



THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS

Volume 1

**1st – 20th ICHO
1968 – 1988**

Edited by Anton Sirota

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 1

Editor: Anton Sirota

ISBN 978-80-8072-082-7

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Issued by IUVENTA in 2008
with the financial support of the Ministry of Education of the Slovak Republic

Number of copies: 250
Not for sale.

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Preface

This publication contains the competition problems from the first twenty International Chemistry Olympiads (ICHO) organized in the years 1968 – 1988. It has been published by the ICHO International Information Centre in Bratislava (Slovakia) on the occasion of the 40th anniversary of this international competition.

Not less than 125 theoretical and 50 practical problems were set in the ICHO in the mentioned twenty years. In the elaboration of this collection the editor had to face certain difficulties because the aim was not only to make use of past recordings but also to give them such a form that they may be used in practice and further chemical education. Consequently, it was necessary to make some corrections in order to unify the form of the problems. However, they did not concern the contents and language of the problems.

Many of the first problems were published separately in various national journals, in different languages and they were hard to obtain. Some of them had to be translated into English. Most of the xerox copies of the problems could not be used directly and many texts, schemes and pictures had to be re-written and created again. The changes concern in particular solutions of the problems set in the first years of the ICHO competition that were often available in a brief form and necessary extent only, just for the needs of members of the International Jury. Some practical problems, in which experimental results and relatively simple calculations are required, have not been accompanied with their solutions. Recalculations of the solutions were made in some special cases only when the numeric results in the original solutions showed to be obviously not correct. Although the numbers of significant figures in the results of several solutions do not obey the criteria generally accepted, they were left without change.

In this publication SI quantities and units are used and a more modern method of chemical calculations is introduced. Only some exceptions have been made when, in an effort to preserve the original text, the quantities and units have been used that are not SI.

Unfortunately, the authors of the particular competition problems are not known and due to the procedure of the creation of the ICHO competition problems, it is impossible to assign any author's name to a particular problem. Nevertheless, responsibility for the scientific content and language of the problems lies exclusively with the organizers of the particular International Chemistry Olympiads.

Nowadays many possibilities for various activities are offered to a gifted pupil. If we want to gain the gifted and talented pupil for chemistry we have to look for ways how to evoke his interest. The International Chemistry Olympiad fulfils all preconditions to play this role excellently.

This review of the competition problems from the first twenty International Chemistry Olympiads should serve to both competitors and their teachers as a source of further ideas in their preparation for this difficult competition. For those who have taken part in some of these International Chemistry Olympiads the collection of the problems could be of help as archival and documentary material. The edition of the competition problems will continue with its second part and will contain the problems set in the International Chemistry Olympiads in the years 1989 – 2008.

The International Chemistry Olympiad has its 40th birthday. In the previous forty years many known and unknown people - teachers, authors, pupils, and organizers - proved their abilities and knowledge and contributed to the success of this already well known and world-wide competition. We wish to all who will organize and attend the future International Chemistry Olympiads, success and happiness.

Bratislava, July 2008

Anton Sirota, editor

1st



International Chemistry Olympiad

**4 theoretical problems
2 practical problems**

THE FIRST INTERNATIONAL CHEMISTRY OLYMPIAD 18–21 JULY 1968, PRAGUE, CZECHOSLOVAKIA

THEORETICAL PROBLEMS

PROBLEM 1

A mixture of hydrogen and chlorine kept in a closed flask at a constant temperature was irradiated by scattered light. After a certain time the chlorine content decreased by 20 % compared with that of the starting mixture and the resulting mixture had the composition as follows: 60 volume % of chlorine, 10 volume % of hydrogen, and 30 volume % of hydrogen chloride.

Problems:

- 1.1 What is the composition of the initial gaseous mixture?
- 1.2 How chlorine, hydrogen, and hydrogen chloride are produced?

SOLUTION



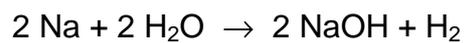
30 volume parts of hydrogen chloride could only be formed by the reaction of 15 volume parts of hydrogen and 15 volume parts of chlorine. Hence, the initial composition of the mixture had to be:

$$\text{Cl}_2: 60 + 15 = 75 \%$$

$$\text{H}_2: 10 + 15 = 25 \%$$

- 1.2 Chlorine and hydrogen are produced by electrolysis of aqueous solutions of NaCl:
- $$\text{NaCl(aq)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$$





Hydrogen chloride is produced by the reaction of hydrogen with chlorine.

PROBLEM 2

Write down equations for the following reactions:

- 2.1 Oxidation of chromium(III) chloride with bromine in alkaline solution (KOH).
 - 2.2 Oxidation of potassium nitrite with potassium permanganate in acid solution (H₂SO₄).
 - 2.3 Action of chlorine on lime water (Ca(OH)₂) in a cold reaction mixture.
-

SOLUTION

- 2.1 $2 \text{CrCl}_3 + 3 \text{Br}_2 + 16 \text{KOH} \rightarrow 2 \text{K}_2\text{CrO}_4 + 6 \text{KBr} + 6 \text{KCl} + 8 \text{H}_2\text{O}$
 - 2.2 $5 \text{KNO}_2 + 2 \text{KMnO}_4 + 3 \text{H}_2\text{SO}_4 \rightarrow 2 \text{MnSO}_4 + \text{K}_2\text{SO}_4 + 5 \text{KNO}_3 + 3 \text{H}_2\text{O}$
 - 2.3. $\text{Cl}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaOCl}_2 + \text{H}_2\text{O}$
-
-

PROBLEM 3

The gas escaping from a blast furnace has the following composition:

12.0 volume % of CO ₂	28.0 volume % of CO
3.0 volume % of H ₂	0.6 volume % of CH ₄
0.2 volume % of C ₂ H ₄	56.2 volume % of N ₂

Problems:

- 3.1** Calculate the theoretical consumption of air (in m³) which is necessary for a total combustion of 200 m³ of the above gas if both the gas and air are measured at the same temperature. (Oxygen content in the air is about 20 % by volume).
- 3.2** Determine the composition of combustion products if the gas is burned in a 20 % excess of air.

SOLUTION

	O ₂
3.1 2 CO + O ₂ → 2 CO ₂	14
2 H ₂ + O ₂ → 2 H ₂ O	1.5
CH ₄ + 2 O ₂ → CO ₂ + 2 H ₂ O	1.2
C ₂ H ₄ + 3 O ₂ → 2 CO ₂ + 2 H ₂ O	0.6
	17.3 parts × 5 = 86.5 parts of the air

$$\begin{array}{r}
 200 \text{ m}^3 \text{ of the gas} \dots\dots\dots 2 \times 86.5 = 173.0 \text{ m}^3 \text{ of the air} \\
 \phantom{200 \text{ m}^3 \text{ of the gas}} + 20 \% 34.6 \text{ m}^3 \\
 \hline
 207.6 \text{ m}^3 \text{ of the air}
 \end{array}$$

- 3.2** 207.6 : 5 = 41.52 parts of O₂ : 2 = 20.76 parts of O₂ for 100 m³ of the gas
 20.76 × 4 = 83.04 parts of N₂ for 100 m³ of the gas

Balance:	CO ₂	H ₂ O	N ₂	O ₂
(volume parts)	12.00	3.00	56.20	20.76
	28.00	1.20	83.04	- 17.30
	0.60	0.40		
	0.40			
	<hr/>			
	41.00	4.60	139.24	3.46

Total: $41.00 + 4.60 + 139.24 + 3.46 = 188.30$ of volume parts of the gaseous components.

$$\% \text{H}_2\text{O} = \frac{4.60}{188.30} \times 100 = 2.44$$

$$\% \text{N}_2 = \frac{139.24}{188.30} \times 100 = 73.95$$

$$\% \text{O}_2 = \frac{3.46}{188.30} \times 100 = 1.84$$

PROBLEM 4

A volume of 31.7 cm³ of a 0.1-normal NaOH is required for the neutralization of 0.19 g of an organic acid whose vapour is thirty times as dense as gaseous hydrogen.

Problem:

4.1 Give the name and structural formula of the acid.

(The acid concerned is a common organic acid.)

SOLUTION

4.1

a) The supposed acid may be: HA, H₂A, H₃A, etc.

$$n(\text{NaOH}) = c V = 0.1 \text{ mol dm}^{-3} \times 0.0317 \text{ dm}^3 = 3.17 \times 10^{-3} \text{ mol}$$

$$n(\text{acid}) = \frac{3.17 \times 10^{-3}}{\nu} \text{ mol}$$

where $\nu = 1, 2, 3, \dots$

$$n(\text{acid}) = \frac{m(\text{acid})}{M(\text{acid})}$$

$$M(\text{acid}) = \nu \times \frac{0.19 \text{ g}}{3.17 \times 10^{-3} \text{ mol}} = \nu \times 60 \text{ g mol}^{-1} \quad (1)$$

b) From the ideal gas law we can obtain:

$$\frac{\rho_1}{\rho_2} = \frac{M_1}{M_2}$$

$$M(\text{H}_2) = 2 \text{ g mol}^{-1}$$

$$M(\text{acid}) = 30 \times 2 = 60 \text{ g mol}^{-1}$$

By comparing with (1): $\nu = 1$

The acid concerned is a monoprotic acid and its molar mass is 60 g mol⁻¹.

The acid is acetic acid: CH₃-COOH

PRACTICAL PROBLEMS**PROBLEM 1 (Practical)**

There are ten test tubes in the rack at your disposal (1 – 10) and each test tube contains one of aqueous solutions of the following salts: Na_2SO_4 , AgNO_3 , KI , $\text{Ba}(\text{OH})_2$, NH_4Cl , Ag_2SO_4 , $\text{Pb}(\text{NO}_3)_2$, NaOH , NH_4I , KCl .

For identification of the particular test tubes you can use mutual reactions of the solutions in the test tubes only.

