THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS

Volume 1

1st – 20th IChO
1968 – 1988

Edited by Anton Sirota

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THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 1

Editor: Anton Sirota

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The competition problems of the:

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 simply calculations are required, have not been accompanied with their solutions. Recalculations of the solutions were made in some special cases ony 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

IChO

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

1.1 $H_2 + Cl_2 \rightarrow 2\ HCl$

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:

Cl_2: 60 + 15 = 75 %

H_2: 10 + 15 = 25 %

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

anode: $2\ Cl^- - 2\ e \rightarrow Cl_2$

cathode: $2\ Na^+ + 2\ e \rightarrow 2\ Na$

$$2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$$

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 (H_2SO_4).

2.3 Action of chlorine on lime water ($Ca(OH)_2$) in a cold reaction mixture.

SOLUTION

2.1 $2\ CrCl_3 + 3\ Br_2 + 16\ KOH \rightarrow 2\ K_2CrO_4 + 6\ KBr + 6\ KCl + 8\ H_2O$

2.2 $5\ KNO_2 + 2\ KMnO_4 + 3\ H_2SO_4 \rightarrow 2\ MnSO_4 + K_2SO_4 + 5\ KNO_3 + 3\ H_2O$

2.3. $Cl_2 + Ca(OH)_2 \rightarrow CaOCl_2 + H_2O$

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_2H_4	56.2 volume % of N_2

Problems:

3.1 Calculate the theoretical consumption of air (in m^3) which is necessary for a total combustion of 200 m^3 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 $2\,CO + O_2 \rightarrow 2\,CO_2$	14
$2\,H_2 + O_2 \rightarrow 2\,H_2O$	1.5
$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$	1.2
$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$	0.6
	17.3 parts x 5 = 86.5 parts of the air

200 m^3 of the gas .... 2 x 86.5 = 173.0 m^3 of the air
+ 20 % 34.6 m^3
207.6 m^3 of the air

3.2 207.6 **:** 5 = 41.52 parts of O_2 **:** 2 = 20.76 parts of O_2 for 100 m^3 of the gas

20.76 x 4 = 83.04 parts of N_2 for 100 m^3 of the gas

Balance: (volume parts)	CO_2	H_2O	N_2	O_2
	12.00	3.00	56.20	20.76
	28.00	1.20	83.04	- 17.30
	0.60	0.40		
	0.40			
	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.

$$\% \, H_2O = \frac{4.60}{188.30} \times 100 = 2.44$$

$$\% \, N_2 = \frac{139.24}{188.30} \times 100 = 73.95$$

$$\% \, O_2 = \frac{3.46}{188.30} \times 100 = 1.84$$

PROBLEM 4

A volume of 31.7 cm^3 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, H_2A, H_3A, etc.

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

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

where v = 1, 2, 3,......

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

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

b) From the ideal gas law we can obtain:

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

$M(H_2)$ = 2 g mol^{-1}

M(acid) = 30 x 2 = 60 g mol^{-1}

By comparing with (1): v = 1

The acid concerned is a monoprotic acid and its molar mass is 60 g mol^{-1}.

The acid is <u>acetic acid:</u> CH_3–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, $Ba(OH)_2$, NH_4Cl, Ag_2SO_4, $Pb(NO_3)_2$, 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

IChO

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 cm^3 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 $\rho = 1\ g\ cm^{-3}$): $m(H_2O) = 150\ g$

1.2 After electrolysis:

$$m(H_2O) = m(\text{solution}) - m(K_2SO_4) = \frac{20\ g}{0.15} - 20\ g = 113.3\ g$$

The mass of water decomposed on electrolysis:

$m(H_2O) = 150 - 113.3 = 36.7$ g, i. e.

$n(H_2O) = 2.04$ mol

Since, $2\ H_2O \rightarrow 2\ H_2 + O_2$

thus, $n(H_2) = 2.04$ mol

$n(O_2) = 1.02$ mol

$$V(\mathrm{H_2}) = \frac{n(\mathrm{H_2})RT}{p} = \frac{2.04\ \mathrm{mol} \times 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}} \times\ 293.15\ \mathrm{K}}{101325\ \mathrm{Pa}}$$

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

$V(O_2)$ = ½ $V(H_2)$ ≈ 0.0245 m^3 ≈ 24.5 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**:

$K_xN_yO_z$ $$x : y : z = \frac{38.67}{39.1} = \frac{13.85}{14} = \frac{47.48}{16} = 0.989 : 0.989 : 2.968 = 1 : 1 : 3$$

A : KNO_3

Compound **B**:

$K_pN_qO_r$ $$p : q : r = \frac{45.85}{39.1} = \frac{16.47}{14} = \frac{37.66}{16} = 1.173 : 1.176 : 2.354 = 1 : 1 : 2$$

B : KNO_2

2.2 Equation: $2\ KNO_3 \rightarrow 2\ KNO_2 + O_2$

PROBLEM 3

A 10 cm^3 sample of an unknown gaseous hydrocarbon was mixed with 70 cm^3 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 cm^3. This mixture then reacted with a potassium hydroxide solution and the volume of gases decreased to 45 cm^3.

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

$$n(C_xH_y) = \frac{0.010\ dm^3}{22.4\ dm^3\ mol^{-1}} = \frac{0.010}{22.4}\ mol$$

Balance of oxygen:

- Before the reaction: 70 cm^3, i. e. $\frac{0.070}{22.4}$ mol
- After the reaction: 45 cm^3, i. e. $\frac{0.045}{22.4}$ mol

Consumed in the reaction: $\frac{0.025}{22.4}$ mol of O_2

According to the equation:

$$C_xH_y + (x + \frac{y}{4})\ O_2 = x\ CO_2 + \frac{y}{2}\ H_2O$$

Hence, $\frac{0.020}{22.4}$ mol of O_2 reacted with carbon and $\frac{0.020}{22.4}$ mol of CO_2 was formed ($C + O_2 = CO_2$),

$\frac{0.005}{22.4}$ mol O_2 combined with hydrogen and $\frac{0.010}{22.4}$ mol of water was obtained ($2\ H_2 + O_2 = 2\ H_2O$).

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

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

x : y = n(C) : n(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:

a) ethanol

b) acetic acid

c) ethylene and polyethylene

d) vinyl chloride

e) benzene

Problem:

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

SOLUTION

Basic reaction: $CaC_2 + 2\ H_2O = Ca(OH)_2 + C_2H_2$

From acetylene can be obtained:

a) ethanol

$$CH \equiv CH + H_2O \xrightarrow[\text{diluted } H_2SO_4]{HgSO_4\ \text{(catalyst)}} \underset{\text{vinyl alcohol}}{CH_2 = CH - OH} \longrightarrow$$

$$\xrightarrow{\text{rearrangement}} \underset{\text{acetaldehyde}}{CH_3 - CH = O} \xrightarrow{\text{reduction}} \underset{\text{ethanol}}{CH_3 - CH_2 - OH}$$

b) acetic acid

$$CH \equiv CH + H_2O \xrightarrow[\text{diluted } H_2SO_4]{HgSO_4\ \text{(catalyst)}} \underset{\text{vinyl alcohol}}{CH_2 = CH - OH} \longrightarrow$$

$$\xrightarrow{\text{rearrangement}} \underset{\text{acetaldehyde}}{CH_3 - CH = O} \xrightarrow{\text{oxidation}} \underset{\text{acetic acid}}{CH_3 - COOH}$$

c) ethylene, polyethylene

$$CH{\equiv}CH + H_2O \xrightarrow{\text{catalyst}} CH_2{=}CH_2$$

ethylene

$$CH_2{=}CH_2 \xrightarrow[\text{catalyst}]{\text{pressure, temperature}} (-CH_2-CH_2-)_n$$

polyethylene

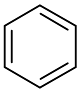
d) vinyl chloride

$$CH{\equiv}CH + HCl \longrightarrow CH_2{=}CH-Cl$$

vinyl chloride

e) benzene

$$3\ CH{\equiv}CH \xrightarrow{400-500\ ^\circ C}$$



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_4Cl
2.	$AlCl_3$ - KBr	$CaCl_2$ - $NaNO_3$	$ZnCl_2$ - $(NH_4)_2SO_4$
3.	KNO_3 - Na_2CO_3	KCl - $MgSO_4$	NH_4Cl - $Ba(NO_3)_2$
4.	$MgCl_2$ - KNO_3	K_2CO_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 H_2SO_4, concentrated H_2SO_4, $FeSO_4$, 2 N NaOH, 20 % NaOH, 2 N NH_4Cl, 2 N $CuSO_4$, 2 N $BaCl_2$, 0,1 N $AgNO_3$, 0,1 % $KMnO_4$, distilled water, phenolphtalein, methyl orange. In addition, further laboratory facilities, such as platinum wire, cobalt glass, etc., were available.

PROBLEM 2 (Practical)

Allow to react 10 cm^3 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

IChO

International Chemistry Olympiad

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 ρ = 2.05 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

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

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

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

n(C) = 1 mol

m(C) = 12 g

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

n(H) = 3 mol

m(H) = 3 g

The compound contains also oxygen, since

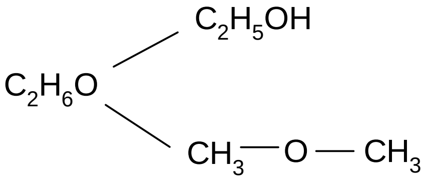
$m(\mathrm{C}) + m(\mathrm{H}) = 12\ \mathrm{g} + 3\ \mathrm{g} = 15\ \mathrm{g} < 23\ \mathrm{g}$

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

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

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

The empirical formula of the compound is C_2H_6O.



ethanol

dimethyl ether

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 cm^3 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 cm^3 of 0.2 N sulphuric acid.

After total decomposition of soda, the excess of the sulphuric acid was neutralized which required 50 cm^3 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 Na_2CO_3 are contained in the first sample of soda?

2.2 Have both samples of soda the same composition?

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

SOLUTION

2.1 Sample **A**: $Na_2CO_3 . x H_2O$

$m(A) = 1.287$ g

$$n(CO_2) = \frac{p\,V}{R\,T} = 0.0045 \text{ mol} = n(A)$$

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

$M(A) = M(Na_2CO_3) + x\ M(H_2O)$

$$x = \frac{M(A) - M(Na_2CO_3)}{M(H_2O)} = \frac{(286 - 106) \text{ g mol}^{-1}}{18 \text{ g mol}^{-1}} = 10$$

Sample **A**: $Na_2CO_3 .10\ H_2O$

2.2 Sample **B**: $Na_2CO_3 \cdot x\ H_2O$

$m(B) = 0.715$ g

$H_2SO_4 + 2\ NaOH = Na_2SO_4 + 2\ H_2O$

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

Excess of H_2SO_4: $n(H_2SO_4) = 0.0025$ mol

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

$n(H_2SO_4) = 0.0025\ mol = n(B)$

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

Sample **B**: $Na_2CO_3 \cdot 10\ H_2O$

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

$CO + H_2O \rightleftharpoons CO_2 + H_2$

Assumption:

$n(CO) = 1$ mol

$n(H_2O) = 1.5$ mol

After reaction:

$n(CO) = 0.2$ mol

$n(H_2O) = 0.7$ mol

$n(CO_2) = 0.8$ mol

$n(H_2) = 0.8$ mol

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

$$\varphi(H_2O) = \frac{V(H_2O)}{V} = \frac{0.7\text{ mol}}{2.5\text{ mol}} = 0.28 \text{ i.e. } 28 \text{ vol. \% of } H_2O$$

$$\varphi(CO_2) = \frac{V(CO_2)}{V} = \frac{0.8\text{ mol}}{2.5\text{ mol}} = 0.32 \text{ i.e. } 32 \text{ vol. \% of } CO_2$$

$$\varphi(H_2) = \frac{V(H_2)}{V} = \frac{0.8\text{ mol}}{2.5\text{ mol}} = 0.32 \text{ i.e. } 32 \text{ vol. \% of } H_2$$

Before reaction:

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

$m(H_2O) = 1.5 \text{ mol} \times 18 \text{ g mol}^{-1} = 27 \text{ g}$

After reaction:

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

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

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

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

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

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

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

$$w(H_2) = \frac{m(\text{H}_2)}{m} = \frac{1.6 \text{ g}}{55.0 \text{ g}} = 0.029 \text{ i.e. } 2.9 \text{ mass \% of } \text{H}_2$$

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 dm^3 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(Li) = 7; A_r(Na) = 23; A_r(K) = 39; A_r(Rb) = 85.5; A_r(Cs) = 133

SOLUTION

4.1 M - alkali metal

Reaction: $2\ M + 2\ H_2O \rightarrow 2\ MOH + H_2$

$n(H_2) = 0.1$ mol

$n(M) = 0.2$ 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.

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

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

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

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

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

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

$n(\text{Li}) = 0.1592$ 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 cooper (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 ($CuSO_4 . 5\ H_2O$) have crystallised when the solution is cooled to 20 ℃?

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

Solubility of $CuSO_4$ at 20 °C: s = 20.9 g of $CuSO_4$ in 100 g of H_2O.

SOLUTION

$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$

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

$$n(H_2SO_4) = n(CuSO_4) = 0.2516\text{ mol}$$

Mass of the $CuSO_4$ solution obtained by the reaction:

$m(\text{solution } CuSO_4) = m(CuO) + m(\text{solution } H_2SO_4) =$

$$= m(\text{CuO}) + \frac{n(H_2SO_4) \times M(H_2SO_4)}{w(H_2SO_4)} = 20\text{ g} + \frac{0.2516\text{ mol} \times 98\text{ g mol}^{-1}}{0.20}$$

$m(\text{solution } CuSO_4) = 143.28$ g

Mass fraction of $CuSO_4$:

a) in the solution obtained:

$$w(CuSO_4) = \frac{m(CuSO_4)}{m(\text{solution } CuSO_4)} = \frac{n(CuSO_4) \times M(CuSO_4)}{m(\text{solution } CuSO_4)} = 0.28$$

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

$$w(CuSO_4) = \frac{20.9\text{ g}}{120.9\text{ g}} = 0.173$$

c) in crystalline $CuSO_4 . 5\,H_2O$:

$$w(\mathrm{CuSO_4}) = \frac{M(\mathrm{CuSO_4})}{M(\mathrm{CuSO_4 . 5H_2O})} = 0.639$$

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 $CuSO_4 . 5H_2O$.

