

8th



International Chemistry Olympiad

**7 theoretical problems
3 practical problems**

THE EIGHTH INTERNATIONAL CHEMISTRY OLYMPIAD

HALLE 1976
GERMAN DEMOCRATIC REPUBLIC

THEORETICAL PROBLEMS

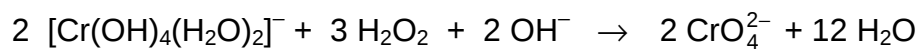
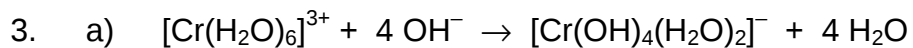
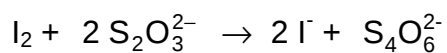
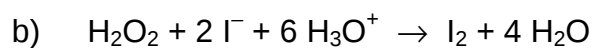
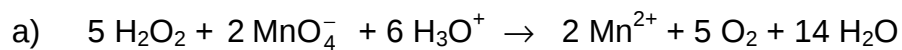
PROBLEM 1

1. Explain by means of generally used international symbols and formulas which compounds are named as peroxo compounds. Write summary formulas for six of them.
2. Write chemical equations for two methods of quantitative determination of the content of peroxide in calcium(II) peroxide.
3. By means of chemical equations express the following chemical reactions:
 - a) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ dissolved in water, is mixed with an excess of sodium hydroxide solution. A clear green solution is formed. The colour of the solution changes to yellow when an aqueous hydrogen peroxide solution is added.
 - b) If an aqueous solution of a violet manganese compound is mixed with a hydrogen peroxide solution, the resulting solution is decolourised and a gas is released from it.

SOLUTION

1. Peroxo compounds contain the functional group: O_2^{2-}
Examples: H_2O_2 , Na_2O_2 , BaO_2 , H_2SO_5 , $\text{H}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{C}_2\text{O}_6$, CrO_5 , $[\text{VO}_2]^{3+}$
2. Calcium(II) peroxide is decomposed by an aqueous solution of a suitable acid, and H_2O_2 which is liberated, is determined by:
 - a) manganometric method,
 - b) iodometric method.

Equations:



b) Equation is given in 2a.

PROBLEM 2

A sample of 2.3793 g of crystallohydrate of the type $M_xA_y \cdot zH_2O$, where M is a metal, reacted with an excess of $SOCl_2$. Gaseous products formed by the reaction were introduced into a barium chloride solution containing hydrochloric acid and hydrogen peroxide. Small quantities of $SOCl_2$ carried by the gaseous products were removed by freezing out. The mass of the precipitate that is deposited from the solution, was 14.004 g. It was found to contain 13.74 mass % of sulphur.

In another experiment, 1.1896 g of the initial substance were dissolved in water and the solution was diluted to a volume of 100 cm^3 . One fifth of this solution required to react with 10 cm^3 of a 0.2-molar $AgNO_3$ solution. The mass of the precipitate formed by the titration was 0.28664 g. (The end point of the titration was determined by the conductometric method.)

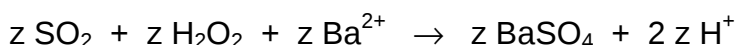
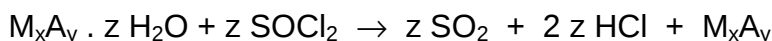
Problems:

1. Calculate the summary formula of the crystallohydrate. (Use the relative atomic mass values given in the attached Periodical Table of Elements.)
2. If you know that the sample can contain a maximum of seven moles of water per one mole of the crystallohydrate, give an example of another possible hydrate that cannot come into consideration due to the given limitation.

SOLUTION

1. a) The content of sulphur confirms that the precipitate is $BaSO_4$.