Determine in which order the solutions of the salts in your rack are and write chemical equations of the reactions you used for identification of the salts.

PROBLEM 2 (Practical)

Each of the six test tubes (A – F) in the rack contains one of the following substances:

benzoic acid, salicylic acid, citric acid, tartaric acid, oxalic acid and glucose.

Determine the order in which the substances in the test tubes are placed in your rack and give chemical reactions you used for identification of the substances.

For identification of the substances the following aqueous solutions are at your disposal: HCl , H_2SO_4 , NaOH , NH_4OH , CuSO_4 , KMnO_4 , FeCl_3 , KCl , and distilled water.

2nd



International Chemistry Olympiad

**4 theoretical problems
2 practical problems**

THE SECOND INTERNATIONAL CHEMISTRY OLYMPIAD 16–20 JUNE 1969, KATOWICE, POLAND

THEORETICAL PROBLEMS

PROBLEM 1

An amount of 20 g of potassium sulphate was dissolved in 150 cm³ of water. The solution was then electrolysed. After electrolysis, the content of potassium sulphate in the solution was 15 % by mass.

Problem:

What volumes of hydrogen and oxygen were obtained at a temperature of 20 °C and a pressure of 101 325 Pa?

SOLUTION

On electrolysis, only water is decomposed and the total amount of potassium sulphate in the electrolyte solution is constant. The mass of water in the solution:

1.1 Before electrolysis (on the assumption that $\rho = 1 \text{ g cm}^{-3}$): $m(\text{H}_2\text{O}) = 150 \text{ g}$

1.2 After electrolysis:

$$m(\text{H}_2\text{O}) = m(\text{solution}) - m(\text{K}_2\text{SO}_4) = \frac{20 \text{ g}}{0.15} - 20 \text{ g} = 113.3 \text{ g}$$

The mass of water decomposed on electrolysis:

$$m(\text{H}_2\text{O}) = 150 - 113.3 = 36.7 \text{ g, i. e.}$$

$$n(\text{H}_2\text{O}) = 2.04 \text{ mol}$$



thus, $n(\text{H}_2) = 2.04 \text{ mol}$

$$n(\text{O}_2) = 1.02 \text{ mol}$$

$$V(\text{H}_2) = \frac{n(\text{H}_2)RT}{p} = \frac{2.04 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 293.15 \text{ K}}{101325 \text{ Pa}}$$

$$\approx 0.049 \text{ m}^3, \text{ resp. } 49 \text{ dm}^3$$

$$V(\text{O}_2) = \frac{1}{2} V(\text{H}_2) \approx 0.0245 \text{ m}^3 \approx 24.5 \text{ dm}^3$$

PROBLEM 2

A compound **A** contains 38.67 % of potassium, 13.85 % of nitrogen, and 47.48 % of oxygen. On heating, it is converted to a compound **B** containing 45.85 % of potassium, 16.47 % of nitrogen, and 37.66 % of oxygen.

Problem:

2.1 What are the stoichiometric formulas of the compounds?

2.2 Write the corresponding chemical equation.

SOLUTION

2.1 Compound **A**:

$$\text{K}_x\text{N}_y\text{O}_z \quad x : y : z = \frac{38.67}{39.1} = \frac{13.85}{14} = \frac{47.48}{16} = 0.989 : 0.989 : 2.968 = 1 : 1 : 3$$

A : KNO_3

Compound **B**:

$$\text{K}_p\text{N}_q\text{O}_r \quad p : q : r = \frac{45.85}{39.1} = \frac{16.47}{14} = \frac{37.66}{16} = 1.173 : 1.176 : 2.354 = 1 : 1 : 2$$

B : KNO_2

2.2 Equation: $2 \text{KNO}_3 \rightarrow 2 \text{KNO}_2 + \text{O}_2$

PROBLEM 3

A 10 cm³ sample of an unknown gaseous hydrocarbon was mixed with 70 cm³ of oxygen and the mixture was set on fire by means of an electric spark. When the reaction was over and water vapours were liquefied, the final volume of gases decreased to 65 cm³. This mixture then reacted with a potassium hydroxide solution and the volume of gases decreased to 45 cm³.

Problem:

What is the molecular formula of the unknown hydrocarbon if volumes of gases were measured at standard temperature and pressure (STP) conditions?

SOLUTION

The unknown gaseous hydrocarbon has the general formula: C_xH_y

$$n(\text{C}_x\text{H}_y) = \frac{0.010 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = \frac{0.010}{22.4} \text{ mol}$$

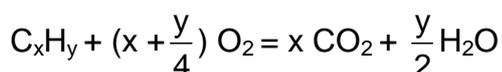
Balance of oxygen:

- Before the reaction: 70 cm³, i. e. $\frac{0.070}{22.4}$ mol

- After the reaction: 45 cm³, i. e. $\frac{0.045}{22.4}$ mol

Consumed in the reaction: $\frac{0.025}{22.4}$ mol of O₂

According to the equation:



Hence, $\frac{0.020}{22.4}$ mol of O₂ reacted with carbon and $\frac{0.020}{22.4}$ mol of CO₂ was formed

(C + O₂ = CO₂),

$\frac{0.005}{22.4}$ mol O₂ combined with hydrogen and $\frac{0.010}{22.4}$ mol of water was obtained

(2 H₂ + O₂ = 2 H₂O).

$$3 n(\text{C}) = n(\text{CO}_2) = \frac{0.020}{22.4} \text{ mol}$$

$$n(\text{H}_2) = 2 n(\text{H}_2\text{O}) = \frac{0.020}{22.4} \text{ mol}$$

$$x : y = n(\text{C}) : n(\text{H}_2) = 0.020 : 0.020 = 1 : 1$$

From the possible solutions C_2H_2 , C_3H_3 , C_4H_4 , C_5H_5 . only C_2H_2 satisfies to the conditions given in the task, i. e. the unknown hydrocarbon is acetylene.

PROBLEM 4

Calcium carbide and water are the basic raw materials in the production of:

- ethanol
- acetic acid
- ethylene and polyethylene
- vinyl chloride
- benzene

Problem:

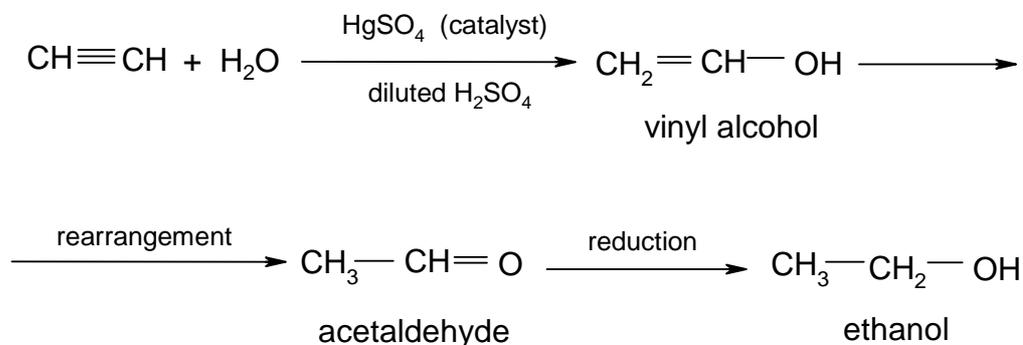
Give basic chemical equations for each reaction by which the above mentioned compounds can be obtained.

SOLUTION

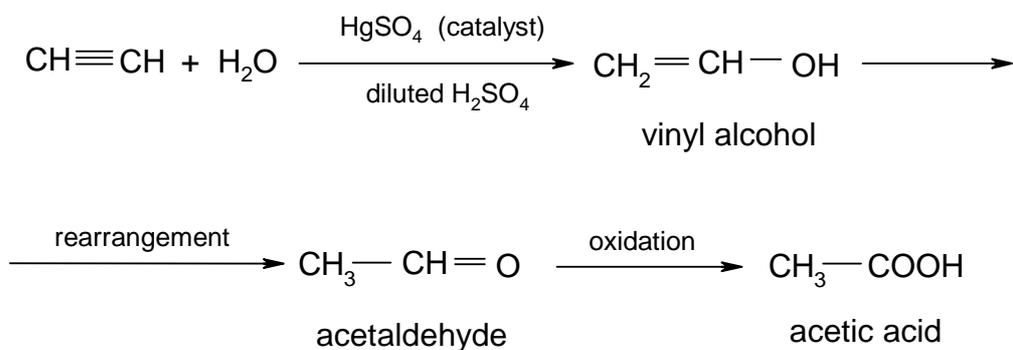
Basic reaction: $\text{CaC}_2 + 2 \text{H}_2\text{O} = \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$

From acetylene can be obtained:

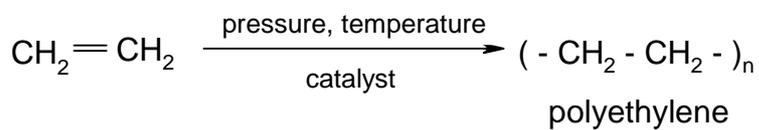
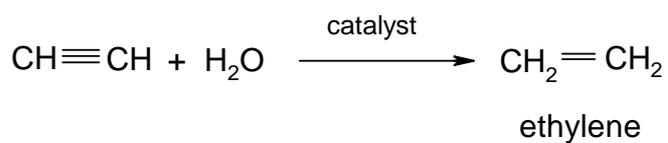
- ethanol



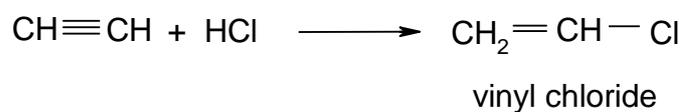
- acetic acid



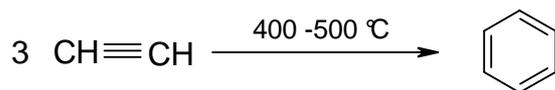
c) ethylene, polyethylene



d) vinyl chloride



e) benzene



PRACTICAL PROBLEMS**PROBLEM 1 (Practical)**

a) Three numbered test-tubes (1-3) contain mixtures of two substances from the following pairs (4 variants):

- | | | |
|---|--|---|
| 1. ZnSO ₄ - NaBr | NaCl - Ca(NO ₃) ₂ | MgSO ₄ - NH ₄ Cl |
| 2. AlCl ₃ - KBr | CaCl ₂ - NaNO ₃ | ZnCl ₂ - (NH ₄) ₂ SO ₄ |
| 3. KNO ₃ - Na ₂ CO ₃ | KCl - MgSO ₄ | NH ₄ Cl - Ba(NO ₃) ₂ |
| 4. MgCl ₂ - KNO ₃ | K ₂ CO ₃ - ZnSO ₄ | Al(NO ₃) ₃ - NaCl |

b) Each of the test-tubes numbered 4 and 5 contains one of the following substances: glucose, saccharose, urea, sodium acetate, oxalic acid.