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

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

$m_1 = 32.9$ g

The yield of the crystallisation is 32.9 g of $CuSO_4 . 5H_2O$.

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

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

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

Oxide 2: M_2O_y

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

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

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):

$A_r(\text{M}) = 54.95$

M = Mn

Oxide 1 = MnO

Oxide 2 = Mn_2O_7

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

An unknown sample is a mixture of 1.2-molar H_2SO_4 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 dm^3 of the solution,
2. the mass of sulphuric acid as well as hydrochloric acid present in 1 dm^3 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

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 dm^3 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 dm^3 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 dm^3 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 = *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 dm^3 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

Reaction: Mg + 2 HCl → $MgCl_2$ + H_2

b) Reaction with sodium hydroxide:

1.52 g – 0.96 g = 0.56 g of an element reacted, 0.896 dm^3 (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

Reaction: Si + 2 NaOH + H_2O → Na_2SiO_3 + 2 H_2

c) Combining of both elements:

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

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

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

silicide: Mg_2Si

d) Reaction of the silicide with acid:

$Mg_2Si + 4\ HCl \rightarrow 2\ MgCl_2 + SiH_4$

$$n(Mg_2Si) = \frac{1.52\ g}{76\ g\ mol^{-1}} = 0.02\ mol$$

$$n(SiH_4) = \frac{0.448\ dm^3}{22.4\ dm^3\ mol^{-1}} = 0.02\ mol$$

e) Reaction of silane with oxygen:

$SiH_4 + 2\ O_2 \rightarrow SiO_2 + 2\ H_2O$

$V = 1\ dm^3$

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

$$n_1(O_2) = \frac{1\ dm^3}{22.4\ dm^3\ mol^{-1}} = 0.0446\ mol$$

Consumption of oxygen in the reaction: $n(O_2) = 0.04\ mol$

The remainder of oxygen in the closed vessel:

$n_2(O_2) = 0.0446\ mol - 0.04\ mol = 0.0046\ mol$

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

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 (ρ = 1.03 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(O) = 16; A_r(S) = 32; A_r(Cl) = 35.5; A_r(Fe) = 56; A_r(Cu) = 64

SOLUTION

2.1 a) Reduction by hydrogen:

$FeO + H_2 \rightarrow Fe + H_2O$

$n(Fe) = n(FeO)$; $n(H_2O) = n(FeO)$

$Fe_2O_3 + 3\,H_2 \rightarrow 2\,Fe + 3\,H_2O$

$n(Fe) = 2\,n(Fe_2O_3)$; $n(H_2O) = 3\,n(Fe_2O_3)$

The mass of iron after reduction: 3.92 g

The total amount of substance of iron after reduction:

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

b) Reaction with copper(II) sulphate:

$Fe + CuSO_4 \rightarrow Cu + FeSO_4$

Increase of the mass: 4.96 g – 4.72 g = 0.24 g

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

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

Amount of substance of iron in the mixture:

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

c) Formation of water after reduction:

0.90 g H_2O, i.e. 0.05 mol

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

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

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

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

d) Consumption of acid:

$\text{Fe} + 2\ \text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$

$\text{FeO} + 2\ \text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2\text{O}$

$\text{Fe}_2\text{O}_3 + 6\ \text{HCl} \rightarrow 2\ \text{FeCl}_2 + 3\ \text{H}_2\text{O}$

$n(\text{HCl}) = 2\, n(\text{Fe}) + 2\, n(\text{FeO}) + 6\, n(\text{Fe}_2\text{O}_3) =$

$= 0.06\ \text{mol} + 0.04\ \text{mol} + 0.06\ \text{mol} = 0.16\ \text{mol}$

A part of iron reacts according to the equation:

$\text{Fe} + 2\ \text{FeCl}_3 \rightarrow 3\ \text{FeCl}_2$

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

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

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

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

$\text{Fe} + 2\ \text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$

Iron in the mixture: 0.03 mol

Iron reacted with FeCl_3: 0.01 mol

Iron reacted with acid: 0.02 mol

Hence, 0.02 mol of hydrogen, i.e. 0.448 dm^3 of hydrogen are formed.

PROBLEM 3

A volume of 200 cm^3 of a 2-normal sodium chloride solution (ρ = 1.10 g cm^{-3}) was electrolysed at permanent stirring in an electrolytic cell with copper electrodes. Electrolysis was stopped when 22.4 dm^3 (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(H) = 1; A_r(O) = 16; A_r(Na) = 23; A_r(Cl) = 35.5; A_r(Cu) = 64.

SOLUTION

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

$2\ NaCl \rightarrow 2\ Na^+ + 2\ Cl^-$

cathode: $2\ Na^+ + 2\ e^- \rightarrow 2\ Na$

anode: $2\ Cl^- - 2\ e^- \rightarrow Cl^-$

$Cl_2 + Cu \rightarrow CuCl_2$

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

$CuCl_2 + 2\ NaOH \rightarrow Cu(OH)_2 + 2\ NaCl$

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

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

$V(H_2) = 22.4\text{ dm}^3$, i. e. $n(H_2) = 1$ mol

The amount of water is decreased in the solution by:

$n(H_2O) = 2$ mol

$m(H_2O) = 36$ g

Before electrolysis:

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

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

After electrolysis:

m(solution NaCl) = 220 g – 36 g = 184 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 J g^{-1} K^{-1}.

Relative atomic masses:

A_r(H) = 1; A_r(O) = 16; A_r(Na)= 23; A_r(S) = 32; A_r(Cl) = 35.5.

SOLUTION

4.1 a) $NaOH + HCl \rightarrow NaCl + H_2O$

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

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

unreacted: n(NaOH) = 0.025 mol

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

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

c) $NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$

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

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

$c_1 = c_2 = c$

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

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

d) The temperature increase due to the reaction of NaOH with H_2SO_4 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: $t = 22 + 2 = 24\ ^\text{o}\text{C}$

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

$\text{NaCl} + \text{NaHSO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{HCl}$

Na_2SO_4 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: $A_r(H) = 1$; $A_r(C) = 12$; $A_r(Br) = 80$.

SOLUTION

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

$M_r(RBr) = 29 \times 5.207 = 151$

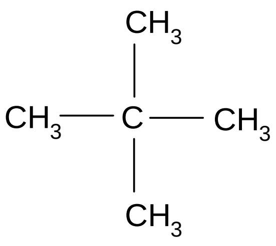
Monobromo derivative can only come into consideration because the relative molecular mass of dibromo derivative should be greater:

$M_r(RBr_2) > 160$

$M_r(RH) = 151 - 80 + 1 = 72$

The corresponding summary formula: C_5H_{12}

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



$$\begin{array}{c} CH_3 \\ | \\ CH_3 - C - CH_3 \\ | \\ CH_3 \end{array}$$

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 cm^3 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(H) = 1; A_r(C) = 12; A_r(O) = 16; A_r(K) = 39.

SOLUTION

6.1 Stoichiometric formulas of compounds:

A : $C_xH_yC_z$

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

B : $C_mH_nO_p$

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

D : $C_aH_bO_c$

$$a : b : c = \frac{35.82}{12} : \frac{4,48}{1} : \frac{59.70}{16} = 4 : 6 : 5$$

20 cm^3 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, ...

1 mol of compound **D** = $v \times 67$ g

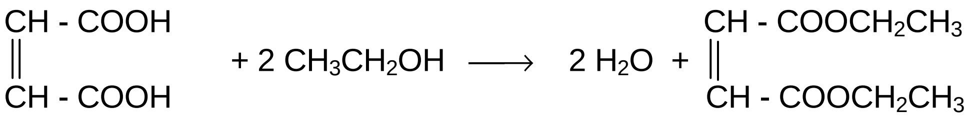
$M_r(\mathbf{D})$ = 67 or 134 or 201, etc.

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:

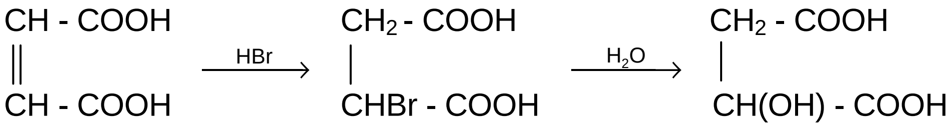
A: $C_4H_4O_4$ **B**: $C_8H_{12}O_4$ **C**: $C_4H_5O_4Br$

6.2 Equations:



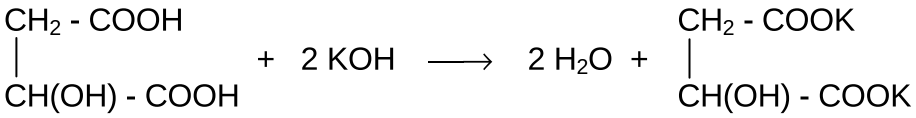
$$\begin{array}{l}\text{CH - COOH}\\ \| \\ \text{CH - COOH}\end{array} + 2\,CH_3CH_2OH \longrightarrow 2\,H_2O + \begin{array}{l}\text{CH - COOCH}_2\text{CH}_3\\ \| \\ \text{CH - COOCH}_2\text{CH}_3\end{array}$$

A **B**

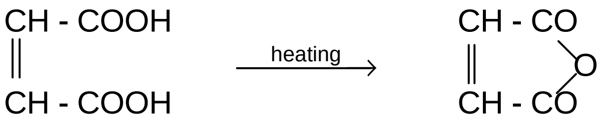


$$\begin{array}{l}\text{CH - COOH}\\ \| \\ \text{CH - COOH}\end{array} \xrightarrow{HBr} \begin{array}{l}\text{CH}_2\text{ - COOH}\\ | \\ \text{CHBr - COOH}\end{array} \xrightarrow{H_2O} \begin{array}{l}\text{CH}_2\text{ - COOH}\\ | \\ \text{CH(OH) - COOH}\end{array}$$

A **C** **D**



$$\begin{array}{l}\text{CH}_2\text{ - COOH}\\ | \\ \text{CH(OH) - COOH}\end{array} + 2\,KOH \longrightarrow 2\,H_2O + \begin{array}{l}\text{CH}_2\text{ - COOK}\\ | \\ \text{CH(OH) - COOK}\end{array}$$



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

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 (Faraday's charge) = 96 500 C mol^{-1}

SOLUTION

1.1 a) Formula of the compound: $C_6H_xO_yN_z$

The compound is a hydroxy nitroderivative of benzene:

$C_6H_{6-(y-2z)-z}(OH)_{y-2z}(NO_2)_z$

b) Equation of the reduction:

$R\text{-}NO_2 + 6\ H \rightarrow\ R\text{-}NH_2 + 2\ H_2O$

Combining mass of the compound:

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

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

$Q = 4350\ C \times 0.8 = 3480\ C$

Combining mass of the compound:

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

In relation to (1): M_r (compound) = 76.2 × z (2)

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

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

M_r(compound) = 32.7 y

d) M_r(compound) = 6 M_r (C) + x M_r (H) + y M_r (O) + z M_r (N)

M_r (compound) = 6 × 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 (4)

Then: M_r(compound) = 72 + 6 – z + 16 y + 14 z

M_r(compound) = 78 + 16 y + 13 z (5)

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

<u>M_r(compound) = 229</u>

x = 3

y = 7

z = 3

The molecular formula of the compound is: $C_6H_3O_7N_3$ or $C_6H_2(OH)(NO_2)_3$.

The compound is <u>2, 4, 6-trinitrophenol</u>

PROBLEM 2

A mixture of a gaseous hydrocarbon and oxygen is in a vessel of a volume of 1 dm^3 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:

Equation: $C_xH_y + (x + \frac{y}{4})O_2 = x\,CO_2 + \frac{y}{2}\,H_2O$

$$n(H_2O) = \frac{m(H_2O)}{M(H_2O)} = \frac{0.162\text{ g}}{18\text{ g mol}^{-1}} = 0.009\text{ mol}$$

$$n(C_xH_y) = \frac{0.009\text{ mol}}{\frac{y}{2}} = \frac{0.018}{y}\text{ mol} \qquad (1)$$

$$n(O_2) = (x + \frac{y}{4}) \times \frac{0.009\text{ mol}}{\frac{y}{2}} = \frac{x + \frac{y}{4}}{y} \times 0.018\text{ mol} \qquad (2)$$

$$n(CO_2) = x\,\frac{0.009\text{ mol}}{\frac{y}{2}} = \frac{x}{y} \times 0.018\text{ mol} \qquad (3)$$

Before reaction:

$$n(\text{mixture}) = \frac{p\,V}{R\,T} = \frac{101.325\text{ kPa} \times 1\text{ dm}^3}{8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 406.5\text{ K}} = 0.03\text{ mol}$$

$$n(C_xH_y) + 2\,n(O_2) = 0.03\text{ mol} \qquad (4)$$

After reaction: p = 101. 325 kPa × 1.05 = 106.4 kPa

$$n(\text{mixture}) = \frac{p\,V}{R\,T} = \frac{106.4\text{ kPa} \times 1\text{ dm}^3}{8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 406.5\text{ K}} = 0.0315\text{ mol}$$

$n(CO_2) + n(O_2) + n(H_2O) = 0.0315$ mol

$n(CO_2) + n(O_2) = 0.0225$ mol (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; y = 6

The stoichiometric formula of the unknown hydrocarbon is: C_3H_6.

PROBLEM 3

Equal volumes (10 cm^3) of 0.01-molar solutions of CH_3COOH and HClO were mixed and then diluted to a total volume of 100 cm^3. Ionisation constant of CH_3COOH 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 CH_3COOH,

3.3 pH value for the solution containing at the same time CH_3COOH and HClO.