Reactions:

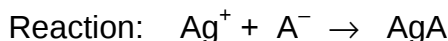


$$n(BaSO_4) = \frac{m(BaSO_4)}{M(BaSO_4)} = \frac{14.004\text{ g}}{233.4\text{ g mol}^{-1}} = 0.06\text{ mol}$$

Amount of substance of H_2O in the hydrate:

$$n(H_2O) = 0.06\text{ mol}$$

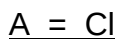
b) Amount of substance of A^- in the sample:



$$n(Ag^+) = c V = 0.2 \text{ mol dm}^{-3} \times 0.01 \text{ dm}^3 = 0.002 \text{ mol}$$

$$n(AgA) = 0.002 \text{ mol}$$

$$M(AgA) = \frac{m(AgA)}{n(AgA)} = \frac{0.28664 \text{ g}}{0.002 \text{ mol}} = 143.32 \text{ g mol}^{-1}$$



The precipitate being formed by the titration is AgCl, thus the hydrate is a chloride.

$$\frac{1.1896}{5} \text{ g, i. e. } 0.23792 \text{ g of the hydrate contain } 0.002 \text{ mol } Cl^-$$

$$2.3792 \text{ g of the hydrate contain } 0.02 \text{ mol } Cl^-.$$

The molar ratio of Cl^- to H_2O in the hydrate:

$$n(Cl^-) : n(H_2O) = 0.02 : 0.06 = 1 : 3$$

Assumption:

i) $MCl \cdot 3 H_2O$

$$n(Cl^-) = 0.02 \text{ mol}$$

$$n(MCl \cdot 3 H_2O) = 0.02 \text{ mol}$$

$$M(MCl_3 \cdot 3 H_2O) = \frac{2,3793 \text{ g}}{0,02 \text{ mol}} = 118.965 \text{ g mol}^{-1}$$

$$\begin{aligned} M(M) &= M(MCl \cdot 3 H_2O) - M(Cl) - 3 M(H_2O) = \\ &= 118.965 - 35.453 - 54.046 = 29.466 \text{ g mol}^{-1} \end{aligned}$$

Elements with similar molar masses are non-metals, therefore the first assumption is not suitable.

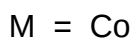
ii) $MCl_2 \cdot 6 H_2O$

$$n(Cl^-) = 0.02 \text{ mol}$$

$$n(MCl_2 \cdot 6 H_2O) = 0.01 \text{ mol}$$

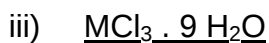
$$M(MCl_2 \cdot 6 H_2O) = \frac{2,3793 \text{ g}}{0,01 \text{ mol}} = 237.93 \text{ g mol}^{-1}$$

$$\begin{aligned} M(M) &= M(MCl_2 \cdot 6 H_2O) - 2 M(Cl) - 6 M(H_2O) = \\ &= 237.93 - 70.906 - 108.092 = 58.932 \text{ g mol}^{-1} \end{aligned}$$



The second assumption satisfies the conditions of the task.

The formula of the hydrate is: **CoCl₂ · 6 H₂O**



$$n(\text{Cl}^-) = 0.02 \text{ mol}$$

$$n(\text{MCl}_3 \cdot 9 \text{H}_2\text{O}) = \frac{0.02}{3} \text{ mol}$$

$$M(\text{MCl}_3 \cdot 9 \text{H}_2\text{O}) = 356.895 \text{ g mol}^{-1}$$

$$\begin{aligned} M(\text{M}) &= M(\text{MCl}_3 \cdot 9 \text{H}_2\text{O}) - 3 M(\text{Cl}) - 9 M(\text{H}_2\text{O}) = \\ &= 356.895 - 106.359 - 162.138 = 88.398 \text{ g mol}^{-1} \end{aligned}$$

M = Y

The hydrate YCl₃ · 9 H₂O as well as the other hydrate SnCl₄ · 12 H₂O cannot come into account because of the limitation in the task (a maximum of seven moles of H₂O per one mole of the hydrate).

PROBLEM 3

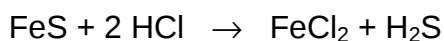
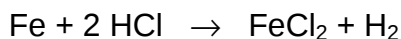
A sample of 5 g of a technical iron(II) sulphide FeS, which contains 5 % metallic iron reacted with hydrochloric acid.

Problems:

1. Calculate the volume of the gaseous products at STP conditions.
2. What is the composition (in volume %) of the gaseous mixture?