Problem:

By means of reagents that are available on the laboratory desk determine the content of the individual test-tubes. Give reasons for both the tests performed and your answers and write the chemical equations of the corresponding reactions.

Note:

For the identification of substances given in the above task, the following reagents were available to competing pupils: 1 N HCl, 3 N HCl, 1 N H₂SO₄, concentrated H₂SO₄, FeSO₄, 2 N NaOH, 20 % NaOH, 2 N NH₄Cl, 2 N CuSO₄, 2 N BaCl₂, 0,1 N AgNO₃, 0,1 % KMnO₄, distilled water, phenolphthalein, methyl orange. In addition, further laboratory facilities, such as platinum wire, cobalt glass, etc., were available.

PROBLEM 2 (Practical)

Allow to react 10 cm³ of a 3 N HCl solution with the metal sample (competing pupils were given precisely weighed samples of magnesium, zinc or aluminium) and collect the hydrogen evolved in the reaction in a measuring cylinder above water. Perform the task by means of available device and procedure.

In order to simplify the problem, calculate the mass of your metal sample from the volume of hydrogen on the assumption that it was measured at STP conditions.

3rd



**6 theoretical problems
2 practical problems**

THE THIRD INTERNATIONAL CHEMISTRY OLYMPIAD 1–5 JULY 1970, BUDAPEST, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

An amount of 23 g of gas (density $\rho = 2.05 \text{ g dm}^{-3}$ at STP) when burned, gives 44 g of carbon dioxide and 27 g of water.

Problem:

What is the structural formula of the gas (compound)?

SOLUTION

The unknown gas : X

$$\text{From the ideal gas law : } M(X) = \frac{\rho(X) R T}{p} = 46 \text{ g mol}^{-1}$$

$$n(X) = \frac{23 \text{ g}}{46 \text{ g mol}^{-1}} = 0.5 \text{ mol}$$

$$n(\text{CO}_2) = \frac{44 \text{ g}}{44 \text{ g mol}^{-1}} = 1 \text{ mol}$$

$$n(\text{C}) = 1 \text{ mol}$$

$$m(\text{C}) = 12 \text{ g}$$

$$n(\text{H}_2\text{O}) = \frac{27 \text{ g}}{18 \text{ g mol}^{-1}} = 1.5 \text{ mol}$$

$$n(\text{H}) = 3 \text{ mol}$$

$$m(\text{H}) = 3 \text{ g}$$

The compound contains also oxygen, since

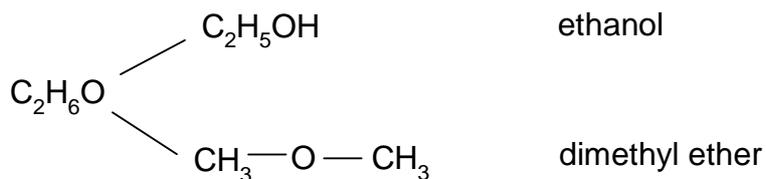
$$m(\text{C}) + m(\text{H}) = 12 \text{ g} + 3 \text{ g} = 15 \text{ g} < 23 \text{ g}$$

$$m(\text{O}) = 23 \text{ g} - 15 \text{ g} = 8 \text{ g}$$

$$n(\text{O}) = 0,5 \text{ mol}$$

$$n(\text{C}) : n(\text{H}) : n(\text{O}) = 1 : 3 : 0,5 = 2 : 6 : 1$$

The empirical formula of the compound is $\text{C}_2\text{H}_6\text{O}$.



Ethanol is liquid in the given conditions and therefore, the unknown gas is dimethyl ether.

PROBLEM 2

A sample of crystalline soda (**A**) with a mass of 1.287 g was allowed to react with an excess of hydrochloric acid and 100.8 cm³ of a gas was liberated (measured at STP).

Another sample of different crystalline soda (**B**) with a mass of 0.715 g was decomposed by 50 cm³ of 0.2 N sulphuric acid.

After total decomposition of soda, the excess of the sulphuric acid was neutralized which required 50 cm³ of 0.1 N sodium hydroxide solution (by titration on methyl orange indicator).

Problems:

- 2.1** How many molecules of water in relation to one molecule of Na₂CO₃ are contained in the first sample of soda?
- 2.2** Have both samples of soda the same composition?

Relative atomic masses: $A_r(\text{Na}) = 23$; $A_r(\text{H}) = 1$; $A_r(\text{C}) = 12$; $A_r(\text{O}) = 16$.

SOLUTION

2.1 Sample **A**: Na₂CO₃ · x H₂O

$$m(\text{A}) = 1.287 \text{ g}$$

$$n(\text{CO}_2) = \frac{pV}{RT} = 0.0045 \text{ mol} = n(\text{A})$$

$$M(\text{A}) = \frac{1.287 \text{ g}}{0.0045 \text{ mol}} = 286 \text{ g mol}^{-1}$$

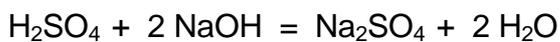
$$M(\text{A}) = M(\text{Na}_2\text{CO}_3) + x M(\text{H}_2\text{O})$$

$$x = \frac{M(\text{A}) - M(\text{Na}_2\text{CO}_3)}{M(\text{H}_2\text{O})} = \frac{(286 - 106) \text{ g mol}^{-1}}{18 \text{ g mol}^{-1}} = 10$$

Sample **A**: Na₂CO₃ · 10 H₂O

2.2 Sample **B**: $\text{Na}_2\text{CO}_3 \cdot x \text{H}_2\text{O}$

$$m(\text{B}) = 0.715 \text{ g}$$



$$n(\text{NaOH}) = c V = 0.1 \text{ mol dm}^{-3} \times 0.05 \text{ dm}^3 = 0.005 \text{ mol}$$

$$\text{Excess of H}_2\text{SO}_4: n(\text{H}_2\text{SO}_4) = 0.0025 \text{ mol}$$

Amount of substance combined with sample **B**:

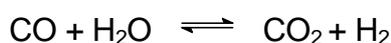
$$n(\text{H}_2\text{SO}_4) = 0.0025 \text{ mol} = n(\text{B})$$

$$M(\text{B}) = \frac{0.715 \text{ g}}{0.0025 \text{ g mol}^{-1}} = 286 \text{ g mol}^{-1}$$

Sample **B**: $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$

PROBLEM 3

Carbon monoxide was mixed with 1.5 times greater volume of water vapours. What will be the composition (in mass as well as in volume %) of the gaseous mixture in the equilibrium state if 80 % of carbon monoxide is converted to carbon dioxide?

SOLUTION

Assumption:

$$n(\text{CO}) = 1 \text{ mol}$$

$$n(\text{H}_2\text{O}) = 1.5 \text{ mol}$$

After reaction:

$$n(\text{CO}) = 0.2 \text{ mol}$$

$$n(\text{H}_2\text{O}) = 0.7 \text{ mol}$$

$$n(\text{CO}_2) = 0.8 \text{ mol}$$

$$n(\text{H}_2) = 0.8 \text{ mol}$$

$$\varphi(\text{CO}) = \frac{V(\text{CO})}{V} = \frac{0.2 \text{ mol}}{2.5 \text{ mol}} = 0.08 \text{ i.e. } 8 \text{ vol. \% of CO}$$

$$\varphi(\text{H}_2\text{O}) = \frac{V(\text{H}_2\text{O})}{V} = \frac{0.7 \text{ mol}}{2.5 \text{ mol}} = 0.28 \text{ i.e. } 28 \text{ vol. \% of H}_2\text{O}$$

$$\varphi(\text{CO}_2) = \frac{V(\text{CO}_2)}{V} = \frac{0.8 \text{ mol}}{2.5 \text{ mol}} = 0.32 \text{ i.e. } 32 \text{ vol. \% of CO}_2$$

$$\varphi(\text{H}_2) = \frac{V(\text{H}_2)}{V} = \frac{0.8 \text{ mol}}{2.5 \text{ mol}} = 0.32 \text{ i.e. } 32 \text{ vol. \% of H}_2$$

Before reaction:

$$m(\text{CO}) = n(\text{CO}) \times M(\text{CO}) = 1 \text{ mol} \times 28 \text{ g mol}^{-1} = 28 \text{ g}$$

$$m(\text{H}_2\text{O}) = 1.5 \text{ mol} \times 18 \text{ g mol}^{-1} = 27 \text{ g}$$

After reaction:

$$m(\text{CO}) = 0,2 \text{ mol} \times 28 \text{ g mol}^{-1} = 5.6 \text{ g}$$

$$m(\text{H}_2\text{O}) = 0.7 \text{ mol} \times 18 \text{ g mol}^{-1} = 12.6 \text{ g}$$

$$m(\text{CO}_2) = 0.8 \text{ mol} \times 44 \text{ g mol}^{-1} = 35.2 \text{ g}$$

$$m(\text{H}_2) = 0.8 \times 2 \text{ g mol}^{-1} = 1.6 \text{ g}$$

$$w(\text{CO}) = \frac{m(\text{CO})}{m} = \frac{5.6 \text{ g}}{55.0 \text{ g}} = 0.102 \text{ i.e. } 10.2 \text{ mass \% of CO}$$

$$w(\text{H}_2\text{O}) = \frac{m(\text{H}_2\text{O})}{m} = \frac{12.6 \text{ g}}{55.0 \text{ g}} = 0.229 \text{ i.e. } 22.9 \text{ mass \% of H}_2\text{O}$$

$$w(\text{CO}_2) = \frac{m(\text{CO}_2)}{m} = \frac{35.2 \text{ g}}{55.0 \text{ g}} = 0.640 \text{ i.e. } 64.0 \text{ mass \% of CO}_2$$

$$w(\text{H}_2) = \frac{m(\text{H}_2)}{m} = \frac{1.6 \text{ g}}{55.0 \text{ g}} = 0.029 \text{ i.e. } 2.9 \text{ mass \% of H}_2$$

PROBLEM 4

An alloy consists of rubidium and one of the other alkali metals. A sample of 4.6 g of the alloy when allowed to react with water, liberates 2.241 dm³ of hydrogen at STP.