SOLUTION

CH_3COOH: K_1, α_1, c_1

HClO: K_2, α_2, c_2

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

3.1 $$K_1 = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(\alpha_1 + \alpha_2)c \times \alpha_1 c}{(1-\alpha_1)\,c} = \frac{(\alpha_1 + \alpha_2)\,\alpha_1 c}{1-\alpha_1} \qquad (1)$$

$$K_2 = \frac{[H_3O^+][ClO^-]}{[HClO]} = \frac{(\alpha_1 + \alpha_2)\,\alpha_1 c}{1-\alpha_2} \qquad (2)$$

$K_1 >> K_2$, therefore also $\alpha_1 >> \alpha_2$ 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 $K_2 = \frac{\alpha_2^2\, c}{1-\alpha_2}$

$\alpha_2 << 1$

$K_2 = \alpha_2^2\, c$

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

3.3 $[H_3O^+] = \alpha_1 c + \alpha_2 c = (\alpha_1 + \alpha_2)\, c = (0,125 + 2,94 \times 10^{-4}) \times 10^{-3} \approx 1,25 \times 10^{-4}$ mol dm^{-3}

<u>pH = 3,9</u>

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 ℃ 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 ℃: a gaseous oxide and 0.90 g of water vapour. The total volume of the gaseous mixture is 1.68 dm^3 (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

H_2O: 0.90 g, i. e. 0.05 mol

Gaseous oxide A_xO_y: 1.1 g

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

$$n(A_xO_y) = n(\text{mixture}) - n(H_2O) = 0.025\ \text{mol}$$

$$M(A_xO_y) = \frac{1.1\ \text{g}}{0.025\ \text{mol}} = 44\ \text{g mol}^{-1}$$

$$x\,M(A) = M(A_xO_y) - y\,M(O)$$

Solution 1:

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

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

Solution 2:

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

A = N and the gaseous oxide is N_2O.

Solution 3:

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

A = C and the gaseous oxide is CO_2.

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:

$$M(\text{dry residue}) = \frac{2.0\ \text{g}}{0.025\ \text{mol}} = 80\ \text{g mol}^{-1} = M(NH_4NO_3)$$

Reaction of the thermal decomposition:

$NH_4NO_3 \rightarrow N_2O + 2\ H_2O$

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

$M(NO_3)_2 + (NH_4)_2B \rightarrow MB + 2\ NH_4NO_3$

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

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

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

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 $CaCO_3$.

Reaction:

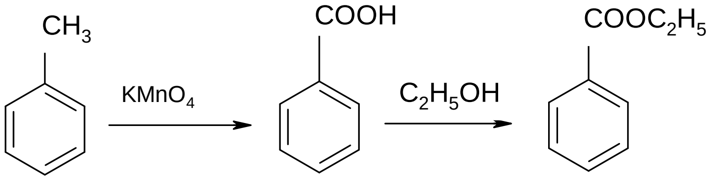
$Ca(NO_3)_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2\ NH_4NO_3$

PROBLEM 5

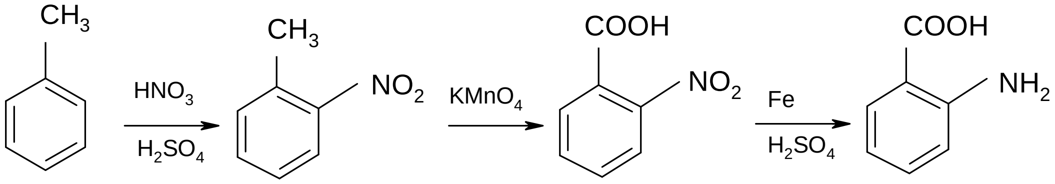
Using your knowledge about the properties of benzene and its derivatives, write chemical equations for reactions by which ethyl ester of benzoic acid as well as o-, m-, and p-amino benzoic acids are prepared in the shortest way.

SOLUTION

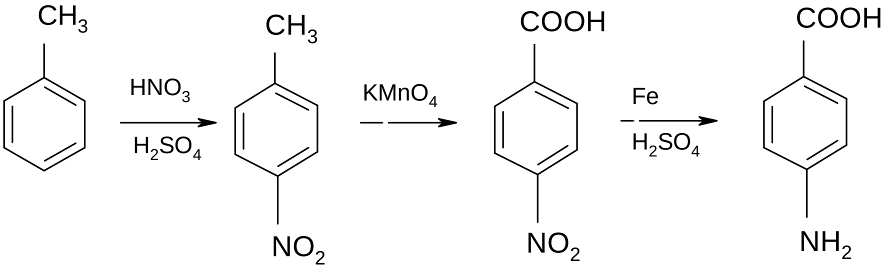
a) Synthesis of ethyl ester of benzoic acid



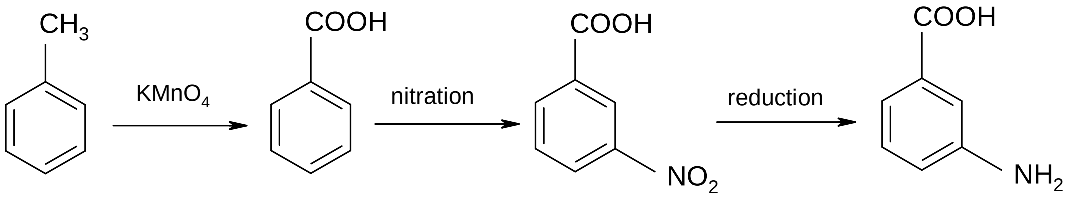
b) Synthesis of o- and p-amino benzoic acid



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 dm^3 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 cm^3 of a 1 N silver(I) nitrate solution. Unreacted Ag_2O 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 dm^3. 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 by formed from $CH \equiv CH$ (M_r = 26) and $CH_3 - CH \equiv CH$ (M_r = 40)

6.2 (1) $CH \equiv CH + H_2O \rightarrow CH_3CHO$

(2) $CH_3C \equiv CH + H_2O \rightarrow CH_3COCH_3$

(3) $2\ AgNO_3 + 2\ NH_3 + 2\ H_2O \rightarrow Ag_2O + 2\ NH_4NO_3$

(4) $CH_3CHO + Ag_2O \rightarrow CH_3COOH + 2\ Ag$

(5) $Ag_2O + 4\ NH_3 + H_2O \rightarrow 2\ [Ag(NH_3)_2]OH$

(6) $CH_3COOH + NH_3 \rightarrow CH_3COONH_4$

(7) $[Ag(NH_3)_2]OH + 3\ HNO_3 \rightarrow AgNO_3 + 2\ NH_4NO_3 + H_2O$

(8) $CH_3COONH_4 + HNO_3 \rightarrow NH_4NO_3 + CH_3COOH$

(9) $NH_3 + HNO_3 \rightarrow NH_4NO_3$

(10) $AgNO_3 + NaBr \rightarrow AgBr + NaNO_3$

(11) $CH \equiv CH + 2\ H_2 \rightarrow CH_3 - CH_3$

(12) $CH_3C \equiv CH + 2\ H_2 \rightarrow CH_3 - CH_2 - CH_3$

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

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

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

$x = 0.2$

$n(C_2H_2) = 0.2$ mol

$n(C_3H_4) = 0.05$ mol

Before hydration:

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

$n(AgNO_3) = c\,V = 1\ \text{mol dm}^{-3} \times 0.07\ \text{dm}^3 = 0.070\ \text{mol}$

According to (3):

$n(Ag_2O) = 0.035$ mol

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

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

unreacted: $n(Ag_2O) = 0.025$ mol

reacted: $n(Ag_2O) = 0.035 - 0.025 = 0.010$ mol

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

$n(CH_3CHO) = n(C_2H_2) = 0.35$ mol

	hydration	hydrogenation	total
C_2H_2	0.35 mol	0.20 mol	0.55 mol
C_3H_4	0.15 mol	0.05 mol	0.20 mol
			$\sum$ = 0.75 mol

$$\text{vol. \% } C_2H_2 = \frac{0.55 \text{ mol}}{0.75 \text{ mol}} \times 100 = 73.3$$

$$\text{vol. \% } C_3H_4 = \frac{0.20 \text{ mol}}{0.75 \text{ mol}} \times 100 = 26.7$$

6.4

$$\text{vol. \% } C_2H_2 = \frac{0.35 \text{ mol}}{0.55 \text{ mol}} \times 100 = 63.64$$

$$\text{vol. \% } C_3H_4 = \frac{0.15 \text{ mol}}{0.20 \text{ mol}} \times 100 = 75.0$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

The following solutions of salts are available in twelve numbered test-tubes: $AgNO_3$, $BaCl_2$, $(NH_4)_2CO_3$, NaCl, KI, $ZnCl_2$, NH_4Cl, $Pb(NO_3)_2$, $Al(NO_3)_3$, $CrCl_3$, $Cr(NO_3)_3$, $Hg(NO_3)_2$.

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 $NaHCO_3$
$AgNO_3$ or $Pb(NO_3)_2$
$ZnSO_4$ or KI
$NiCl_2$ or $CuCl_2$
$ZnCl_2$ or $Al(NO_3)_3$
NH_4NO_3 or $Ba(NO_3)_2$

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.

6th

IChO

International Chemistry Olympiad

5 theoretical problems
3 practical problems

THE SIXTH
INTERNATIONAL CHEMISTRY OLYMPIAD
1–10 JULY 1974, BUCURESTI, ROMANIA

THEORETICAL PROBLEMS

PROBLEM 1

By electrochemical decomposition of water, there are in an electric circuit a voltmeter, platinum electrodes and a battery containing ten galvanic cells connected in series, each of it having the voltage of 1.5 V and internal resistance of 0.4 Ω. The resistance of the voltmeter is 0.5 Ω and the polarisation voltage of the battery is 1.5 V. Electric current flows for 8 hours, 56 minutes and 7 seconds through the electrolyte. Hydrogen obtained in this way was used for a synthesis with another substance, thus forming a gaseous substance **A** which can be converted by oxidation with oxygen via oxide to substance **B**.

By means of substance **B** it is possible to prepare substance **C** from which after reduction by hydrogen substance **D** can be obtained. Substance **D** reacts at 180 °C with a concentration solution of sulphuric acid to produce sulphanilic acid. By diazotization and successive copulation with p-N,N-dimethylaniline, an azo dye, methyl orange is formed.

Problems:

1. Write chemical equations for all the above mentioned reactions.
2. Calculate the mass of product **D**.
3. Give the exact chemical name for the indicator methyl orange. Show by means of structural formulas what changes take place in dependence on concentration of H_3O^+ ions in the solution.

Relative atomic masses: $A_r(N) = 14$; $A_r(O) = 16$; $A_r(C) = 12$; $A_r(H) = 1$.

SOLUTION

1. $N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$

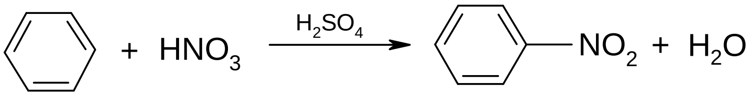
(**A**)

$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$

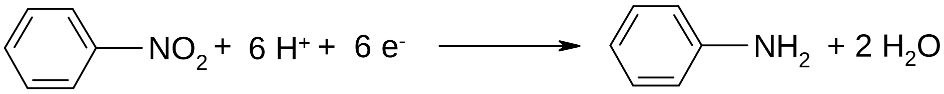
$2\ NO + O_2 \rightarrow 2\ NO_2$

$2\ NO_2 + H_2O + 1/2\ O_2 \rightarrow 2\ HNO_3$

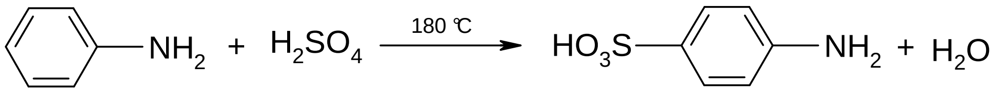
(**B**)

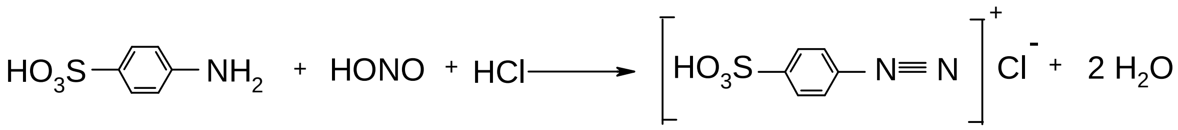


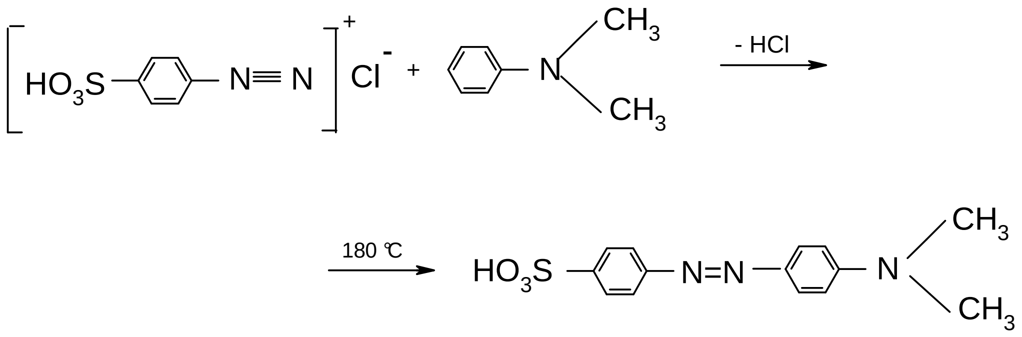
(**C**)



(**D**)