SOLUTION

1. Reactions:



$$n(\text{Fe}) = \frac{m(\text{Fe})}{M(\text{Fe})} = \frac{0.25 \text{ g}}{55.85 \text{ g mol}^{-1}} = 4.48 \times 10^{-3} \text{ mol}$$

$$n(\text{FeS}) = \frac{m(\text{FeS})}{M(\text{FeS})} = \frac{4.75 \text{ g}}{87.91 \text{ g mol}^{-1}} = 5.40 \times 10^{-2} \text{ mol}$$

$$V(\text{H}_2) = n(\text{H}_2) \times V_0 = 4.48 \times 10^{-3} \text{ mol} \times 22.4 \text{ dm}^3 \text{ mol}^{-1} = \underline{0.1 \text{ dm}^3}$$

$$V(\text{H}_2\text{S}) = n(\text{H}_2\text{S}) \times V_0 = 5.40 \times 10^{-2} \text{ mol} \times 22.4 \text{ dm}^3 \text{ mol}^{-1} = \underline{1.21 \text{ dm}^3}$$

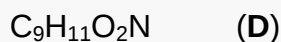
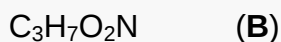
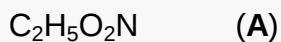
2. Composition of the gaseous mixture:

$$\frac{0.1 \text{ dm}^3}{1.31 \text{ dm}^3} \times 100 = 7.63 \text{ volume \% of H}_2$$

$$\frac{1.21 \text{ dm}^3}{1.31 \text{ dm}^3} \times 100 = 92.37 \text{ volume \% of H}_2\text{S}$$

PROBLEM 4

Four often occurring natural substances have the following summary (empirical) formulas:



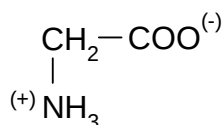
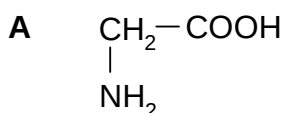
The given substances when allowed to react with an alkali hydroxide solution yield alkali salts. However, in a neutral or acidic solution the reaction takes place on the nitrogen atom.

Problems:

1. Write structural formulas for the compounds **A**, **B**, **C**, and **D**.
2. Which of the given substances are optically active and which ones are inactive?
3. Write the formula of the functional group which is typical of certain natural substances and which is contained also in the product formed by the reaction of two molecules of compound **A**. Give the name of the natural substances to which belongs the above mentioned product.
4. A cyclic organic compound being of technical importance contains also the functional group mentioned in passage 3.
 - a) Write the structural formula of this cyclic compound.
 - b) Write the characteristic part of the structural formula of a macromolecular substance that can be obtained from the mentioned compound.
 - c) Write the characteristic part of the structural formula of an isomeric macromolecular substance that is also technically important.
 - d) Give the name for the group of compounds to which belong the above mentioned macromolecular substances.

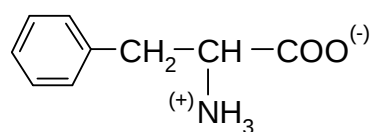
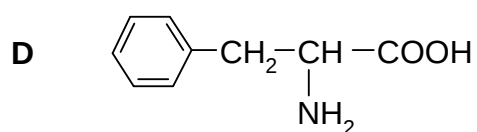
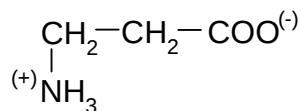
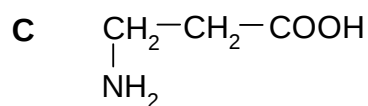
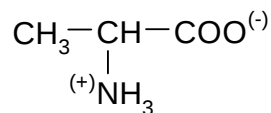
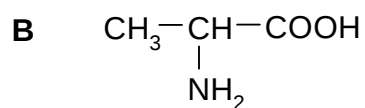
SOLUTION

1.