Problems:

4.1 Which alkali metal is the component of the alloy?

4.2 What composition in % by mass has the alloy?

Relative atomic masses:

$A_r(\text{Li}) = 7$; $A_r(\text{Na}) = 23$; $A_r(\text{K}) = 39$; $A_r(\text{Rb}) = 85.5$; $A_r(\text{Cs}) = 133$

SOLUTION

4.1 M - alkali metal



$$n(\text{H}_2) = 0.1 \text{ mol}$$

$$n(\text{M}) = 0.2 \text{ mol}$$

Mean molar mass:

$$M = \frac{4.6 \text{ g}}{0.2 \text{ mol}} = 23 \text{ g mol}^{-1}$$

4.2 Concerning the molar masses of alkali metals, only lithium can come into consideration, i.e. the alloy consists of rubidium and lithium.

$$n(\text{Rb}) + n(\text{Li}) = 0.2 \text{ mol}$$

$$m(\text{Rb}) + m(\text{Li}) = 4.6 \text{ g}$$

$$n(\text{Rb}) M(\text{Rb}) + n(\text{Li}) M(\text{Li}) = 4.6 \text{ g}$$

$$n(\text{Rb}) M(\text{Rb}) + (0.2 - n(\text{Rb})) M(\text{Li}) = 4.6$$

$$n(\text{Rb}) \cdot 85.5 + (0.2 - n(\text{Rb})) \times 7 = 4.6$$

$$n(\text{Rb}) = 0.0408 \text{ mol}$$

$$n(\text{Li}) = 0.1592 \text{ mol}$$

$$\% \text{ Rb} = \frac{0.0408 \text{ mol} \times 85.5 \text{ g mol}^{-1}}{4.6 \text{ g}} \times 100 = 76$$

$$\% \text{ Li} = \frac{0.1592 \text{ mol} \times 7 \text{ g mol}^{-1}}{4.6 \text{ g}} \times 100 = 24$$

PROBLEM 5

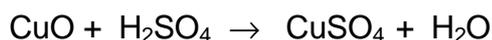
An amount of 20 g of copper (II) oxide was treated with a stoichiometric amount of a warm 20% sulphuric acid solution to produce a solution of copper (II) sulphate.

Problem:

How many grams of crystalline copper(II) sulphate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) have crystallised when the solution is cooled to 20 °C?

Relative atomic masses: $A_r(\text{Cu}) = 63.5$; $A_r(\text{S}) = 32$; $A_r(\text{O}) = 16$; $A_r(\text{H}) = 1$

Solubility of CuSO_4 at 20 °C: $s = 20.9 \text{ g of CuSO}_4 \text{ in } 100 \text{ g of H}_2\text{O}$.

SOLUTION

$$n(\text{CuO}) = \frac{m(\text{CuO})}{M(\text{CuO})} = \frac{20 \text{ g}}{79.5 \text{ g mol}^{-1}} = 0.2516 \text{ g}$$

$$n(\text{H}_2\text{SO}_4) = n(\text{CuSO}_4) = 0.2516 \text{ mol}$$

Mass of the CuSO_4 solution obtained by the reaction:

$$\begin{aligned} m(\text{solution CuSO}_4) &= m(\text{CuO}) + m(\text{solution H}_2\text{SO}_4) = \\ &= m(\text{CuO}) + \frac{n(\text{H}_2\text{SO}_4) \times M(\text{H}_2\text{SO}_4)}{w(\text{H}_2\text{SO}_4)} = 20 \text{ g} + \frac{0.2516 \text{ mol} \times 98 \text{ g mol}^{-1}}{0.20} \end{aligned}$$

$$m(\text{solution CuSO}_4) = 143.28 \text{ g}$$

Mass fraction of CuSO_4 :

a) in the solution obtained:

$$w(\text{CuSO}_4) = \frac{m(\text{CuSO}_4)}{m(\text{solution CuSO}_4)} = \frac{n(\text{CuSO}_4) \times M(\text{CuSO}_4)}{m(\text{solution CuSO}_4)} = 0.28$$

b) in saturated solution of CuSO_4 at 20°C:

$$w(\text{CuSO}_4) = \frac{20.9 \text{ g}}{120.9 \text{ g}} = 0.173$$

c) in crystalline $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$:

$$w(\text{CuSO}_4) = \frac{M(\text{CuSO}_4)}{M(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})} = 0.639$$

Mass balance equation for CuSO_4 :

$$0.28 m = 0.639 m_1 + 0.173 m_2$$

m - mass of the CuSO_4 solution obtained by the reaction at a higher temperature.

m_1 - mass of the crystalline $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

m_2 - mass of the saturated solution of CuSO_4 at 20 °C.

$$0.28 \times 143.28 = 0.639 m_1 + 0.173 \times (143.28 - m_1)$$

$$m_1 = 32.9 \text{ g}$$

The yield of the crystallisation is 32.9 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

PROBLEM 6

Oxide of a certain metal contains 22.55 % of oxygen by mass. Another oxide of the same metal contains 50.48 mass % of oxygen.

Problem:

1. What is the relative atomic mass of the metal?
-

SOLUTION

Oxide 1: M_2O_x

$$2 : x = \frac{w(M)}{A_r(M)} : \frac{w(O)}{A_r(O)}$$

$$2 : x = \frac{0.7745}{A_r(M)} : \frac{0.2255}{16} = \frac{54.95}{A_r(M)} \quad (1)$$

Oxide 2: M_2O_y

$$2 : y = \frac{w(M)}{A_r(M)} : \frac{w(O)}{A_r(O)}$$

$$2 : y = \frac{0.4952}{A_r(M)} : \frac{0.5048}{16} = \frac{15.695}{A_r(M)} \quad (2)$$

When (1) is divided by (2):

$$\frac{y}{x} = \frac{54.95}{15.695} = 3.5$$

$$\frac{y}{x} = \frac{7}{2}$$

By substituting $x = 2$ into equation (1):

$$A_r(M) = 54.95$$

$$M = \text{Mn}$$

$$\text{Oxide 1} = \text{MnO}$$

$$\text{Oxide 2} = \text{Mn}_2\text{O}_7$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

An unknown sample is a mixture of 1.2-molar H₂SO₄ and 1.47-molar HCl. By means of available solutions and facilities determine:

1. the total amount of substance (in val) of the acid being present in 1 dm³ of the solution,
 2. the mass of sulphuric acid as well as hydrochloric acid present in 1 dm³ of the sample.
-
-

PROBLEM 2 (Practical)

By means of available reagents and facilities perform a qualitative analysis of the substances given in numbered test tubes and write down their chemical formulas.

Give 10 equations of the chemical reactions by which the substances were proved:

5 equations for reactions of precipitation,

2 equations for reactions connected with release of a gas,

3 equations for redox reactions.

4th



International Chemistry Olympiad

**6 theoretical problems
2 practical problems**

THE FOURTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–10 JULY 1972, MOSCOW, SOVIET UNION

THEORETICAL PROBLEMS

PROBLEM 1

A mixture of two solid elements with a mass of 1.52 g was treated with an excess of hydrochloric acid. A volume of 0.896 dm³ of a gas was liberated in this process and 0.56 g of a residue remained which was undissolved in the excess of the acid.

In another experiment, 1.52 g of the same mixture were allowed to react with an excess of a 10 % sodium hydroxide solution. In this case 0.896 dm³ of a gas were also evolved but 0.96 g of an undissolved residue remained.

In the third experiment, 1.52 g of the initial mixture were heated to a high temperature without access of the air. In this way a compound was formed which was totally soluble in hydrochloric acid and 0.448 dm³ of an unknown gas were released. All the gas obtained was introduced into a one litre closed vessel filled with oxygen. After the reaction of the unknown gas with oxygen the pressure in the vessel decreased by approximately ten times ($T = \text{const}$).

Problem:

1.1 Write chemical equations for the above reactions and prove their correctness by calculations.

In solving the problem consider that the volumes of gases were measured at STP and round up the relative atomic masses to whole numbers.