4'-dimethyl amino 4-azo benzene sulphonic acid

2. $$m = \frac{M}{F\,z}\,I\,t$$

$$F = 96500 \text{ C mol}^{-1}$$

$$I = \frac{\text{b}\,E_b - E_p}{R_v + \text{b}\,R_i} = \frac{(10 \times 1.5 \text{ V}) - 1.5 \text{ V}}{0.5\ \Omega + (10 \times 0.4\ \Omega)} = 3 \text{ A}$$

b - number of batteries,

E_b - voltage of one battery,

E_p - polarisation voltage,

R_v - resistance of voltmeter,

R_i - internal resistance of one battery

$$m(\text{H}_2) = \frac{1 \text{ g mol}^{-1}}{96500 \text{ C mol}^{-1}} \times 3 \text{ A} \times 32167 \text{ s} = 1 \text{ g}$$

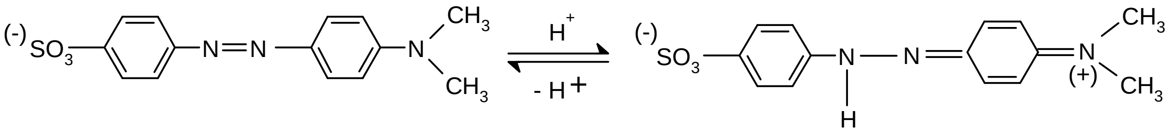
From equations:

1 g H_2 i. e. 0.5 mol H_2 corresponds $\frac{1}{3}$ mol NH_3 .... $\frac{1}{3}$ mol HNO_3 .... $\frac{1}{3}$ mol $C_6H_5NO_2$ .... $\frac{1}{3}$ mol $C_6H_5NH_2$ (**D**)

The mass of product **D**:

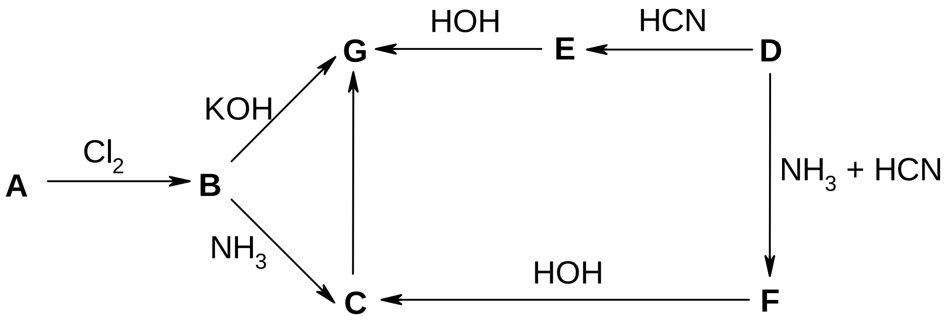
$m = n\,M = 31$ g $C_6H_5NH_2$

3.



PROBLEM 2

Substance **G** can be prepared by several methods according to the following scheme:



<u>Compound **A**</u> is 48.60 mass % carbon, 8.10 % hydrogen, and 43.30 % oxygen. It reacts with a freshly prepared silver(I) oxide to form an undissolved salt. An amount of 1.81 g of silver(I) salt is formed from 0.74 g of compound **A**.

<u>Compound **D**</u> contains 54.54 mass % of carbon, 9.09 % of hydrogen, and 36.37 % of oxygen. It combines with $NaHSO_3$ to produce a compound containing 21.6 % of sulphur.

Problems:

1. Write summary as well as structural formulas of substances **A** and **D**.
2. Write structural formulas of substances **B**, **C**, **E**, **F**, and **G**.
3. Classify the reactions in the scheme marked by arrows and discuss more in detail reactions **B** → **G** and **D** → **E**.
4. Write structural formulas of possible isomers of substance **G** and give the type of isomerism.

Relative atomic masses:

A_r(C) = 12; A_r(H) = 1; A_r (O) = 16; A_r (Ag) = 108; A_r (Na) = 23; A_r (S) = 32.

SOLUTION

1. <u>Compound **A** :</u>

R-COOH + AgOH → R-COOAg + H_2O

A : $(C_xH_yO_z)_n$

$$x : y : z = \frac{48.60}{12} : \frac{8.10}{1} : \frac{43.30}{16} = 1 : 2 : 0.67$$

If n = 3, then the summary formula of substance **A** is: $C_3H_6O_2$.

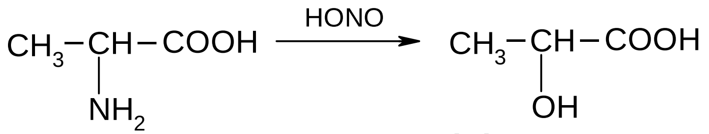
M(**A**) = 74 g mol^{-1}

A = CH_3-CH_2-COOH

<u>Compound **D**:</u>

$(C_pH_qO_r)_n$

$$p:q:r = \frac{54.54}{12} : \frac{9.09}{1} : \frac{36.37}{16} = 1 : 2 : 0.5$$



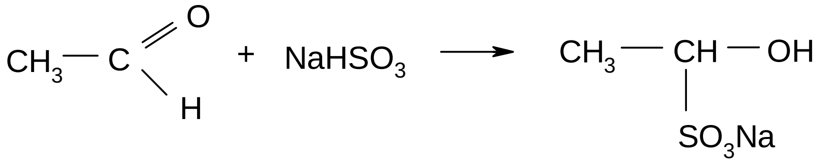
$$CH_3-\underset{NH_2}{CH}-COOH \xrightarrow{HONO} CH_3-\underset{OH}{CH}-COOH$$

(C) **(G)**

IV

If n = 2, then the summary formula of substance **D** is: C_2H_4O.

M(**D**) = 44 g mol^{-1}



$$CH_3-CHO + NaHSO_3 \longrightarrow CH_3-\underset{SO_3Na}{CH}-OH$$

D = CH_3-CHO

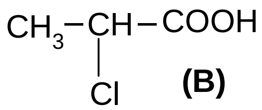
Reaction:

The reduction product contains 21.6 % of sulphur.

2.

CH_3-CH_2-COOH

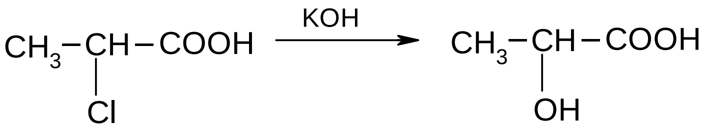
(A)



$$CH_3-\underset{Cl}{CH}-COOH$$

(B)

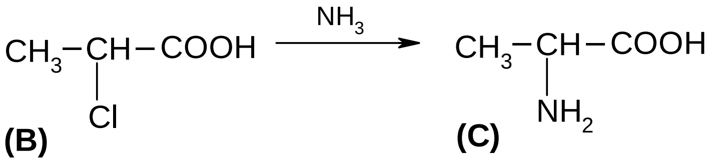
I



$$CH_3-\underset{Cl}{CH}-COOH \xrightarrow{KOH} CH_3-\underset{OH}{CH}-COOH$$

(B) **(G)**

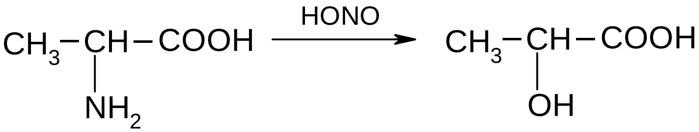
II



$$CH_3-\underset{Cl}{CH}-COOH \xrightarrow{NH_3} CH_3-\underset{NH_2}{CH}-COOH$$

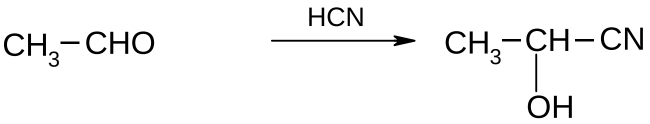
(B) **(C)**

III



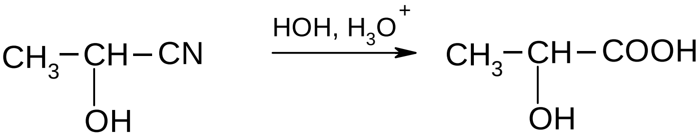
$$CH_3-\underset{\underset{\displaystyle NH_2}{|}}{CH}-COOH \xrightarrow{HONO} CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-COOH \qquad IV$$

(C) **(G)**



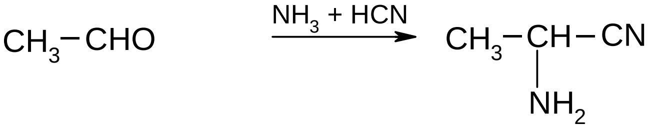
$$CH_3-CHO \xrightarrow{HCN} CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CN \qquad V$$

(D) **(E)**



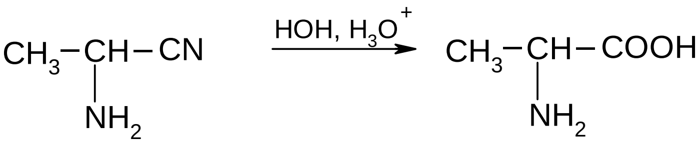
$$CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CN \xrightarrow{HOH,\ H_3O^+} CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-COOH \qquad VI$$

(E) **(G)**



$$CH_3-CHO \xrightarrow{NH_3\ +\ HCN} CH_3-\underset{\underset{\displaystyle NH_2}{|}}{CH}-CN \qquad VII$$

(D) **(F)**



$$CH_3-\underset{\underset{\displaystyle NH_2}{|}}{CH}-CN \xrightarrow{HOH,\ H_3O^+} CH_3-\underset{\underset{\displaystyle NH_2}{|}}{CH}-COOH \qquad VIII$$

(F) **(C)**

3\. I - substitution reaction

II - substitution nucleophilic reaction

III - substitution nucleophilic reaction

IV - substitution reaction

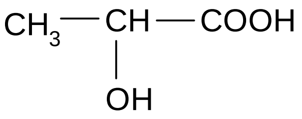
V - additive nucleophilic reaction

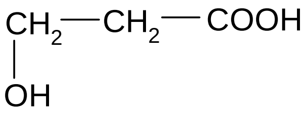
VI - additive reaction, hydrolysis

VII - additive reaction

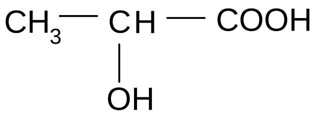
VIII - additive reaction, hydrolysis

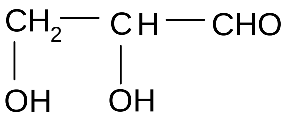
4.

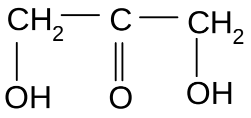

$$CH_3-\underset{\underset{OH}{|}}{CH}-COOH$$


$$\underset{\underset{OH}{|}}{CH_2}-CH_2-COOH$$

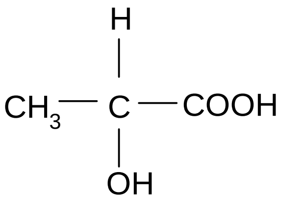
position isomerism


$$CH_3-\underset{\underset{OH}{|}}{CH}-COOH$$

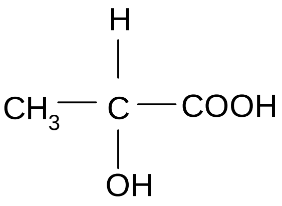

$$\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH}-CHO$$


$$\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH_2}$$

structural isomerism

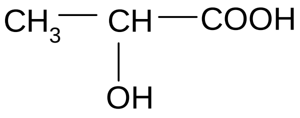

$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-COOH$$

d(+)


$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-COOH$$

l(-)

stereoisomerism
(optical isomerism)


$$CH_3-\underset{\underset{OH}{|}}{CH}-COOH$$

racemic mixture

PROBLEM 3

The following 0.2 molar solutions are available:

A: HCl **B**: HSO_4^- **C**: CH_3COOH **D**: NaOH

E: CO_3^{2-} **F**: CH_3COONa **G**: HPO_4^{2-} **H**: H_2SO_4

Problems:

1. Determine the concentration of H_3O^+ ions in solution **C**.
2. Determine pH value in solution **A**.
3. Write an equation for the chemical reaction that takes place when substances **B** and **E** are allowed to react and mark conjugate acid-base pairs.
4. Compare acid-base properties of substances **A**, **B**¸ and **C** and determine which one will show the most basic properties. Explain your decision.
5. Write a chemical equation for the reaction between substances **B** and **G**, and explain the shift of equilibrium.
6. Write a chemical equation for the reaction between substances **C** and **E**, and explain the shift of equilibrium.
7. Calculate the volume of **D** solution which is required to neutralise 20.0 cm^3 of **H** solution.
8. What would be the volume of hydrogen chloride being present in one litre of **A** solution if it were in gaseous state at a pressure of 202.65 kPa and a temperature of 37 ℃?

Ionisation constants:

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ $K_a = 1.8 \times 10^{-5}$

$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$ $K_a = 4.4 \times 10^{-7}$

$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$ $K_a = 4.7 \times 10^{-11}$

$HSO_4^{2-} + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$ $K_a = 1.7 \times 10^{-2}$

$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$ $K_a = 4.4 \times 10^{-13}$

Relative atomic masses:

A_r(Na) = 23; A_r(S) = 32; A_r(O) = 16.

SOLUTION

1. $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{[H_3O^+]^2}{c}$$

$$[H_3O^+] = \sqrt{K_a\, c} = \sqrt{1.8\times10^{-5}\times0.2} = 1.9\times10^{-3}\ \text{mol dm}^{-3}$$

2. $\text{pH} = -\log[H_3O^+] = -\log 0.2 = 0.7$

3. $$\underset{A_1}{HSO_4^{2-}} + \underset{B_2}{CO_3^{2-}} \rightleftharpoons \underset{B_1}{SO_4^{2-}} + \underset{A_2}{HCO_3^-}$$

4. By comparison of the ionisation constants we get:

$K_a(HCl) > K_a(HSO_4^-) > K_a(CH_3COOH)$

Thus, the strength of the acids in relation to water decreases in the above given order.