2. **A** - optically inactive

B - optically active

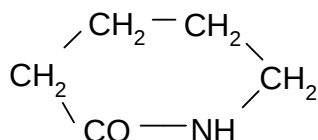


C - optically inactive

D - optically active

3. $-\text{NH}-\text{CO}-$ peptides

4. a)



b) $-\text{CO}-(\text{CH}_2)_5-\text{NH}-$

c) $-\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO}-$

d) polyamides

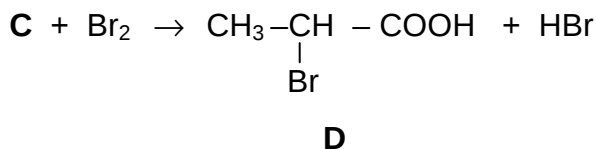
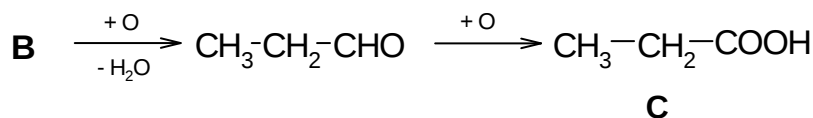
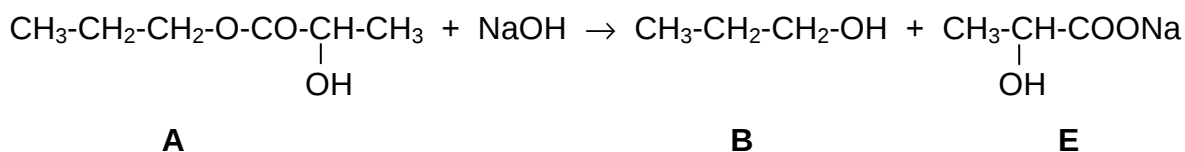
PROBLEM 5

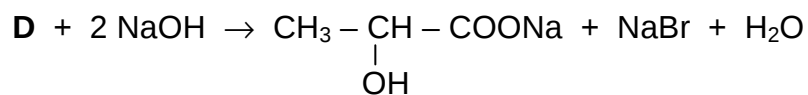
- Compounds **B** and **E** are formed when an organic substance **A** (summary formula $C_6H_{12}O_3$) reacts with a sodium hydroxide solution (saponification).
- Substance **B** can be oxidised in a two-step process to a substance **C**.
- Substance **C** when reacted with bromine yields a substitution product **D** which can be hydrolysed by the reaction with sodium hydroxide solution to produce a substance **E**.
- Substance **E** when allowed to react with a stoichiometric amount of hydrochloric acid gives a compound **F** (40.0 % C, 6.66 % H, the rest is oxygen).
- Substance **F** is an important product of metabolism in biological processes.
- Compound **F** when allowed to stand, splits off one mole of water from two moles of the substance that results in the formation of an unstable compound **G**.
- Substance **F** can also be obtained from a compound **H** containing nitrogen, by one-step reaction with nitrous acid. Assuming the quantitative course of the reaction, 4.5 g of substance **F** are formed from 4.45 g of substance **H**.

Problems:

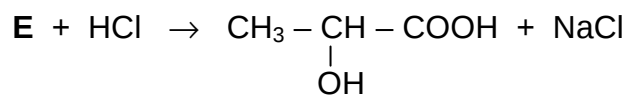
- Write all equations for the above mentioned chemical reactions.
- Give structural formulas of the organic compounds **A – H**.

SOLUTION

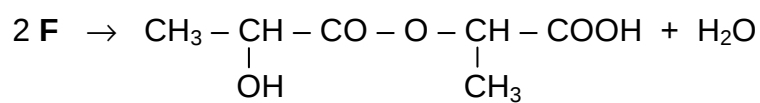




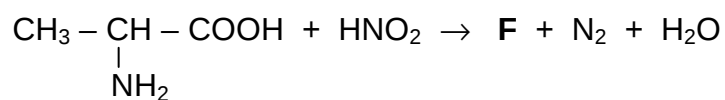
E



F



G



H

PROBLEM 6

Temperature in a larger room should be measured by means of a gaseous thermometer. A glass tube with the internal volume of 80 cm^3 was for this purpose filled with nitrogen at a temperature of 20°C and a pressure of 101.325 kPa . The tube was then slowly and steadily moved throughout the room. Due to the thermal expansion the gas at the higher temperature escapes from the tube and is captured above the liquid whose vapour pressure is negligible. The total volume of the gas escaped from the tube was 35 cm^3 at a temperature of 20°C and a pressure of 101.325 kPa .