SOLUTION

1.1 a) Reaction with hydrochloric acid:

1.52 g – 0.56 g = 0.96 g of a metal reacted and 0.896 dm³ of hydrogen (0.04 mol) were formed.

$$\text{combining mass of the metal: } 11.2 \times \frac{0.96}{0.896} = 12 \text{ g}$$

Possible solutions:

Relative atomic mass of the metal	Oxidation number	Element	Satisfying?
12	I	C	No
24	II	Mg	Yes
36	III	Cl	No



b) Reaction with sodium hydroxide:

1.52 g – 0.96 g = 0.56 g of an element reacted, 0.896 dm³ (0.04 mol) of hydrogen were formed.

$$\text{combining mass of the metal: } 11.2 \times \frac{0.56}{0.896} = 7 \text{ g}$$

Possible solutions:

Relative atomic mass of the element	Oxidation number	Element	Satisfying?
7	I	Li	No
14	II	N	No
21	III	Ne	No
28	IV	Si	Yes



c) Combining of both elements:

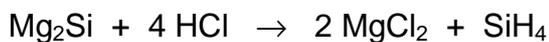
0.96 g Mg + 0.56 g Si = 1.52 g of silicide Mg_xSi_y

$$w(\text{Mg}) = \frac{0.96 \text{ g}}{1.52 \text{ g}} = 0.63 \quad w(\text{Si}) = \frac{0.56 \text{ g}}{1.52 \text{ g}} = 0.37$$

$$x : y = \frac{0.63}{24} : \frac{0.37}{28} = 2 : 1$$

silicide: Mg₂Si

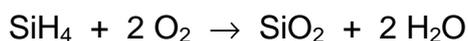
d) Reaction of the silicide with acid:



$$n(\text{Mg}_2\text{Si}) = \frac{1.52 \text{ g}}{76 \text{ g mol}^{-1}} = 0.02 \text{ mol}$$

$$n(\text{SiH}_4) = \frac{0.448 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.02 \text{ mol}$$

e) Reaction of silane with oxygen:



$$V = 1 \text{ dm}^3$$

On the assumption that $T = \text{const}$: $p_2 = \frac{n_2}{n_1} p_1$

$$n_1(\text{O}_2) = \frac{1 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.0446 \text{ mol}$$

Consumption of oxygen in the reaction: $n(\text{O}_2) = 0.04 \text{ mol}$

The remainder of oxygen in the closed vessel:

$$n_2(\text{O}_2) = 0.0446 \text{ mol} - 0.04 \text{ mol} = 0.0046 \text{ mol}$$

$$p_2 = \frac{0.0046 \text{ mol}}{0.0446 \text{ mol}} \times p_1 \approx 0.1 p_1$$

PROBLEM 2

A mixture of metallic iron with freshly prepared iron (II) and iron (III) oxides was heated in a closed vessel in the atmosphere of hydrogen. An amount of 4.72 g of the mixture when reacted, yields 3.92 g of iron and 0.90 g of water.

When the same amount of the mixture was allowed to react with an excess of a copper(II) sulphate solution, 4.96 g of a solid mixture were obtained.

Problems:

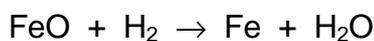
- 2.1 Calculate the amount of 7.3 % hydrochloric acid ($\rho = 1.03 \text{ g cm}^{-3}$) which is needed for a total dissolution of 4.72 g of the starting mixture.
- 2.2 What volume of a gas at STP is released?

Relative atomic masses:

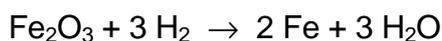
$$A_r(\text{O}) = 16; \quad A_r(\text{S}) = 32; \quad A_r(\text{Cl}) = 35.5; \quad A_r(\text{Fe}) = 56; \quad A_r(\text{Cu}) = 64$$

SOLUTION

- 2.1 a) Reduction by hydrogen:



$$n(\text{Fe}) = n(\text{FeO}); \quad n(\text{H}_2\text{O}) = n(\text{FeO})$$



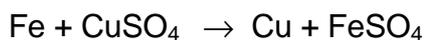
$$n(\text{Fe}) = 2 n(\text{Fe}_2\text{O}_3); \quad n(\text{H}_2\text{O}) = 3 n(\text{Fe}_2\text{O}_3)$$

The mass of iron after reduction: 3.92 g

The total amount of substance of iron after reduction:

$$n(\text{Fe}) + n(\text{FeO}) + 2 n(\text{Fe}_2\text{O}_3) = \frac{3.92 \text{ g}}{56 \text{ g mol}^{-1}} = 0.07 \text{ mol} \quad (1)$$

- b) Reaction with copper(II) sulphate:



Increase of the mass: $4.96 \text{ g} - 4.72 \text{ g} = 0.24 \text{ g}$

After reaction of 1 mol Fe, an increase of the molar mass would be:

$$M(\text{Cu}) - M(\text{Fe}) = 64 \text{ g mol}^{-1} - 56 \text{ g mol}^{-1} = 8 \text{ g mol}^{-1}$$

Amount of substance of iron in the mixture:

$$n(\text{Fe}) = \frac{0.24 \text{ g}}{8 \text{ g mol}^{-1}} = 0.03 \text{ mol} \quad (2)$$

c) Formation of water after reduction:

0.90 g H₂O, i.e. 0.05 mol

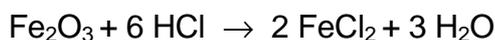
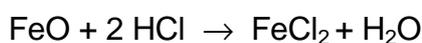
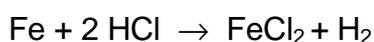
$$0.05 \text{ mol} = n(\text{Fe}) + 3 n(\text{Fe}_2\text{O}_3) \quad (3)$$

By solving equations (1), (2), and (3):

$$n(\text{FeO}) = 0.02 \text{ mol}$$

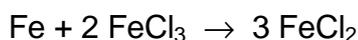
$$n(\text{Fe}_2\text{O}_3) = 0.01 \text{ mol}$$

d) Consumption of acid:



$$\begin{aligned} n(\text{HCl}) &= 2 n(\text{Fe}) + 2 n(\text{FeO}) + 6 n(\text{Fe}_2\text{O}_3) = \\ &= 0.06 \text{ mol} + 0.04 \text{ mol} + 0.06 \text{ mol} = 0.16 \text{ mol} \end{aligned}$$

A part of iron reacts according to the equation:



$$n(\text{Fe}) = 0.5 \times n(\text{FeCl}_3) = n(\text{Fe}_2\text{O}_3)$$

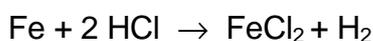
$$n(\text{Fe}) = 0.01 \text{ mol}$$

It means that the consumption of acid decreases by 0.02 mol.

The total consumption of acid: $n(\text{HCl}) = 0.14 \text{ mol}$

$$V(7.3\% \text{ HCl}) = \frac{n M}{w \rho} = \frac{0.14 \text{ mol} \times 36.5 \text{ g mol}^{-1}}{0.073 \times 1.03 \text{ g cm}^{-3}} = 68 \text{ cm}^3$$

2.2 Volume of hydrogen:



Iron in the mixture: 0.03 mol

Iron reacted with FeCl₃: 0.01 mol

Iron reacted with acid: 0.02 mol

Hence, 0.02 mol of hydrogen, i.e. 0.448 dm³ of hydrogen are formed.

PROBLEM 3

A volume of 200 cm³ of a 2-normal sodium chloride solution ($\rho = 1.10 \text{ g cm}^{-3}$) was electrolysed at permanent stirring in an electrolytic cell with copper electrodes. Electrolysis was stopped when 22.4 dm³ (at STP) of a gas were liberated at the cathode.

Problem:

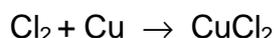
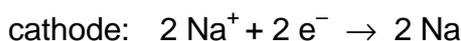
3.1 Calculate the mass percentage of NaCl in the solution after electrolysis.

Relative atomic masses:

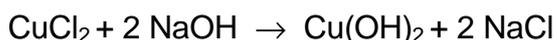
$$A_r(\text{H}) = 1; \quad A_r(\text{O}) = 16; \quad A_r(\text{Na}) = 23; \quad A_r(\text{Cl}) = 35.5; \quad A_r(\text{Cu}) = 64.$$

SOLUTION

3.1 Calculations are made on the assumption that the following reactions take place:



Because the electrolyte solution is permanently being stirred the following reaction comes into consideration:



On the assumption that all chlorine reacts with copper, the mass of NaCl in the electrolyte solution remains unchanged during the electrolysis.

$$m(\text{NaCl}) = n M = c V M = 2 \text{ mol dm}^{-3} \times 0.2 \text{ dm}^3 \times 58.5 \text{ g mol}^{-1} = 23.4 \text{ g}$$

$$V(\text{H}_2) = 22.4 \text{ dm}^3, \text{ i. e. } n(\text{H}_2) = 1 \text{ mol}$$

The amount of water is decreased in the solution by:

$$n(\text{H}_2\text{O}) = 2 \text{ mol}$$

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

Before electrolysis:

$$m(\text{solution NaCl}) = V \rho = 200 \text{ cm}^3 \times 1.10 \text{ g cm}^{-3} = 220 \text{ g}$$

$$\% \text{ NaCl} = \frac{23.4 \text{ g}}{220 \text{ g}} \times 100 = 10.64$$

After electrolysis:

$$m(\text{solution NaCl}) = 220 \text{ g} - 36 \text{ g} = 184 \text{ g}$$

$$\% \text{ NaCl} = \frac{23.4 \text{ g}}{184 \text{ g}} \times 100 = 12.72$$

PROBLEM 4

Amount of 50 g of a 4 % sodium hydroxide solution and 50 g of a 1.825 % solution of hydrochloric acid were mixed in a heat insulated vessel at a temperature of 20 °C. The temperature of the solution obtained in this way increased to 23.4 °C. Then 70 g of a 3.5 % solution of sulphuric acid at a temperature of 20 °C were added to the above solution.

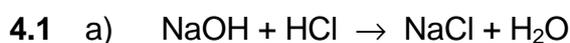
Problems:

- 4.1 Calculate the final temperature of the resulting solution.
 4.2 Determine the amount of a dry residue that remains after evaporation of the solution.

In calculating the first problem use the heat capacity value $c = 4.19 \text{ J g}^{-1} \text{ K}^{-1}$.