CH_3COO^- is the strongest conjugate base, whereas Cl^- is the weakest one.

5. $HSO_4^- + HPO_4^{2-} \rightleftharpoons H_2PO_4^- + SO_4^{2-}$

$K_a(HSO_4^-) \gg K_a(HPO_4^{2-})$

Equilibrium is shifted to the formation of $H_2PO_4^-$ and SO_4^{2-}.

6. $CH_3COOH + CO_3^{2-} \rightleftharpoons CH_3COO^- + HCO_3^-$

$CH_3COO^- + HCO_3^- \rightleftharpoons CH_3COO^- + H_2CO_3$

$K_a(CH_3COOH) > K_a(H_2CO_3) > K_a(HCO_3^-)$

Equilibrium is shifted to the formation of CH_3COO^- a H_2CO_3.

7. $n(H_2SO_4) = c\,V = 0.2\ \text{mol dm}^{-3} \times 0.02\ \text{dm}^3 = 0.004\ \text{mol}$

$$V(0.2\ \text{molar NaOH}) = \frac{n}{c} = \frac{0.008\ \text{mol}}{0.2\ \text{mol dm}^{-3}} = 0.04\ \text{dm}^3$$

8. $$V(\text{HCl}) = \frac{n\,R\,T}{p} = \frac{0.2\ \text{mol} \times 8.314\ \text{J mol}^{-1}\,\text{K}^{-1} \times 310\ \text{K}}{202.65\ \text{kPa}} = 2.544\ \text{dm}^3$$

PROBLEM 4

A mixture contains two organic compounds, **A** and **B**. Both of them have in their molecules oxygen and they can be mixed together in arbitrary ratios. Oxidation of this mixture on cooling yields the only substance **C** that combines with $NaHSO_3$. The ratio of the molar mass of the substance being formed in the reaction with $NaHSO_3$ to that of substance **C**, is equal to 2.7931.

The mixture of substances **A** and **B** is burned in the presence of a stoichiometric amount of air (20 % O_2 and 80 % of N_2 by volume) in an eudiometer to produce a mixture of gases with a total volume of 5.432 dm^3 at STP. After the gaseous mixture is bubbled through a $Ba(OH)_2$ solution, its volume is decreased by 15.46 %.

Problems:

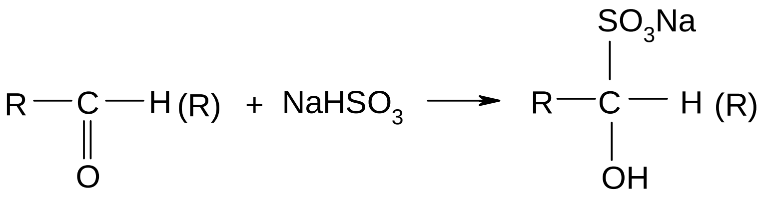
4.1 Write structural formulas of substance **A** and **B**.

4.2 Calculate the molar ratio of substances **A** and **B** in the mixture.

$A_r(C) = 12$; $A_r(O) = 16$; $A_r(S) = 32$; $A_r(Na) = 23$.

SOLUTION

4.1

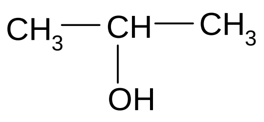


$$R-\overset{\displaystyle O}{\overset{\|}{C}}-H\,(R) + NaHSO_3 \longrightarrow R-\underset{\displaystyle OH}{\overset{\displaystyle SO_3Na}{C}}-H\,(R)$$

$M_r(\mathbf{C})$ $M_r(NaHSO_3) = 104$ $M_r(\mathbf{C}) + 104$

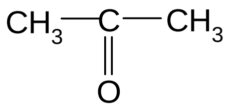
$$\frac{M_r(\mathbf{C}) + 104}{M_r(\mathbf{C})} = 2.7931 \qquad M_r(\mathbf{C}) = 58$$

A ...



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

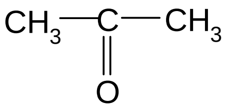
C ...



$$CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$$

4.2 At STP conditions the gaseous mixture can only contain CO_2 and N_2. Carbon dioxide is absorbed in a barium hydroxide solution and therefore:

B ...



$CH_3-C(=O)-CH_3$

(a) $V(CO_2) = 5.432 \text{ dm}^3 \times 0.1546 = 0.84 \text{ dm}^3$

(b) $V(N_2) = 5.432 \text{ dm}^3 - 0.84 \text{ dm}^3 = 4.592 \text{ dm}^3$

(c) $CH_3\text{-}CHOH\text{-}CH_3 + 9/2\ (O_2 + 4\ N_2) = 3\ CO_2 + 4\ H_2O + 18\ N_2$

(d) $CH_3\text{-}CO\text{-}CH_3 + 4\ (O_2 + 4\ N_2) = 3\ CO_2 + 3\ H_2O + 16\ N_2$

Let us mark the amounts of substances as:

$n(CH_3\text{-}CHOH\text{-}CH_3) = x$

$n(CH_3\text{-}CO\text{-}CH_3) = y$

From equations (a), (c) and (d):

(e) $(3x \times 22.4) + (3y \times 22.4) = 0.84$

From equations (b), (c) and (d):

(f) $(18x \times 22.4) + (16y \times 22.4) = 4.592$

In solving equations (e) and (f) we get:

$x = 0.0025$ mol $y = 0.01$ mol

$$\frac{x}{y} = \frac{1}{4}$$

PROBLEM 5

A mixture of two metals found in Mendelejev's periodical table in different groups, reacted with 56 cm^3 of hydrogen on heating (measured at STP conditions) to produce two ionic compounds. These compounds were allowed to react with 270 mg of water but only one third of water reacted. A basic solution was formed in which the content of hydroxides was 30 % by mass and at the same time deposited a precipitate with a mass that represented 59.05 % of a total mass of the products formed by the reaction. After filtration the precipitate was heated and its mass decreased by 27 mg.

When a stoichiometric amount of ammonium carbonate was added to the basic solution, a slightly soluble precipitate was obtained, at the same time ammonia was liberated and the content of hydroxides in the solution decreased to 16.81 %.

Problem:

5.1 Determine the metals in the starting mixture and their masses.

SOLUTION

Ionic hydrides are formed by combining of alkali metals or alkaline earth metals with hydrogen. In relation to the conditions in the task, there will be an alkali metal (M^I) as well as an alkaline earth metal (M^{II}) in the mixture.

Equations:

(1) $M^I + 1/2\ H_2 \rightarrow M^IH$

(2) $M^{II} + H_2 \rightarrow M^{II}H_2$

(3) $M^IH + H_2O \rightarrow M^IOH + H_2$

(4) $M^{II}H_2 + 2\ H_2O \rightarrow M^{II}(OH)_2 + 2\ H_2$

reacted: 0.09 g H_2O, i. e. 0.005 mol

unreacted: 0.18 g H_2O, i. e. 0.01 mol

Since all hydroxides of alkali metals are readily soluble in water, the undissolved precipitate is $M^{II}(OH)_2$, however, it is slightly soluble in water, too.

Thus, the mass of hydroxides dissolved in the solution:

(5) $m'(M^IOH + M^{II}(OH)_2) = Z$

Therefore:

$$30 = \frac{Z}{Z + 0.18} \times 100 \qquad\qquad Z = 0.077 \text{ g}$$

(6) $m'(M^IOH + M^{II}(OH)_2) = 0.077$ g

It represents 40.95 % of the total mass of the hydroxides, i. e. the total mass of hydroxides is as follows:

(7) $m'(M^IOH + M^{II}(OH)_2) = \dfrac{0.077 \text{ g} \times 100}{40.95} = 0.188$ g

The mass of solid $M^{II}(OH)_2$:

(8) 0.188 g – 0.077 g = 0.111 g

Heating:

(9) $M^{II}(OH)_2 \rightarrow M^{II}O + H_2O$

Decrease of the mass: 0.027 g (H_2O)

(10) Mass of $M^{II}O$: 0.084 g

In relation to (8), (9), and (10):

$$\frac{M_r(M^{II}O)}{M_r(M^{II}O) + 18} = \frac{0.084}{0.111}$$

$M_r(M^{II}O) = 56 \text{ g mol}^{-1}$

$M_r(M^{II}) = M_r(M^{II}O) - M_r(O) = 56 - 16 = 40$

M^{II} = Ca

Precipitation with (NH_4CO_3):

(11) $Ca(OH)_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2\, NH_3 + 2\, H_2O$

According to (5) and (6) the mass of the solution was:

0.18 g + 0.077 g = 0.257 g

After precipitation with $(NH_4)_2CO_3$:

$$16.81 = \frac{m(M^IOH)}{m(\text{solution})} \times 100$$

Let us mark as *n*' the amount of substance of $Ca(OH)_2$ being present in the solution.

$M(Ca(OH)_2) = 74 \text{ g mol}^{-1}$

Taking into account the condition in the task as well as equation (11), we get:

$$16.81 = \frac{(0.077 - 74n') \times 100}{0.257 - 74n' + 2n' \times 18}$$

$n' = 5 \times 10^{-4}$ mol

The <u>total amount of substance of $Ca(OH)_2$</u> (both in the precipitate and in the solution):

(12) $$n(Ca(OH)_2) = \frac{0.111\ g}{74\ g\ mol^{-1}} + 5 \times 10^{-4}\ mol = 0.002\ mol \quad (i.\ e.\ 0.148\ g)$$

According to equations (3) and (4):

$n(H_2O) = 0.004$ mol (for $M^{II}H_2$)

$n(H_2O) = 0.001$ mol (for $M^{I}H$)

$n(M^{I}OH) = 0.001$ mol

According to equations (7) and (11):

$m(M^{I}OH) = 0.188\ g - 0.148\ g = 0.04\ g$

$$M(M^{I}OH) = \frac{m(M^{I}OH)}{n(M^{I}OH)} = \frac{0.04\ g}{0.001\ mol} = 40\ g\ mol^{-1}$$

$M^{I}OH$ = NaOH

Composition of the mixture:

0.002 mol Ca + 0.001 mol Na

or

0.080 g Ca + 0.023 g Na

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Test tubes with unknown samples contain:

- a salt of carboxylic acid,
- a phenol,
- a carbohydrate,
- an amide.

Determine the content of each test tube using reagents that are available on the laboratory desk.

PROBLEM 2 (practical)

Determine cations in solutions No 5, 6, 8 and 9 using the solution in test tube 7.

Without using any indicator find out whether the solution in test tube 7 is an acid or a hydroxide.

SOLUTION

Test tube: No 5 - NH_4^+; No 6 - Hg^{2+}; No 7 - OH^-; No 8 – Fe^{3+} ; No 9 – Cu^{2+}

PROBLEM 3 (practical)

The solution in test tube No 10 contains two cations and two anions.

Prove those ions by means of reagents that are available on the laboratory desk.

SOLUTION

The solution in test tube No 10 contained: Ba^{2+}, Al^{3+}, Cl^-, CO_3^{2-}

7th

International Chemistry Olympiad

8 theoretical problems
4 practical problems

THE SEVENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
1–10 JULY 1975, VESZPRÉM, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

How many grams of alum $KAl(SO_4)_2 \,.\, 12\,H_2O$ are crystallised out from 320 g $KAl(SO_4)_2$ solution saturated at 20 °C if 160 g of water are evaporated from the solution at 20 °C?

(The solution saturated at 20 °C contains 5.50 % of $KAl(SO_4)_2$ by mass.)

Relative atomic masses:

$A_r(K) = 39.10$; $A_r(Al) = 26.98$; $A_r(S) = 32.06$; $A_r(O) = 16.0$; $A_r(H) = 1.01$

SOLUTION

Let us mark

x - mass of crystallised alum,

y - mass of the saturated solution of $AlK(SO_4)_2$ which remains after crystallisation

Mass fraction of $KAl(SO_4)_2$ in the crystallohydrate is equal to 0.544.

Then: $320 = x + y + 160$

i. e. $y = 160 - x$

Mass balance equation for $AlK(SO_4)_2$:

$$320 \times 0.055 = x \,.\, 0.544 + (160 - x)\, 0.055$$

$$x = 18.0 \text{ g}$$

PROBLEM 2

An alloy prepared for experimental purposes contains aluminium, zinc, silicon, and copper. If 1000 mg of the alloy are dissolved in hydrochloric acid, 843 cm^3 of hydrogen (0 °C, 101.325 kPa) are evolved and 170 mg of an undissolved residue remain. A sample of 500 mg of the alloy when reacted with a NaOH solution produces 517 cm^3 of hydrogen at the above conditions and in this case remains also an undissolved fraction.

Problem:

2.1 Calculate the composition of the alloy in % by mass.

Relative atomic masses:

A_r(Al) = 26.98; A_r(Zn) = 65.37; A_r(Si) = 28.09; A_r(Cu) = 63.55.