Problems:

1. How many moles of nitrogen were used to fill the glass tube?
2. How many moles of nitrogen escaped from the tube at the higher temperature?
3. Calculate the average temperature in the room under investigation if the thermal expansion of the glass tube is assumed to be negligible.
4. Does anything change if instead of pure nitrogen, a mixture containing 50 volume % of nitrogen and 50 volume % of hydrogen is used?

SOLUTION

1. Filling of the tube:

$$n_1(\text{N}_2) = \frac{p V_1}{R T} = \frac{101.325 \text{ kPa} \times 0.080 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 293.15 \text{ K}} = 3.33 \times 10^{-3} \text{ mol}$$

2. Escaped from the tube:

$$n_2(\text{N}_2) = \frac{p V_2}{R T} = \frac{101.325 \text{ kPa} \times 0.035 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 293.15 \text{ K}} = 1.46 \times 10^{-3} \text{ mol}$$

Remained in the tube:

$$n_3(\text{N}_2) = n_1 - n_2 = 1.87 \times 10^{-3} \text{ mol}$$

3. Temperature at which the amount of substance of nitrogen (n_3) takes a volume of V_1 (the mean temperature in the room under investigation):

$$T = \frac{p V_1}{R n_3} = \frac{101.325 \text{ kPa} \times 0.080 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 1.87 \times 10^{-3} \text{ mol}} = 521 \text{ K}$$

$$\underline{t = 248 \text{ }^{\circ}\text{C}}$$

4. No change can occur in comparison with the preceding experiment.
-

PROBLEM 7

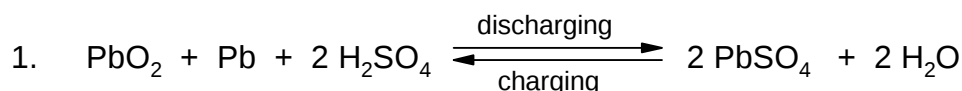
The density of a sulphuric acid solution in a charged lead accumulator should be equal to $\rho = 1.28 \text{ g cm}^{-3}$ which corresponds to the solution containing 36.87 % of H_2SO_4 by mass. In a discharged lead accumulator it should not decrease under the value of $\rho = 1.10 \text{ g cm}^{-3}$ which corresponds to the 14.35 % solution of sulphuric acid.

(Faraday's constant F is equal to 26.8 Ah mol^{-1} .)

Problems:

1. Write the equation for a total electrochemical reaction that takes place in the lead accumulator when it is charged and discharged.
2. Calculate the masses of H_2O and H_2SO_4 being consumed or formed according to the equation in No 1.
3. Calculate the mass of H_2SO_4 that is required to be added to a led accumulator with a capacity of 120 Ah if the content of H_2SO_4 is to be in the range as given in the task.
4. Calculate the difference in volumes of the sulphuric acid solutions in a charged and a discharged lead accumulator with a capacity of 120 Ah.

SOLUTION



$$2. \quad n(\text{H}_2\text{SO}_4) = 2 \text{ mol} \qquad n(\text{H}_2\text{O}) = 2 \text{ mol}$$

$$m(\text{H}_2\text{SO}_4) = 196 \text{ g} \qquad m(\text{H}_2\text{O}) = 36 \text{ g}$$

$$\text{Discharging: } \Delta m(\text{H}_2\text{SO}_4) = -196 \text{ g}$$

$$\Delta m(\text{H}_2\text{O}) = +36 \text{ g}$$

$$\text{Charging: } \Delta m(\text{H}_2\text{SO}_4) = +196 \text{ g}$$

$$\Delta m(\text{H}_2\text{O}) = -36 \text{ g}$$

3. The mass of H_2SO_4 required:

$$26.8 \text{ Ah corresponds to } 98 \text{ g H}_2\text{SO}_4$$

$$120 \text{ Ah corresponds to } 438.8 \text{ g H}_2\text{SO}_4$$

Analogously:

26.8 Ah corresponds to 18 g H₂O

120 Ah corresponds to 80.6 g H₂O

Discharged lead accumulator:

mass of H ₂ SO ₄ solution	–	m
mass of H ₂ SO ₄	–	m_1
mass fraction of H ₂ SO ₄	–	$w_1 = 0.1435$
density of H ₂ SO ₄ solution	–	$\rho_1 = 1.10 \text{ g cm}^{-3}$