Relative atomic masses:

$A_r(\text{H}) = 1$; $A_r(\text{O}) = 16$; $A_r(\text{Na}) = 23$; $A_r(\text{S}) = 32$; $A_r(\text{Cl}) = 35.5$.

SOLUTION

$$n(\text{NaOH}) = \frac{m(\text{solution NaOH}) \times w(\text{NaOH})}{M(\text{NaOH})} = \frac{50 \text{ g} \times 0.04}{40 \text{ g mol}^{-1}} = 0.05 \text{ mol}$$

$$n(\text{HCl}) = \frac{50 \text{ g} \times 0.01825}{36.5 \text{ g mol}^{-1}} = 0.025 \text{ mol}$$

unreacted: $n(\text{NaOH}) = 0.025 \text{ mol}$

b) When 1 mol of water is formed, neutralization heat is:

$$\Delta H_{\text{neutr}} = - \frac{m c \Delta t}{n(\text{H}_2\text{O})} = \frac{100 \text{ g} \times 4.19 \text{ J g}^{-1} \text{ K}^{-1} \times 3.4 \text{ K}}{0.025 \text{ mol}} = - 57\,000 \text{ J mol}^{-1}$$



The temperature of the resulting solution is calculated according to the equation:

$$m_1 c_1 t_1 + m_2 c_2 t_2 = m c t$$

$$c_1 = c_2 = c$$

$$m_1 t_1 + m_2 t_2 = m t$$

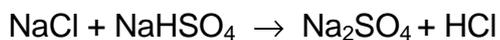
$$t = \frac{m_1 t_1 + m_2 t_2}{m} = \frac{(100 \times 23.4) + (70 \times 20.0)}{170} = 22 \text{ }^\circ\text{C}$$

- d) The temperature increase due to the reaction of NaOH with H₂SO₄ is as follows:

$$t = - \frac{n(\text{H}_2\text{O}) \Delta H_{\text{neutr}}}{m c} = - \frac{0.025 \text{ mol} \times 57\,000 \text{ J mol}^{-1}}{170 \text{ g} \times 4.19 \text{ J g}^{-1} \text{ K}^{-1}} = 2 \text{ K}$$

The final temperature of the solution: $t = 22 + 2 = 24 \text{ }^\circ\text{C}$

- 4.2 e) When the solution has evaporated the following reaction is assumed to take place:



Na₂SO₄ is the dry residue.

$$m(\text{Na}_2\text{SO}_4) = n M = 0.025 \text{ mol} \times 142 \text{ g mol}^{-1} = 3.55 \text{ g}$$

PROBLEM 5

Only one product was obtained by the reaction of bromine with an unknown hydrocarbon. Its density was 5,207 times as great as that of the air.

Problem:

5.1 Determine the structural formula of the unknown hydrocarbon.

Relative atomic masses: $A_r(\text{H}) = 1$; $A_r(\text{C}) = 12$; $A_r(\text{Br}) = 80$.

SOLUTION

5.1 Relative molecular mass of the initial hydrocarbon can be calculated from the density value:

$$M_r(\text{RBr}) = 29 \times 5.207 = 151$$

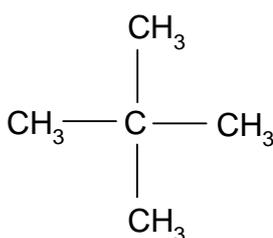
Monobromo derivative can only come into consideration because the relative molecular mass of dibromo derivative should be greater:

$$M_r(\text{RBr}_2) > 160$$

$$M_r(\text{RH}) = 151 - 80 + 1 = 72$$

The corresponding summary formula: C_5H_{12}

The given condition (the only product) is fulfilled by 2,2-dimethyl propane:



PROBLEM 6

Organic compound **A** is 41.38 % carbon, 3.45 % hydrogen and the rest is oxygen. Compound **A** when heated with ethanol in the presence of an acid yields a new substance **B** which contains 55.81 % carbon, 6.97 % hydrogen, and oxygen.

The initial compound **A** when allowed to react with hydrobromide yields product **C** which on boiling in water gives substance **D** containing 35.82 % carbon, 4.48 % hydrogen, and oxygen. An amount of 2.68 g of substance **D** required reacting with 20 cm³ of a 2 N solution of potassium hydroxide.

Problems:

6.1 Determine structural formulas of all the above mentioned substances **A**, **B**, **C** and **D**.

Use the finding that compound **A** splits off water when heated.

6.2 Write chemical equations for the above reactions.

Relative atomic masses: $A_r(\text{H}) = 1$; $A_r(\text{C}) = 12$; $A_r(\text{O}) = 16$; $A_r(\text{K}) = 39$.

SOLUTION

6.1 Stoichiometric formulas of compounds:



$$x : y : z = \frac{41.38}{12} : \frac{3.45}{1} : \frac{55.17}{16} = 1 : 1 : 1$$



$$m : n : p = \frac{55.81}{12} : \frac{6.97}{1} : \frac{37.22}{16} = 2 : 3 : 1$$



$$a : b : c = \frac{35.82}{12} : \frac{4.48}{1} : \frac{59.70}{16} = 4 : 6 : 5$$

20 cm³ of 2 N KOH correspond 0.04 / v mol of substance **D** and it corresponds to 2.68 g of substance **D**

$$v = 1, 2, 3, \dots$$

$$1 \text{ mol of compound } \mathbf{D} = v \times 67 \text{ g}$$

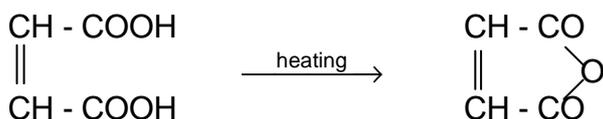
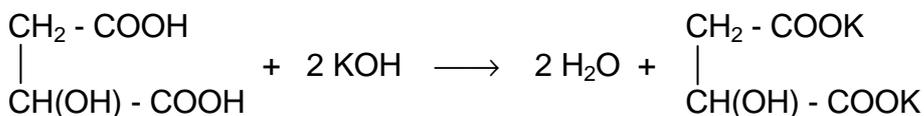
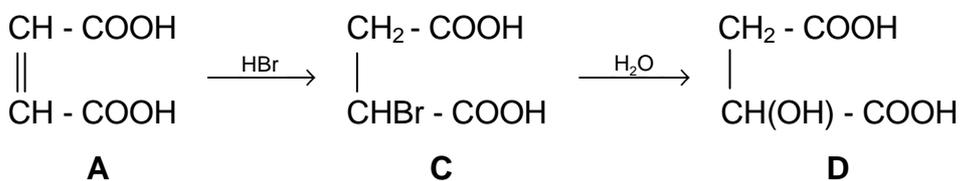
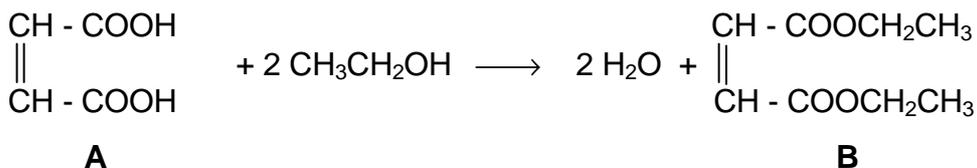
$M_r(\mathbf{D}) = 67$ or 134 or 201 , etc.

Due to both the stoichiometric formula and relative molecular mass of compound **D**, its composition is $C_4H_6O_5$.

Then molecular formulas for compounds **A**, **B**, and **C** are as follows:

A: $C_4H_4O_4$ **B:** $C_8H_{12}O_4$ **C:** $C_4H_5O_4Br$

6.2 Equations:



Compound **A**: maleic acid

PRACTICAL PROBLEMS**PROBLEM 1 (Practical)**

Determine unknown samples in ten numbered test tubes using reagents and facilities available on the laboratory desk. Write chemical equations for the most important reactions that were used to identify each substance. In case that the reactions take place in solutions, write equations in a short ionic form.

PROBLEM 2 (Practical)

On June 10th, a mixture of formic acid with an excess of ethanol was prepared. This mixture was kept in a closed vessel for approximately one month. Determine quantitatively the composition of the mixture on the day of the competition, using only reagents and facilities available on the laboratory desk. Calculate the amounts of the acid and ethanol in per cent by mass which were initially mixed together.

5th



International Chemistry Olympiad

**6 theoretical problems
3 practical problems**

THE FIFTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–10 JULY 1973, SOFIA, BULGARIA

THEORETICAL PROBLEMS

PROBLEM 1

In nitrating a hydroxy derivative of benzene a compound is formed which contains 49.0 % by mass of oxygen. A charge of 4350 C is required for a total electroreduction of 0.458 g of the compound, efficiency being 80 %.

