Ca}(\text{OH})_2$ in the 1.000 g sample dissolved in 100 mL of water was

$$100 \cdot \frac{0,0603}{2} = 3.02 \text{ mmol or } 3.02 \times 74.1 = 224 \text{ mg}$$

After the reaction with aqueous Na_2CO_3 ,



all calcium is present in the form of CaCO_3 .

$$M(\text{Ca}(\text{OCl})_2) = 143,0 \text{ g/mol}$$

$$M(\text{CaCO}_3) = 100.1 \text{ g/mol}$$

$$M(\text{CaCl}_2) = 111.0 \text{ g/mol}$$

$$M(\text{CO}_2) = 44.0 \text{ g/mol}$$

$$M(\text{Cl}_2) = 70.9 \text{ g/mol}$$

$$M(\text{H}_2\text{O}) = 18.0 \text{ g/mol}$$

$$n(\text{Ca}^{2+}) = \frac{828}{100,1} = 8.27 \text{ mmol}$$

Chlorine gas is produced by the reaction:



1 g of the powder produces 640 mg or

$$\frac{640}{70,9} = 9.03 \text{ mmol of Cl}_2.$$

Therefore, the amount of $\text{Ca}(\text{OCl})_2$ is

$$\frac{1}{2} \cdot 9,03 = 4.51 \text{ mmol or } 4.51 \times 143 = 645 \text{ mg}$$

The mixture of gases contains Cl_2 and CO_2 . Its molecular mass is

$$M = \frac{\rho \cdot R \cdot T}{P} = \frac{3,128 \cdot 8,314 \cdot 273,2}{101,3} = 70.14 \text{ g/mol}.$$



If the mole fraction of CO_2 is x , then

$$70.9(1 - x) + 44.0x = 70.14, \text{ which gives } x = 0.0283.$$

Therefore, 1 g of the powder contains

$$4,51 \cdot \frac{2 \cdot 0,0283}{1 - 0,0283} = 0.26 \text{ mmol CaCO}_3 \text{ or } 0.26 \times 100.1 = 26.0 \text{ mg}.$$

Finally, the amount of CaCl_2 can be determined from the electrical neutrality condition:

$$2n(\text{Ca}^{2+}) = n(\text{Cl}^-) + n(\text{OCl}^-) + n(\text{OH}^-) + 2 \cdot n(\text{CO}_3^{2-}),$$

$$\text{which gives } n(\text{CaCl}_2) = \frac{2 \cdot 8,27 - 6,03 - 9,03 - 2 \cdot 0,26}{2} = 0.48 \text{ mmol or}$$

$$0.48 \times 111 = 53.3 \text{ mg of CaCl}_2.$$

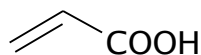
The rest of the mass, $(1000 - 53.3 - 26.0 - 645 - 224) = 51.7 \text{ mg}$ is water

$$n(\text{H}_2\text{O}) = \frac{51,7}{18,0} = 2.87 \text{ mmol}.$$

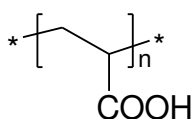
- d) $2\text{Ca}(\text{OH})_2 \cdot 3\text{Ca}(\text{OCl})_2 \cdot 2\text{H}_2\text{O}$, HL-CHM = hydrated lime-calcium hypochlorite mixture. This substance is used for decontamination and disinfection of military equipment exposed to chemical and biological warfare agents.

Problem 11-5

- a) The structural formulas of acrylic acid and PAA are:

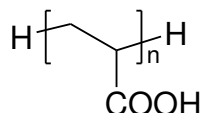


акриловая кислота



ПАК

- b) The molar mass of the 100-unit polymer is



$100M_0 + 2 = (100 \times 72 + 2) = 7202$ g/mol, where M_0 is the molecular mass of one $-\text{CH}_2-\text{CH}(\text{COOH})-$ unit.

- c) The solution contains $\frac{10}{7202} = 1.39 \cdot 10^{-3}$ mol of PAA. Therefore, the initial number of carboxylic groups in the solution is $(1.39 \times 10^{-3})(100)(6.02 \times 10^{23}) = 8.37 \times 10^{22}$.

The concentration of the molecules is $C_0(\text{PAA}) = \frac{1,39 \cdot 10^{-3}}{0,5} = 2.78 \cdot 10^{-3}$ mol/L,

so the concentration of individual carboxyl groups is $C_0(-\text{COOH}) = 0.278$ mol/L.

Thus, the problem boils down to calculating the pH value of a weak acid solution.

We assume that all COOH groups present in the solution ionize independently.

We have

$$[\text{H}^+] = [\text{RCOO}^-] + [\text{OH}^-] \approx [\text{RCOO}^-] \text{ (acidic solution);}$$

$$C_0(-\text{COOH}) = [\text{RCOO}^-] + [\text{RCOOH}] = 0.278.$$

$$K_a = \frac{[\text{H}^+] \cdot [\text{RCOO}^-]}{[\text{RCOOH}]} = \frac{[\text{H}^+]^2}{C_0 - [\text{H}^+]} = 10^{-4.88}.$$

Therefore, $[\text{H}^+] = 1.9 \times 10^{-3}$ and $\text{pH} = 2.72$.

- d) Let us write the degree of dissociation as

$$\alpha = \frac{[-\text{COO}^-]}{[-\text{COO}^-] + [-\text{COOH}]} = \frac{K_a}{K_a + [\text{H}^+]} = \frac{10^{-4.88}}{10^{-4.88} + [\text{H}^+]}$$

Thus, if $\alpha = 0.5$, then $[\text{H}^+] = 10^{-4.88}$, which gives $\text{pH} = 4.88$.