SOLUTION

2.1 HCl dissolves: Al, Zn

NaOH dissolves: Al, Zn, Si

$$\frac{0.843\ \text{dm}^3}{22.414\ \text{dm}^3\ \text{mol}^{-1}} = 37.61\ \text{mmol H}_2 \qquad \text{(Al, Zn)}$$

$$\frac{2 \times 0.517\ \text{dm}^3}{22.414\ \text{dm}^3\ \text{mol}^{-1}} = 46.13\ \text{mmol H}_2 \qquad \text{(Al, Zn, Si)}$$

The difference of 8.52 mmol H_2 corresponds to 4.26 mmol Si

Si: $m(\text{Si}) = 4.26\ \text{mmol} \times 28.09\ \text{g mol}^{-1} = 119.7\ \text{mg}$

$$\%\ \text{Si} = \frac{119.7\ \text{mg}}{1000\ \text{mg}} \times 100 = 11.97$$

Cu: $m(\text{Si + Cu}) = 170\ \text{mg}$

$m(\text{Cu}) = 170\ \text{mg} - 119.7\ \text{mg} = 50.3\ \text{mg}$ (in 1000 mg of the alloy)

% Cu = 5.03

Al: $m(\text{Zn + Al}) = 1000 \text{ mg} - 170 \text{ mg} = 830 \text{ mg}$

x mg Al gives $\frac{3}{2} \times \frac{x}{26.98}$ mmol H_2

(830 – x) mg Zn gives $\frac{830 - x}{65.37}$ mmol H_2

$$\frac{3}{2} \times \frac{x}{26.98} + \frac{830 - x}{65.37} = 37.61 \text{ mmol } H_2$$

x = 618.2 mg Al (in 1000 mg of the alloy)

% Al = 61.82

Zn: $m(\text{Zn}) = 830 \text{ mg} - 618.2 \text{ mg} = 211.8 \text{ mg}$ (in 1000 mg of the alloy)

% Zn = 21.18

PROBLEM 3

A sample of 1500 mg of an alloy that contains silver, copper, and chromium is dissolved and the solution containing Ag^+, Cu^{2+}, and Cr^{3+} ions, is diluted to exactly 500 cm^3. One tenth of the volume of that solution is taken for further procedure:

After elimination of silver and copper, chromium is oxidised in it according to the following unbalanced equation:

$$OH^- + Cr^{3+} + H_2O_2 \rightarrow CrO_4^{2-} + H_2O$$

Then 25.00 cm^3 of a 0.100 molar Fe(II) salt solution are added. The following reaction (written in an unbalanced form) is taking place:

$$H^+ + Fe^{2+} + CrO_4^{2-} \rightarrow Fe^{3+} + Cr^{3+} + H_2O$$

According to the unbalanced equation:

$$H^+ + Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+} + H_2O$$

a volume of 17.20 cm^3 of a 0.020-molar $KMnO_4$ solution is required for an oxidation of the Fe(II) salt which remains unoxidized in the solution.

In another experiment, a volume of 200 cm^3 of the initial solution is electrolysed. Due to secondary reactions, the efficiency of the electrolysis is 90 % for metals under consideration. All three metals are quantitatively deposited in 14.50 minutes by passing a current of 2 A through the solution.

Problem:

3.1 Balance the three chemical equations and calculate the composition of the alloy in % by mass.

Relative atomic masses: $A_r(Cu) = 63.55$; $A_r(Ag) = 107.87$; $A_r(Cr) = 52.00$

SOLUTION

3.1 Equations:

$$10\,OH^- + 2\,Cr^{3+} + 3\,H_2O_2 \rightarrow 2\,CrO_4^{2-} + 8\,H_2O$$

$$8\,H^+ + 3\,Fe^{2+} + CrO_4^{2-} \rightarrow 3\,Fe^{3+} + Cr^{3+} + 4\,H_2O$$

$$8\,H^+ + 5\,Fe^{2+} + MnO_4^- \rightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O$$

Content of Cr:

$17.20 \times 0.020 = 0.344$ mmol $KMnO_4$

$5 \times 0.344 = 1.72$ mmol Fe^{2+}

Reacted: $25 \times 0.1 - 1.72 = 0.78$ mmol Fe^{2+}

It corresponds:

$$\frac{0.78}{3} = 0.26 \text{ mmol Cr in 150 mg of the alloy}$$

m(Cr) = 2.6 mmol × 52 g mol^{-1} = 135.2 mg in 1500 mg of the alloy

% Cr = 9.013

Content of Cu and Ag:

Q = 40.575 mF / 1500 mg (1087.4 mAh)

Q_{Cr} = 2.6 × 3 = 7.8 mF (209 mAh)

$Q_{(Cu+Ag)}$ = 40.575 – 7.8 = 32.775 mF (878.4 mAh)

(F = Faraday's charge)

m(Cu + Ag) = m(alloy) – m(Cr) = 1500 – 135.2 = 1364.8 mg

For deposition of copper: $\frac{2\,x}{63.55}$ mF

For deposition of silver: $\frac{1364.8 - x}{107.87}$ mF

$$32.775 = \frac{2\,x}{63.55} + \frac{1364.8 - x}{107.87}$$

x = 906.26

m(Cu) = 906.26 mg in 1500 mg of the alloy

m(Ag) = 458.54 mg in 1500 mg of the alloy

% Cu = 60.4 % Ag = 30.6

PROBLEM 4

The pH value of a solution containing 3 % by mass of formic acid (ρ = 1.0049 g cm^{-3}) is equal to 1.97.

Problem:

4.1 How many times should the solution be diluted to attain a tenfold increase in the value of ionisation degree?

Relative atomic masses: A_r(H) = 1.01; A_r(C) = 12.01; A_r(O) = 16.

SOLUTION

4.1 $$c_1 = \frac{n_1}{V} = \frac{\dfrac{1004.9\text{ g}\times 0.03}{45.03\text{ g mol}^{-1}}}{1\text{ dm}^3} = 6.55\times10^{-1}\text{ mol dm}^{-3}$$

pH = 1.97; [H$^+$] = 1.0715×10^{-2} mol dm^{-3}

$$\alpha_1 = \frac{[\text{H}^+]}{c_1} = 0.01636 \qquad (1.636\ \%)$$

<u>Calculation of c_2 after dilution</u> (two alternative solutions):

a) α_1 – before dilution; α_2 – after dilution

$$K_a = \frac{\alpha_1\, c_1}{1-c_1} \qquad (1)$$

$$K_a = \frac{\alpha_2^2\, c_2}{1-\alpha_2} = \frac{(10\,\alpha_1)^2\, c_2}{1-10\,\alpha_1} \qquad (2)$$

From equations (1) and (2):

$$\frac{c_1}{c_2} = \frac{100\,(1-\alpha_1)}{1-10\,\alpha_1} = 117.6$$

b) $$K_a = \frac{[\text{H}^+]^2}{c-[\text{H}^+]} = \frac{(1.0715\times10^{-4})^2}{0.655-1.0715\times10^{-2}} = 1.78\times10^{-4}$$

$$c_2 = \frac{K_a\,(1 - 10\,\alpha_1)}{(10\,\alpha_1)^2} = 5.56 \times 10^{-3}\ \text{mol dm}^{-3}$$

$$\frac{c_1}{c_2} = \frac{6.55 \times 10^{-1}\ \text{mol dm}^{-3}}{5.56 \times 10^{-3}\ \text{mol dm}^{-3}} = 117.8$$

PROBLEM 5

A certain aldehyde **B** is subsequent to an aldehyde **A** in the homologous series of aldehydes. An amount of 19 g of aldehyde **B** is added to 100 g of an aqueous solution containing 23 mass % of aldehyde **A**. Addition of $AgNO_3$ in ammonia solution to 2 g of the aldehydes solution results in a precipitation of 4.35 g of silver.

Problems:

5.1 Determine by calculation what aldehydes were used.

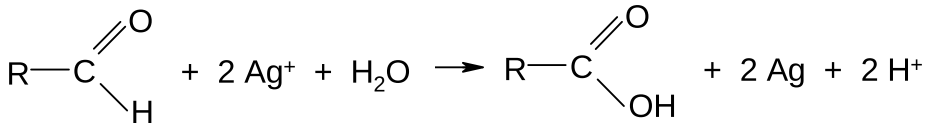
5.2 Give the structural formulas of the aldehydes.

Relative atomic masses:

$A_r(C) = 12.01$; $A_r(O) = 16.00$; $A_r(H) = 1.01$; $A_r(Ag) = 107.87$

SOLUTION

5.1 Equation:



$$n(\text{Ag}) = \frac{4.35\ \text{g}}{107.87\ \text{g mol}^{-1}} = 0.04033\ \text{mol}$$

$$n(\mathbf{A}) + n(\mathbf{B}) = 0.02017\ \text{mol}$$

$$\frac{m(\mathbf{A})}{M(\mathbf{A})} + \frac{m(\mathbf{B})}{M(\mathbf{A}) + 14} = 0.02017\ \text{mol} \qquad (1)$$

$$m(\mathbf{A}) = \frac{23\ \text{g}}{119\ \text{g}} \times 2\ \text{g} = 0.39\ \text{g}$$

$$m(\mathbf{B}) = \frac{19\ \text{g}}{119\ \text{g}} \times 2\ \text{g} = 0.32\ \text{g}$$

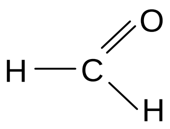
According to equation (1):

$M(\mathbf{A}) = 30\ \text{g mol}^{-1}$

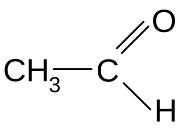
$M(\mathbf{B}) = 44\ \text{g mol}^{-1}$

5.2 **A** = formaldehyde, methanal

B = acetaldehyde, ethanal



A



B

PROBLEM 6

The equilibrium constant of the reaction $H_2 + I_2 \rightleftharpoons 2\,HI$ is at 600 ℃ equal to 70.0 .

Problems:

6.1 How much iodine (in %) is converted till the equilibrium is reached if the reactants are mixed in:

a) 1 : 1 molar ratio at 600 ℃;

b) 2 : 1 molar ratio at 600 ℃ (the amount of hydrogen is twice as great as that of iodine).

6.2 How many moles of hydrogen should be mixed with one mole of iodine when 99 % of iodine is to be converted to hydrogen iodide till the equilibrium is reached at 600 ℃?

SOLUTION

6.1a) (two alternative solutions)

i) $[H_2] = [I_2] = c - x$

$[HI] = 2\,x$

$$K = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{4\,x^2}{(c - x)^2}$$

$$\sqrt{K} = \frac{2\,x}{c - x}$$

$$x = \frac{\sqrt{70}\,.\,c}{2 + \sqrt{70}} \qquad \frac{x}{c} = 0.807 \qquad 80.7\ \%$$

ii) $[H_2] = [I_2] = c - c\alpha$

$[HI] = 2\,c\alpha$

$$K = \frac{4\,\alpha^2\,c^2}{(1-\alpha)^2\,c^2} = \frac{4\,\alpha^2}{(1 - \alpha^2)^2}$$

$$\sqrt{K} = \frac{2\,\alpha}{1 - \alpha}$$

α = 0.807 , i. e. 80.7 %

6.1b) (two alternative solutions)

i) $[H_2] = 2\,c - x$ $[I_2] = c - x$

$[HI] = 2\,x$

$$K = \frac{4\,x^2}{(2c - x)\,(c - x)}$$

$x = 0.951\,c$ $\frac{x}{c} = 0.951$ i. e. 95.1 %

ii) $[H_2] = 2\,c - c\alpha$ $[I_2] = c - c\,\alpha$

$[HI] = 2\,c\,\alpha$

$$K = \frac{4c^2\,\alpha^2}{(2 - \alpha)\,(1 - \alpha)\,c^2}$$

$\alpha = 0.951$ i. e. 95.1 %

6.2 $[H_2] = x\,c - 0.99\,c$ $[I_2] = c - 0.99\,c$

$[HI] = 1.98\,c$

$$K = \frac{1.98^2\;c^2}{c^2\;(1 - 0.99)\,(x - 0.99)} = \frac{1.98^2}{0.01\,(x - 0.99)}$$

x = 6.59 mol H_2

PROBLEM 7

A certain saturated hydrocarbon **A** is transformed by a catalytic oxidation partly into a secondary alcohol **B**, and partly into a ketone **C**. The ketone when oxidised with nitric acid in the presence of catalyst yields a compound **D** with a formula of $C_6H_{10}O_4$. From compound **D** when heated in the presence of acetic anhydride, a ketone **E** is formed, its formation being accompanied by evolution of CO_2 and H_2O. Compounds **E** and **C** have similar structures but compound **E** contains one methylene group less than ketone **C**. Compound **D** is one of the starting materials in the production of an important polycondensation synthetic fibre.

Problem:

7.1 Write the structural formulas of compounds **A**, **B**, **C**, **D**, and **E**.

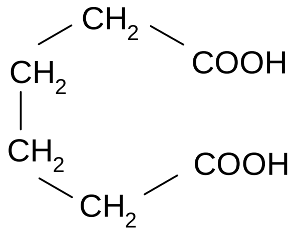
SOLUTION

7.1 In general: ketone $\xrightarrow{\text{oxidation}}$ carboxylic acid

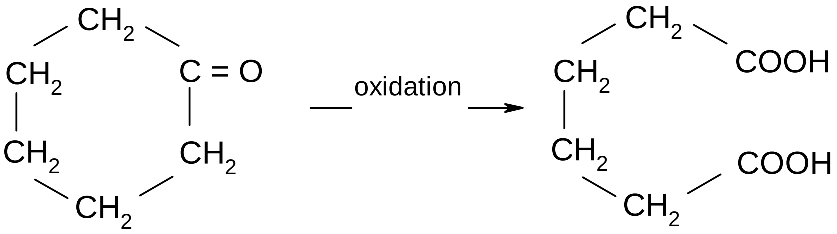
$C_6H_{10}O_4$ = $C_4H_8(COOH)_2$ = $HOOC\text{-}(CH_2)_4\text{-}COOH$

Product **D** is adipic acid which is a basic material in the production of nylon.