Problem:

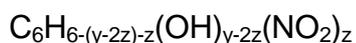
1.1 Determine the stoichiometric as well as structural formulas of the compound if the product of the electrochemical reduction is an aromatic hydroxy amino derivative.

$$F \text{ (Faraday's charge)} = 96\,500 \text{ C mol}^{-1}$$

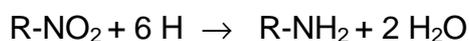
SOLUTION

1.1 a) Formula of the compound: $C_6H_xO_yN_z$

The compound is a hydroxy nitroderivative of benzene:



b) Equation of the reduction:



Combining mass of the compound:

$$E = \frac{M_r(\text{compound})}{6 z} \quad (1)$$

An amount of charge which is required for the electrochemical reduction:

$$Q = 4350 \text{ C} \times 0.8 = 3480 \text{ C}$$

Combining mass of the compound:

$$E = \frac{m}{\frac{3480 \text{ C}}{F}} = 0.458 \times \frac{96500 \text{ C}}{3480 \text{ C}} = 12.7$$

$$\text{In relation to (1): } M_r(\text{compound}) = 76.2 \times z \quad (2)$$

$$\text{c) } \% \text{ O} = \frac{y \times M_r(\text{O}) \times 100}{M_r(\text{compound})}$$

$$49 = \frac{y \times 16 \times 100}{M_r(\text{compound})}$$

$$M_r(\text{compound}) = 32.7 y$$

$$\text{d) } M_r(\text{compound}) = 6 M_r(\text{C}) + x M_r(\text{H}) + y M_r(\text{O}) + z M_r(\text{N})$$

$$M_r(\text{compound}) = 6 \times 12 + x + 16 y + 14 z$$

Taking into consideration the general formula of the unknown hydroxy derivative of benzene:

$$x = 6 - (y - 2 z) - z + y - 2 z$$

$$x = 6 - z \quad (4)$$

$$\text{Then: } M_r(\text{compound}) = 72 + 6 - z + 16 y + 14 z$$

$$M_r(\text{compound}) = 78 + 16 y + 13 z \quad (5)$$

By solving equations (2), (3), (4), and (5) we obtain:

$$\underline{M_r(\text{compound}) = 229}$$

$$x = 3$$

$$y = 7$$

$$z = 3$$

The molecular formula of the compound is: $\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ or $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$.

The compound is 2, 4, 6-trinitrophenol

PROBLEM 2

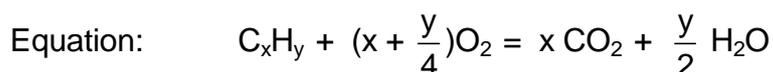
A mixture of a gaseous hydrocarbon and oxygen is in a vessel of a volume of 1 dm³ at a temperature of 406.5 K and a pressure of 101 325 Pa. There is twice as much oxygen in the mixture as is needed for the reaction with the hydrocarbon. After combustion of the hydrocarbon the pressure in the vessel (at the same temperature) is increased by 5 %.

Problem:

2.1 What hydrocarbon was in the mixture when the mass of water formed by the combustion was 0.162 g.

SOLUTION

2.1 Amounts of substances of reactants and reaction products:



$$n(\text{H}_2\text{O}) = \frac{m(\text{H}_2\text{O})}{M(\text{H}_2\text{O})} = \frac{0.162 \text{ g}}{18 \text{ g mol}^{-1}} = 0.009 \text{ mol}$$

$$n(\text{C}_x\text{H}_y) = \frac{0.009 \text{ mol}}{\frac{y}{2}} = \frac{0.018}{y} \text{ mol} \quad (1)$$

$$n(\text{O}_2) = \left(x + \frac{y}{4}\right) \times \frac{0.009 \text{ mol}}{\frac{y}{2}} = \frac{x + \frac{y}{4}}{y} \times 0.018 \text{ mol} \quad (2)$$

$$n(\text{CO}_2) = x \frac{0.009 \text{ mol}}{\frac{y}{2}} = \frac{x}{y} \times 0.018 \text{ mol} \quad (3)$$

Before reaction:

$$n(\text{mixture}) = \frac{pV}{RT} = \frac{101.325 \text{ kPa} \times 1 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 406.5 \text{ K}} = 0.03 \text{ mol}$$

$$n(\text{C}_x\text{H}_y) + 2 n(\text{O}_2) = 0.03 \text{ mol} \quad (4)$$

After reaction: $p = 101.325 \text{ kPa} \times 1.05 = 106.4 \text{ kPa}$

$$n(\text{mixture}) = \frac{pV}{RT} = \frac{106.4 \text{ kPa} \times 1 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 406.5 \text{ K}} = 0.0315 \text{ mol}$$

$$n(\text{CO}_2) + n(\text{O}_2) + n(\text{H}_2\text{O}) = 0.0315 \text{ mol}$$

$$n(\text{CO}_2) + n(\text{O}_2) = 0.0225 \text{ mol} \tag{5}$$

When (1), (2), and (3) are substituted in (4) and (5), an equation of two unknowns is obtained which when solved yields

$$x = 3; \quad y = 6$$

The stoichiometric formula of the unknown hydrocarbon is: C_3H_6 .

PROBLEM 3

Equal volumes (10 cm³) of 0.01-molar solutions of CH₃COOH and HClO were mixed and then diluted to a total volume of 100 cm³. Ionisation constant of CH₃COOH is equal to 1.8×10^{-5} and that for HClO is $3,7 \times 10^{-8}$.

Problems:

Calculate:

- 3.1 degree of ionisation for each of the acids in the solution,
- 3.2 degree of ionisation of HClO if the diluted solution would not contain CH₃COOH,
- 3.3 pH value for the solution containing at the same time CH₃COOH and HClO.

SOLUTION

CH₃COOH: K_1, α_1, c_1

HClO: K_2, α_2, c_2

$c_1 = c_2 = 1 \times 10^{-3} \text{ mol dm}^{-3} = c$

$$3.1 \quad K_1 = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(\alpha_1 + \alpha_2)c \times \alpha_1 c}{(1 - \alpha_1)c} = \frac{(\alpha_1 + \alpha_2)\alpha_1 c}{1 - \alpha_1} \quad (1)$$

$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = \frac{(\alpha_1 + \alpha_2)\alpha_2 c}{1 - \alpha_2} \quad (2)$$

$K_1 \gg K_2$, therefore also $\alpha_1 \gg \alpha_2$ and $\alpha_1 + \alpha_2 \approx \alpha_1$

$$K_1(1 - \alpha_1) = \alpha_1^2 c$$

$$c \alpha_1^2 + K_1 \alpha_1 - K_1 = 0$$

$$\alpha_1 = 0,125$$

When (2) is divided by (1):

$$\frac{K_2}{K_1} = \frac{(1 - \alpha_1)\alpha_2}{(1 - \alpha_2)\alpha_1}$$

After substitution of α_1 : $\alpha_2 = 2.94 \cdot 10^{-4}$

$$3.2 \quad K_2 = \frac{\alpha_2^2 c}{1 - \alpha_2}$$

$$\alpha_2 \ll 1$$

$$K_2 = \alpha_2^2 c$$

$$\alpha_2 = 6,08 \cdot 10^{-3}$$

$$3.3 \quad [\text{H}_3\text{O}^+] = \alpha_1 c + \alpha_2 c = (\alpha_1 + \alpha_2) c = (0,125 + 2,94 \times 10^{-4}) \times 10^{-3} \approx 1,25 \times 10^{-4} \text{ mol dm}^{-3}$$

pH = 3,9

PROBLEM 4

When solutions of two unknown substances are mixed together in stoichiometric ratio, 1.25 g of a precipitate are formed which contain a salt of a bivalent metal M. The precipitate when heated to 1100 °C is decomposed to 0.70 g of a solid metal oxide MO and another gaseous oxide. After evaporation of the filtrate, a dry residue with a mass of 2.0 g remains which yields two products by thermal decomposition at 215 °C: a gaseous oxide and 0.90 g of water vapour. The total volume of the gaseous mixture is 1.68 dm³ (at STP).

Problem:

- 4.1 Determine the unknown compounds and write chemical equations for the above mentioned reactions.

SOLUTION

- 4.1 a) Dry residue: 2.0 g

H₂O: 0.90 g, i. e. 0.05 mol

Gaseous oxide A_xO_y: 1.1 g

$$n(\text{mixture}) = \frac{1.68 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.075 \text{ mol}$$

$$n(\text{A}_x\text{O}_y) = n(\text{mixture}) - n(\text{H}_2\text{O}) = 0.025 \text{ mol}$$

$$M(\text{A}_x\text{O}_y) = \frac{1.1 \text{ g}}{0.025 \text{ mol}} = 44 \text{ g mol}^{-1}$$

$$x M(\text{A}) = M(\text{A}_x\text{O}_y) - y M(\text{O})$$

Solution 1:

$$\text{If } x = 1 \text{ and } y = 1, \text{ then } M(\text{A}) = M(\text{A}_x\text{O}_y) - M(\text{O}) = (44 - 16) \text{ g mol}^{-1} = 28 \text{ g mol}^{-1}$$

A = Si. It does not satisfy the requirements of the task.

Solution 2:

$$\text{If } x = 2 \text{ and } y = 1 \text{ then } M(\text{A}) = 14 \text{ g mol}^{-1}$$

A = N and the gaseous oxide is N₂O.

Solution 3:

$$\text{If } x = 1 \text{ and } y = 2 \text{ then } M(\text{A}) = 12 \text{ g mol}^{-1}$$

A = C and the gaseous oxide is CO₂.

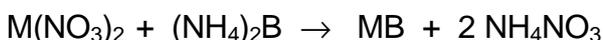
Solution 2 is correct, since it is known that gaseous N_2O is formed by thermal decomposition of NH_4NO_3 . This conclusion is supported by the following calculation:

$$M(\text{dry residue}) = \frac{2.0 \text{ g}}{0.025 \text{ mol}} = 80 \text{ g mol}^{-1} = M(\text{NH}_4\text{NO}_3)$$

Reaction of the thermal decomposition:



b) The precipitation reaction can be described by the following equation:



$$M(\text{MB}) = \frac{1.25 \text{ g}}{0.0125 \text{ mol}} = 100 \text{ g mol}^{-1}$$

$$M(\text{MO}) = \frac{0.70 \text{ g}}{0.0125 \text{ mol}} = 56 \text{ g mol}^{-1}$$

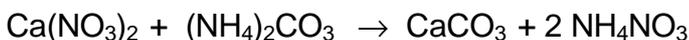
$$M(\text{M}) = M(\text{MO}) - M(\text{O}) = 56 - 16 = 40 \text{ g mol}^{-1}$$

M = Ca

Since

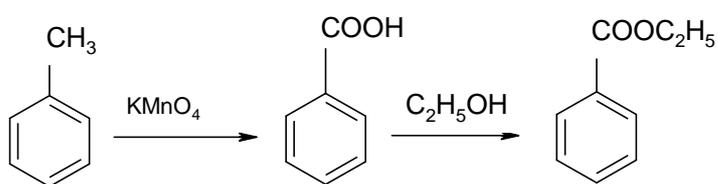
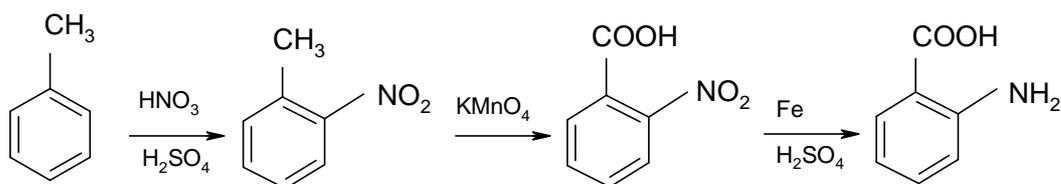
- the decomposition temperature of the precipitate is 1100 °C,
- the product of thermal decomposition is CaO,
- the molar mass of the precipitate is 100 g mol⁻¹,
- the precipitate is CaCO₃.