Charged lead accumulator:

mass of H ₂ SO ₄ formed	–	$m_2 = 438.8 \text{ g}$
mass of H ₂ O consumed	–	$m_3 = 80.6 \text{ g}$
mass fraction of H ₂ SO ₄	–	$w_2 = 0.3687$
density of the H ₂ SO ₄ solution	–	$\rho_2 = 1.28 \text{ g cm}^{-3}$

Because:

$$w_1 = \frac{m_1}{m} \quad (\text{a})$$

$$w_2 = \frac{m_1 + m_2}{m + m_2 - m_3} \quad (\text{b})$$

We get a system of equations (a) and (b) which are solved for m_1 and m :

$$m_1 = 195.45 \text{ g}$$

$$m = 1362 \text{ g}$$

4. Volume of the electrolyte V_1 in a discharged lead accumulator:

$$V_1 = \frac{m}{\rho_1} = \frac{1362 \text{ g}}{1.10 \text{ g cm}^{-3}} = 1238.2 \text{ cm}^3$$

Volume of the electrolyte V_2 in a charged lead accumulator:

$$V_2 = \frac{m + m_2 - m_3}{\rho_2} = \frac{1720.2 \text{ g}}{1.28 \text{ g cm}^{-3}} = 1343.9 \text{ cm}^3$$

Difference in the volumes:

$$\Delta V = V_2 - V_1 = 1343.9 - 1238.2 = 105.7 \text{ cm}^3$$

PRACTICAL PROBLEMS

PROBLEM 1

A sample contains two of the following cations: Ag^+ , Pb^{2+} , Fe^{2+} , Cr^{3+} , Co^{2+} , Al^{3+} , Mn^{2+} , and one of the following anions: SO_4^{2-} , Cl^- , NO_3^- .

Prove the cations and anions in the sample by means of the following reagents:

2 N-HCl, concentrated H_2SO_4 , 2 N- H_2SO_4 , 2 N- HNO_3 , 2 N- CH_3COOH , NaOH, NH_4OH , H_2O_2 , Na_2CO_3 , $\text{KNO}_3/\text{Na}_2\text{CO}_3$, NH_4SCN , $\text{Na}_2\text{B}_4\text{O}_7$, NaF, $\text{C}_2\text{H}_5\text{OH}$, BaCl_2 , AgNO_3 , NH_4Cl , $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, alizarin B.

Write the results into the attached table in the following way:

- into the column "Reagent" write the formula of the reagent which was needed to prove whether the cation or anion is present or absent in the sample;
- into the column "+/—" mark the presence or absence of an ion, proved in the sample, by the sign "+" and "—" , respectively.

PROBLEM 2

A solution contains sodium oxalate and oxalic acid.

Determine how many milligrams of sodium oxalate and oxalic acid are contained in the solution under investigation.

The following solutions are at your disposal: KMnO_4 ($c = 0.01972 \text{ mol dm}^{-3}$), NaOH ($c = 0.1019 \text{ mol dm}^{-3}$), concentrated H_2SO_4 , and a solution of phenolphthalein.

PROBLEM 3

Four unknown organic aliphatic compounds of a general formula $A-CH_2-B$ are numbered from 1 to 4, and given as samples. Some of them may be in an aqueous solution.

Perform the following experiments:

1. Determine the pH value of the solution.
2. Allow the sample to react with hydrochloric acid.
3. Reaction with alkali hydroxide (basic hydrolysis – 5 minutes boiling under a reverse cooler) and a subsequent proof of halides.

Moreover, the following data are at your disposal:

- a) One of the compounds under investigation forms an intra-molecular anhydride.
- b) The content of carbon and hydrogen (in mass %) as well as the relative molecular mass are known for the same compound, the data being given, however, in an arbitrary order which does not correspond to the numbering of samples.

Determine the functional groups A and B for each substance using results of your experiments as well as the available data.

Write your results into the attached table; mark positive results with sign "+" whereas the negative ones with sign "-".