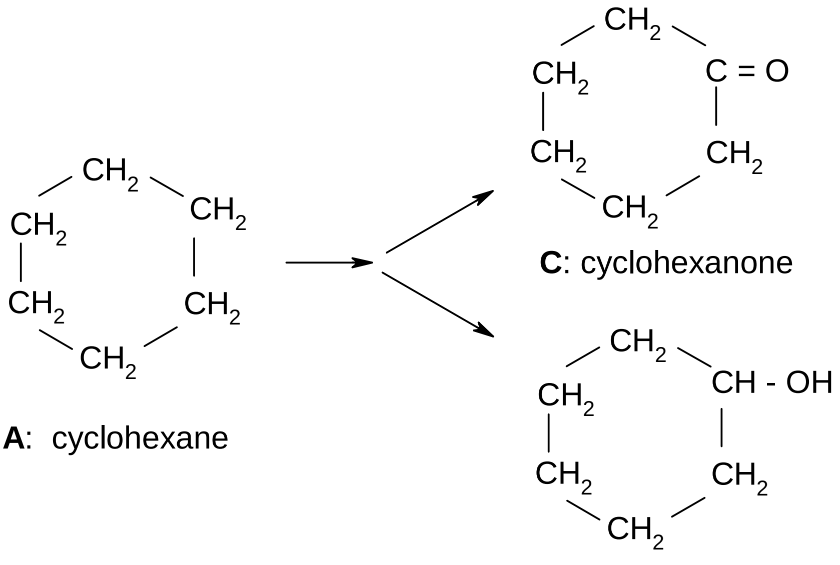
D:



Compound **C** is cyclohexanone, because:



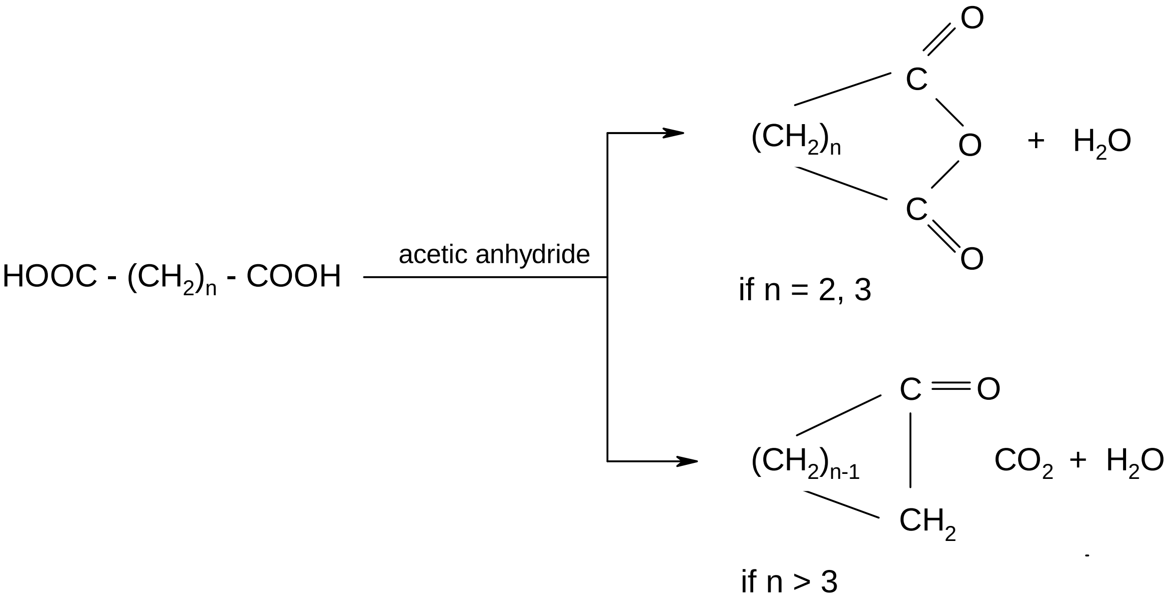
cyclohexanone adipic acid



A: cyclohexane

C: cyclohexanone

B: cyclohexanol



<u>Compound **E**: cyclopentanone</u>

PROBLEM 8

a) Mark by the "+" in a corresponding window those molecules for which the assertions written on the left side of the Table, are true.

Assertion	Molecule			
	C_2H_4	N_2H_4	H_2O_2	H_2F_2
There is a covalent bond between two equal atoms				
The molecule contains a double bond				
The molecule is planar				
The molecule is polar				
There is also a hydrogen bond in the molecule				
It has basic properties in relation to water				

b) The following assertion and Table are incomplete. Fill in the dotted places by a missing word and the missing formulas, respectively.

Assertion: The electronic structures of the molecules (ions) being placed in the Table one under the other are . . . .

CH_4	C_2H_6	CO_3^{2-}	. . . . . .	$C_2O_4^{2-}$	. . . . . .
NH_4^+	$N_2H_6^{2+}$	. . . . . .	NO_2^+	. . . . . .	N_2

SOLUTION

a)

Assertion	Molecule			
	C_2H_4	N_2H_4	H_2O_2	H_2F_2
There is a covalent bond between two equal atoms	+	+	+	
The molecule contains a double bond	+			
The molecule is planar	+			+
The molecule is polar		+	+	+
There is also a hydrogen bond in the molecule				+
It has basic properties in relation to water		+		

b) **Assertion**: The electronic structures of the molecules (ions) being placed in the Table under the other are **isoelectronic**.

CH_4	C_2H_6	CO_3^{2-}	$\mathbf{CO_2}$	$C_2O_4^{2-}$	$\mathbf{C_2^{2-}}$
NH_4^+	$N_2H_6^{2+}$	$\mathbf{NO_3^-}$	NO_2^+	$\mathbf{N_2O_4}$	N_2

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Aqueous solutions of the following compounds: $AgNO_3$, HCl, Ag_2SO_4, $Pb(NO_3)_2$, NH_3 and NaOH are available in numbered bottles. Allow to react each of them with others and align the numbers of the bottles with formulas of the compounds.

Attention! The use of any other reagent is not permitted. In performing the reactions do not use the whole volume of the solutions. A few cm^3 of the solution should remain in each bottle after your work is finished. It is advisable to make a draft at first but only those solutions will be evaluated by the jury that will be written in the Table.

Write your observations into the squares of the Table bellow the diagonal using the following uniform symbols:

white precipitate : ↓

coloured precipitate: ↓↓

formation of a complex soluble in water: [ ]

evolution of a gas: ↑

Write into the corresponding squares above the diagonal the chemical formulas of the precipitate, the complex ion or gas which are formed by the corresponding reactions.

Write into the last line of the Table the final results obtained on the basis of your experiments.

Number of sample	1	2	3	4	5	6
1	▨					
2		▨				
3			▨			
4				▨		
5					▨	
6						▨
Formula of compounds						

PROBLEM 2 (practical)

A solid compound is in each of the numbered test-tubes. It might be chloride, iodide, oxide, hydroxide, sulphide, sulphate or carbonate, each combined with one of the following cations: Ag^+, Pb^{2+}, Cu^{2+}, Cd^{2+}, Sb(V), Sn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, Al^{3+}, Zn^{2+}, Ba^{2+}.

Problem:

Write the chemical formula for each solid compound given as a sample. You can use only reagents that are available on your laboratory desk.

Attention! In carrying out reactions do not use the whole quantity of the sample. A small portion of the sample is to remain in each test tube. Only those results will be evaluated that will be written in the Table below.

Table:

Compound			
Number of sample	Formula	Number of sample	Formula
1		6	
2		7	
3		8	
4		9	
5			

PROBLEM 3 (practical)

Three samples are found in sealed ampoules. All of them are aromatic compounds: a hydrocarbon, a phenol, and an aldehyde.

Determine the group of compounds to which your numbered samples belong, using only the reagents which are at your disposal.

Attention! Be careful when opening the ampoules. The identification of the samples based upon physical characteristics only (colour, smell), is not sufficient. Only those results will be taken into account that will be written in the Table below.

Table:

No of sample	Reagent	Observation	Type of compound
1			
2			
3			

PROBLEM 4 (practical)

A crystalline sodium carbonate loses a part of water when stored for a long time, i. e. its water content is not constant. After a long storage it has an average content of crystal water.

A solution of Na_2CO_3 is in the test-tube and the mass of $Na_2CO_3 . x H_2O$ used in its preparation is marked on the test-tube.

Determine the content of crystal water per mole of sodium carbonate in the sample. Make calculations with an accuracy of 0.01 mol.

Procedure:

Transfer the solution from the test tube quantitatively into a 100 cm^3 volumetric flask and dilute it up to the mark with distilled water free of carbon dioxide (having been boiled and cooled to room temperature). Measure 10.00 cm^3 of the solution into a 100 cm^3 Erlenmeyer flask and dilute it to about 30 cm^3 with the above mentioned distilled water. Add 2 – 3 drops of methyl orange indicator and titrate with a 0.1-molar HCl volumetric solution to a colour transition of the indicator. On boiling for 1 – 2 minutes the carbon dioxide dissolved in the solution is expelled. If the colour of the solution changes to yellow, cool it and titrate again to the colour transition of the indicator. Calculate the carbonate content in the sample from the total consumption of the 0.1-molar HCl solution.

A_r(Na) = 22.99; A_r(C) = 12.01; A_r(O) = 16.00; A_r(H) = 1.01.

8th

International Chemistry Olympiad

7 theoretical problems
3 practical problems

THE EIGHTH
INTERNATIONAL CHEMISTRY OLYMPIAD
10–19 JULY 1976, HALLE, GERMAN DEMOCRATIC REPUBLIC

THEORETICAL PROBLEMS

PROBLEM 1

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.

1.2 Write chemical equations for two methods of quantitative determination of the content of peroxide in calcium(II) peroxide.

1.3 By means of chemical equations express the following chemical reactions:

a) $[Cr(H_2O)_6]Cl_3$ 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

1.1 Peroxo compounds contain the functional group: O_2^{2-}

Examples: H_2O_2, Na_2O_2, BaO_2, H_2SO_5, $H_2S_2O_8$, $K_2C_2O_6$, CrO_5, $[VO_2]^{3+}$

1.2 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:

a) $5\ H_2O_2 + 2\ MnO_4^- + 6\ H_3O^+ \rightarrow 2\ Mn^{2+} + 5\ O_2 + 14\ H_2O$

b) $H_2O_2 + 2\ I^- + 6\ H_3O^+ \rightarrow I_2 + 4\ H_2O$

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

1.3 a) $[Cr(H_2O)_6]^{3+} + 4\ OH^- \rightarrow [Cr(OH)_4(H_2O)_2]^- + 4\ H_2O$

$2\ [Cr(OH)_4(H_2O)_2]^- + 3\ H_2O_2 + 2\ OH^- \rightarrow 2\ CrO_4^{2-} + 12\ H_2O$

b) Equation is given in 2a.

PROBLEM 2

A sample of 2.3793 g of crystallohydrate of the type $M_xA_y\,.z\,H_2O$, 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:

2.1 Calculate the summary formula of the crystallohydrate. (Use the relative atomic mass values given in the attached Periodical Table of Elements.)

2.2 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

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

Reactions:

$M_xA_y\,.\,z\,H_2O + z\,SOCl_2 \rightarrow z\,SO_2 + 2\,z\,HCl + M_xA_y$

$z\,SO_2 + z\,H_2O_2 + z\,Ba^{2+} \rightarrow z\,BaSO_4 + 2\,z\,H^+$

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

<u>Amount of substance of H_2O in the hydrate</u>:

$n(H_2O) = 0.06$ mol

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

Reaction: $Ag^+ + A^- \rightarrow AgA$

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

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

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

A = Cl

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

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

2.3792 g of the hydrate contain 0.02 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) $MCl\ .\ 3\ H_2O$

$n(Cl^-) = 0.02$ mol

$n(MCl\ .\ 3\ H_2O) = 0.02$ mol

$$M(\text{MCl}_3\ .\ 3\ \text{H}_2\text{0}) = \frac{2{,}3793 \text{ g}}{0{,}02 \text{ mol}} = 118.965 \text{ g mol}^{-1}$$

$M(M) = M(MCl\ .\ 3\ H_2O) - M(Cl) - 3\ M(H_2O) =$

$= 118.965 - 35.453 - 54.046 = 29.466 \text{ g mol}^{-1}$

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

ii) $MCl_2\ .\ 6\ H_2O$

$n(Cl^-) = 0.02$ mol

$n(MCl_2\ .\ 6\ H_2O) = 0.01$ mol

$$M(\text{MCl}_2\ .\ 6\ \text{H}_2\text{0}) = \frac{2{,}3793 \text{ g}}{0{,}01 \text{ mol}} = 237.93 \text{ g mol}^{-1}$$

$M(M) = M(MCl_2\ .\ 6\ H_2O) - 2\ M(Cl) - 6\ M(H_2O) =$

$= 237.93 - 70.906 - 108.092 = 58.932 \text{ g mol}^{-1}$

M = Co

The second assumption satisfies the conditions of the task.

The formula of the hydrate is: **$CoCl_2 . 6 H_2O$**

iii) $\underline{MCl_3 . 9 H_2O}$

$n(Cl^-) = 0.02$ mol

$n(MCl_3 . 9 H_2O) = \frac{0.02}{3}$ mol

$M(MCl_3 . 9 H_2O) = 356.895$ g mol^{-1}

$M(M) = M(MCl_3 . 9 H_2O) - 3 M(Cl) - 9 M(H_2O) =$

$= 356.895 - 106.359 - 162.138 = 88.398$ g mol^{-1}

$\underline{M = Y}$

2.2 The hydrate $YCl_3 . 9 H_2O$ as well as the other hydrate $SnCl_4 . 12 H_2O$ cannot come into account because of the limitation in the task (a maximum of seven moles of H_2O pre 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:

3.1 Calculate the volume of the gaseous products at STP conditions.

3.2 What is the composition (in volume %) of the gaseous mixture?

SOLUTION

3.1 Reactions:

$Fe + 2\,HCl \rightarrow FeCl_2 + H_2$

$FeS + 2\,HCl \rightarrow FeCl_2 + H_2S$

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

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

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

$$V(\text{H}_2\text{S}) = n(\text{H}_2\text{S}) \times V_0 = 5.40 \times 10^{-2}\ \text{mol} \times 22.4\ \text{dm}^3\ \text{mol}^{-1} = 1\underline{.21\ \text{dm}^3}$$

3.2 Composition of the gaseous mixture:

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

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

PROBLEM 4

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

$C_2H_5O_2N$	(**A**)	$C_3H_7O_2N$	(**C**)
$C_3H_7O_2N$	(**B**)	$C_9H_{11}O_2N$	(**D**)

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:

4.1 Write structural formulas for the compounds **A**, **B**, **C**, and **D**.

4.2 Which of the given substances are optically active and which ones are inactive?

4.3 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.