Reaction:

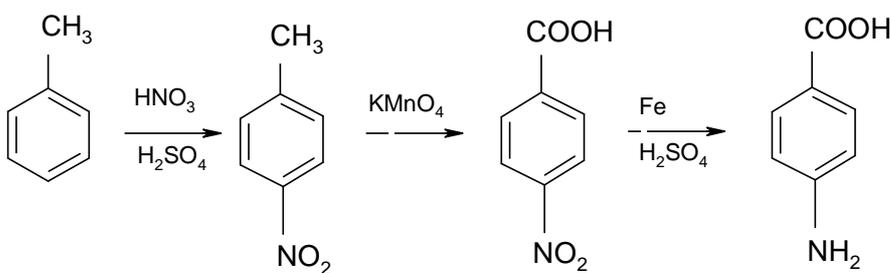
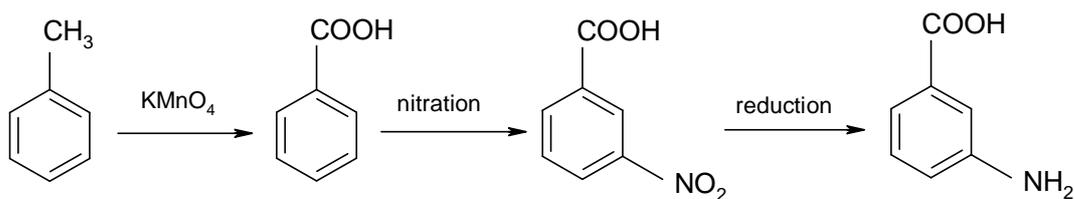


PROBLEM 5

Using your knowledge about the properties of benzene and its derivatives, write chemical equations for reactions by which ethyl ester of benzoic acid as well as o-, m-, and p-amino benzoic acids are prepared in the shortest way.

SOLUTION**a) Synthesis of ethyl ester of benzoic acid****b) Synthesis of o- and p-amino benzoic acid**

and simultaneously

**c) Synthesis of m-aminobenzoic acid**

PROBLEM 6

A gaseous mixture containing two neighbour hydrocarbons of the same homologous series was 14.4 times as dense as hydrogen. This mixture with a volume of 16.8 dm³ was hydrated and 350 g of the solution were obtained when the products of hydration were absorbed in water. Ten grams of this solution were taken and heated in the presence of silver(I) oxide which was prepared from 70 cm³ of a 1 N silver(I) nitrate solution. Unreacted Ag₂O was dissolved in an aqueous ammonia solution and a residual precipitate was filtered off. The filtrate was acidified with nitric acid and addition of an excess of sodium bromide to it resulted in 9.4 g of a precipitate.

When the mixture of the hydrocarbons that remained unreacted, was mixed with a 50 % excess of hydrogen and transmitted above a heated Pt-catalyst, its resulting volume decreased to 11.2 dm³. Volumes of gases were measured in STP conditions.

Problems:

- 6.1 What hydrocarbons were in the starting mixture?
- 6.2 Write chemical equations for the above mentioned reactions.
- 6.3 Calculate the composition of the starting mixture in % by volume.
- 6.4 How much (in %) of each hydrocarbon was hydrated?

SOLUTION

6.1 $M_r = 2 \times 14.4 = 28.8$

When reactivity of the hydrocarbons and the value of M_r are taken into consideration then the mixture can only be formed from CH₃CH=CH₂ ($M_r = 26$) and CH₃-CH₂-CH=CH₂ ($M_r = 40$)

- 6.2 (1) $\text{CH} \equiv \text{CH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO}$
- (2) $\text{CH}_3\text{C} \equiv \text{CH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COCH}_3$
- (3) $2 \text{AgNO}_3 + 2 \text{NH}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Ag}_2\text{O} + 2 \text{NH}_4\text{NO}_3$
- (4) $\text{CH}_3\text{CHO} + \text{Ag}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2 \text{Ag}$
- (5) $\text{Ag}_2\text{O} + 4 \text{NH}_3 + \text{H}_2\text{O} \rightarrow 2 [\text{Ag}(\text{NH}_3)_2]\text{OH}$

- (6) $\text{CH}_3\text{COOH} + \text{NH}_3 \rightarrow \text{CH}_3\text{COONH}_4$
 (7) $[\text{Ag}(\text{NH}_3)_2]\text{OH} + 3 \text{HNO}_3 \rightarrow \text{AgNO}_3 + 2 \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$
 (8) $\text{CH}_3\text{COONH}_4 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 + \text{CH}_3\text{COOH}$
 (9) $\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3$
 (10) $\text{AgNO}_3 + \text{NaBr} \rightarrow \text{AgBr} + \text{NaNO}_3$
 (11) $\text{CH} \equiv \text{CH} + 2 \text{H}_2 \rightarrow \text{CH}_3 - \text{CH}_3$
 (12) $\text{CH}_3\text{C} \equiv \text{CH} + 2 \text{H}_2 \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_3$

6.3 According to (11) and (12) and regarding the excess of hydrogen, amounts of substances before catalytic hydrogenation are as follows:

$$n(\text{mixture}) = \frac{11.2 \text{ dm}^3}{2} = 5.6 \text{ dm}^3, \text{ i. e. } 0.25 \text{ mol}$$

$$26x + 40(0.25 - x) = 28.8 \times 0.25$$

$$x = 0.2$$

$$n(\text{C}_2\text{H}_2) = 0.2 \text{ mol}$$

$$n(\text{C}_3\text{H}_4) = 0.05 \text{ mol}$$

Before hydration:

$$n(\text{mixture}) = \frac{16.8 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.75 \text{ mol}$$

$$n(\text{AgNO}_3) = cV = 1 \text{ mol dm}^{-3} \times 0.07 \text{ dm}^3 = 0.070 \text{ mol}$$

According to (3):

$$n(\text{Ag}_2\text{O}) = 0.035 \text{ mol}$$

$$n(\text{AgBr}) = \frac{9.4 \text{ g}}{188 \text{ g mol}^{-1}} = 0.05 \text{ mol}$$

According to (10), (7) and (5):

$$\text{unreacted: } n(\text{Ag}_2\text{O}) = 0.025 \text{ mol}$$

$$\text{reacted: } n(\text{Ag}_2\text{O}) = 0.035 - 0.025 = 0.010 \text{ mol}$$

Due to dilution, reacted amounts of substances are as follows:

$$n(\text{CH}_3\text{CHO}) = n(\text{C}_2\text{H}_2) = 0.35 \text{ mol}$$

	hydration	hydrogenation	total
C ₂ H ₂	0.35 mol	0.20 mol	0.55 mol
C ₃ H ₄	0.15 mol	0.05 mol	0.20 mol
			Σ = 0.75 mol

$$\text{vol. \% C}_2\text{H}_2 = \frac{0.55 \text{ mol}}{0.75 \text{ mol}} \times 100 = 73.3$$

$$\text{vol. \% C}_3\text{H}_4 = \frac{0.20 \text{ mol}}{0.75 \text{ mol}} \times 100 = 26.7$$

6.4

$$\text{vol. \% C}_2\text{H}_2 = \frac{0.35 \text{ mol}}{0.55 \text{ mol}} \times 100 = 63.64$$

$$\text{vol. \% C}_3\text{H}_4 = \frac{0.15 \text{ mol}}{0.20 \text{ mol}} \times 100 = 75.0$$

PRACTICAL PROBLEMS**PROBLEM 1 (Practical)**

The following solutions of salts are available in twelve numbered test-tubes: AgNO_3 , BaCl_2 , $(\text{NH}_4)_2\text{CO}_3$, NaCl , KI , ZnCl_2 , NH_4Cl , $\text{Pb}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, CrCl_3 , $\text{Cr}(\text{NO}_3)_3$, $\text{Hg}(\text{NO}_3)_2$.

The numbering of the test tubes does not correspond to the order of the salts given above. Prove the content of the test tubes by means of the least number of operations. In your answer align the proper salt with each number of the test tube. Write chemical equations for the reactions.

PROBLEM 2 (Practical)

Six test tubes contain the following compounds:

Na_2CO_3	or	NaHCO_3	NiCl_2	or	CuCl_2
AgNO_3	or	$\text{Pb}(\text{NO}_3)_2$	ZnCl_2	or	$\text{Al}(\text{NO}_3)_3$
ZnSO_4	or	KI	NH_4NO_3	or	$\text{Ba}(\text{NO}_3)_2$

The numbers of the test tubes do not correspond to the order of the compounds. Prove the content of each test tube by available reagents. Describe the reactions by chemical equations.

PROBLEM 3 (Practical)

There are three test tubes marked by numbers 1, 2, and 3. Prove the content of each test-tube by means of available reagents and write the proper formula of the compound to each number. Write chemical equations for the reactions.