4.4 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.

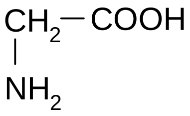
c) Write the characteristic part of the structural formula of an isomeric macromolecular substance that is also technically important.

d) Give the name for the group of compounds to which belong the above mentioned macromolecular substances.

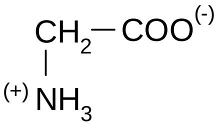
SOLUTION

4.1

A

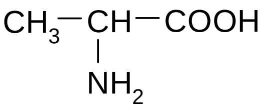


$$\underset{NH_2}{\underset{|}{CH_2}}-COOH$$

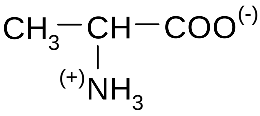


$$\underset{^{(+)}NH_3}{\underset{|}{CH_2}}-COO^{(-)}$$

B

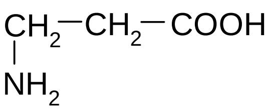


$CH_3-\underset{NH_2}{\underset{|}{CH}}-COOH$

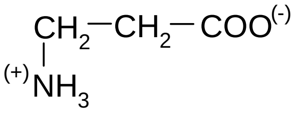


$CH_3-\underset{^{(+)}NH_3}{\underset{|}{CH}}-COO^{(-)}$

C

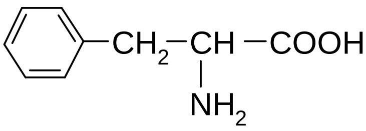


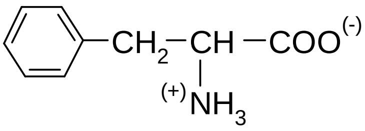
$\underset{NH_2}{\underset{|}{CH_2}}-CH_2-COOH$



$\underset{^{(+)}NH_3}{\underset{|}{CH_2}}-CH_2-COO^{(-)}$

D





4.2 **A** - optically inactive

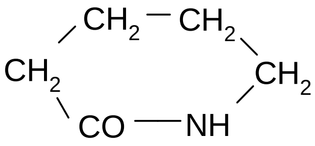
B - optically active

C - optically inactive

D - optically active

4.3 – NH – CO – peptides

4.4 a)



b) – CO – $(CH_2)_5$ – NH –

c) – NH – $(CH_2)_6$ – NH – CO – $(CH_2)_4$ – CO –

d) polyamides

PROBLEM 5

a) 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).

b) Substance **B** can be oxidised in a two-step process to a substance **C**.

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**.

d) 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).

e) Substance **F** is an important product of metabolism in biological processes.

f) 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**.

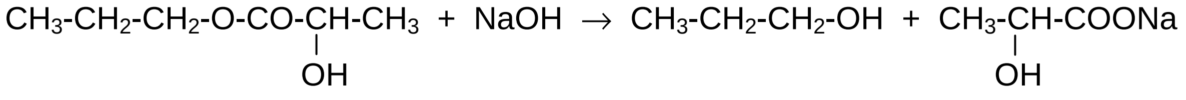
g) Substance **F** can also be obtained from a compound **H** containing nitrogen, by one-step reaction with nitrous acid. Assuming the quantitative course of the reaction, 4.5 g of substance **F** are formed from 4.45 g of substance **H**.

Problems:

5.1 Write all equations for the above mentioned chemical reactions.

5.2 Give structural formulas of the organic compounds **A** – **H**.

SOLUTION

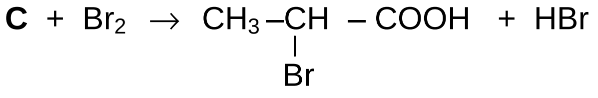


$$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CO\text{-}\underset{\large OH}{\underset{|}{C}}H\text{-}CH_3 + NaOH \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}OH + CH_3\text{-}\underset{\large OH}{\underset{|}{C}}H\text{-}COONa$$

A **B** **E**

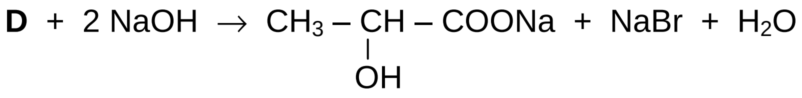
$$\mathbf{B} \xrightarrow[-\,H_2O]{+\,O} CH_3\text{-}CH_2\text{-}CHO \xrightarrow{+\,O} CH_3\text{—}CH_2\text{—}COOH$$

C



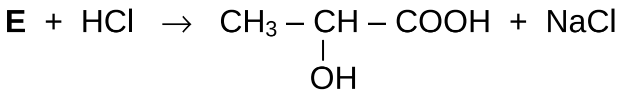
$$\mathbf{C} + Br_2 \rightarrow CH_3\text{–}\underset{\large Br}{\underset{|}{C}}H\text{ – }COOH + HBr$$

D



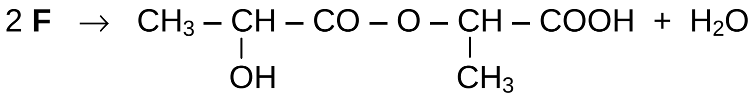
$$\mathbf{D} + 2\,NaOH \rightarrow CH_3-\underset{\substack{|\\ OH}}{CH}-COONa + NaBr + H_2O$$

E



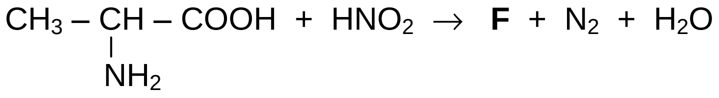
$$\mathbf{E} + HCl \rightarrow CH_3-\underset{\substack{|\\ OH}}{CH}-COOH + NaCl$$

F



$$2\,\mathbf{F} \rightarrow CH_3-\underset{\substack{|\\ OH}}{CH}-CO-O-\underset{\substack{|\\ CH_3}}{CH}-COOH + H_2O$$

G



$$CH_3-\underset{\substack{|\\ NH_2}}{CH}-COOH + HNO_2 \rightarrow \mathbf{F} + N_2 + H_2O$$

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:

6.1 How many moles of nitrogen were used to fill the glass tube?

6.2 How many moles of nitrogen escaped from the tube at the higher temperature?

6.3 Calculate the average temperature in the room under investigation if the thermal expansion of the glass tube is assumed to be negligible.

6.4 Does anything change if instead of pure nitrogen, a mixture containing 50 volume % of nitrogen and 50 volume % of hydrogen is used?

SOLUTION

6.1 Filling of the tube:

$$n_1(\mathrm{N_2}) = \frac{p\,V_1}{R\,T} = \frac{101.325\ \mathrm{kPa} \times 0.080\ \mathrm{dm^3}}{8.314\ \mathrm{J\,mol^{-1}\,K^{-1}} \times 293.15\ \mathrm{K}} = 3.33 \times 10^{-3}\ \mathrm{mol}$$

6.2 Escaped from the tube:

$$n_2(\mathrm{N_2}) = \frac{p\,V_2}{R\,T} = \frac{101.325\ \mathrm{kPa} \times 0.035\ \mathrm{dm^3}}{8.314\ \mathrm{J\,mol^{-1}\,K^{-1}} \times 293.15\ \mathrm{K}} = 1.46 \times 10^{-3}\ \mathrm{mol}$$

Remained in the tube:

$$n_3(\mathrm{N_2}) = n_1 - n_2 = 1.87 \times 10^{-3}\ \mathrm{mol}$$

6.3 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):

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

$\underline{t = 248\ °C}$

6.4 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 ρ = 1.28 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 ρ = 1.10 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:

7.1 Write the equation for a total electrochemical reaction that takes place in the lead accumulator when it is charged and discharged.

7.2 Calculate the masses of H_2O and H_2SO_4 being consumed or formed according to the equation in No 1.

7.3 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.

7.4 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

7.1 $$PbO_2 + Pb + 2\,H_2SO_4 \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftarrows}} 2\,PbSO_4 + 2\,H_2O$$

7.2 $n(H_2SO_4) = 2$ mol $n(H_2O) = 2$ mol

$m(H_2SO_4) = 196$ g $m(H_2O) = 36$ g

Discharging: $\Delta m(H_2SO_4) = -196$ g

$\Delta m(H_2O) = +36$ g

Charging: $\Delta m(H_2SO_4) = +196$ g

$\Delta m(H_2O) = -36$ g

7.3 The mass of H_2SO_4 required:

26.8 Ah corresponds to 98 g H_2SO_4

120 Ah corresponds to 438.8 g H_2SO_4

Analogously:

26.8 Ah corresponds to 18 g H_2O
120 Ah corresponds to 80.6 g H_2O

Discharged lead accumulator:

mass of H_2SO_4 solution – m
mass of H_2SO_4 – m_1
mass fraction of H_2SO_4 – $w_1 = 0.1435$
density of H_2SO_4 solution – $\rho_1 = 1.10\ \text{g cm}^{-3}$

Charged lead accumulator:

mass of H_2SO_4 formed – $m_2 = 438.8\ \text{g}$
mass of H_2O consumed – $m_3 = 80.6\ \text{g}$
mass fraction of H_2SO_4 – $w_2 = 0.3687$
density of the H_2SO_4 solution – $\rho_2 = 1.28\ \text{g cm}^{-3}$

Because:

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

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

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

$$m_1 = 195.45\ \text{g}$$
$$m = 1362\ \text{g}$$

7.4 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 (practical)

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, KNO_3/Na_2CO_3, NH_4SCN, $Na_2B_4O_7$, NaF, C_2H_5OH, $BaCl_2$, $AgNO_3$, NH_4Cl, $(NH_4)_2Fe(SO_4)_2$, alizarin B.

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

a) 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;

b) into the column "+/–" mark the presence or absence of an ion, proved in the sample, by the sign "+" and "–" , respectively.

PROBLEM 2 (practical)

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 mol dm^{-3}), NaOH (c = 0.1019 mol dm^{-3}), concentrated H_2SO_4, and a solution of phenolphthalein.

PROBLEM 3 (practical)

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 "–".

9th

8 theoretical problems
3 practical problems

THE NINTH
INTERNATIONAL CHEMISTRY OLYMPIAD
4–14 JULY 1977, BRATISLAVA, CZECHOSLOVAKIA

THEORETICAL PROBLEMS

PROBLEM 1

Compare three salts of a composition $M_2S_2O_x$ where x are three different small integers and M is an alkali metal. To each of the three salts apply some of the following assertions:

a) The O–O bond is characteristic for the anion.

b) The S–S bond is characteristic for the anion.

c) The S–O–S bond is characteristic for the anion.

d) It is formed by thermal decomposition of hydrogen sulphate.

e) It is formed by anodic oxidation of hydrogen sulphate.

f) It is formed by the reaction of an aqueous solution of sulphite with sulphur.

g) Its aqueous solution dissolves silver bromide.

h) Neutralisation of its aqueous solution with hydroxide MOH yields sulphate M_2SO_4.

i) In aqueous solution, it is able to oxidise Mn(II) salt to permanganate.

Problems:

1.1 Fill in the correct x values in the formulas given in the Table and indicate in the corresponding square by appropriate letters those assertions that may be applied to each of the given salts:

$M_2S_2O_{\square}$					
$M_2S_2O_{\square}$					
$M_2S_2O_{\square}$					

1.2 Write structural formulas of the anions of the above three salts and assign σ-bonds and π-bonds in them.

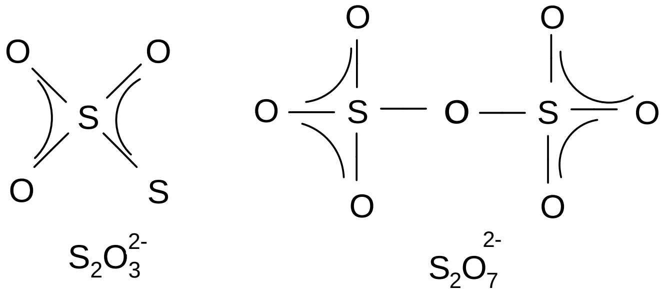
1.3 Write the chemical equations expressing the processes involved in the assertions under the letters d, e, f, g, h, i.

SOLUTION

1.1

$M_2S_2O_3$	b	f	g		
$M_2S_2O_7$	c	d	h		
$M_2S_2O_8$	a	e	i		

1.2



$S_2O_3^{2-}$

$S_2O_7^{2-}$

1.3 d) $2\,HSO_4^- \rightarrow H_2O + S_2O_7^{2-}$

$2\,MHSO_4 \rightarrow H_2O + M_2S_2O_7$

e) $2\,HSO_4^- - 2e \rightarrow 2\,H^+ + S_2O_8^{2-}$

$2\,MHSO_4 - 2e \rightarrow 2\,H^+ + M_2S_2O_8$

f) $SO_3^{2-} + S \rightarrow S_2O_3^{2-}$

$M_2SO_3 + S \rightarrow M_2S_2O_3$

g) $AgBr + 2\,S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$

$AgBr + 2\,M_2S_2O_3 \rightarrow M_3[Ag(S_2O_3)_2] + MBr$

h) $S_2O_7^{2-} + 2\ OH^- \rightarrow 2\ SO_4^{2-} + H_2O$

$M_2S_2O_7 + 2\ MOH \rightarrow 2\ M_2SO_4 + H_2O$

i) $2\ Mn^{2+} + 5\ S_2O_8^{2-} + 8\ H_2O \rightarrow 2\ MnO_4^- + 10\ SO_4^{2-} + 16\ H^+$

$2\ MnSO_4 + 5\ M_2S_2O_8 + 8\ H_2O \rightarrow 2\ MMnO_4 + 4\ M_2SO_4 + 8\ H_2SO_4$

PROBLEM 2a

Note: The International Jury did not choose Task 2a for the competition but the alternative Task 2b.

Attention

Make sure to open only the correct envelopes.

You lose points for an incorrectly opened envelope.

Return unopened envelopes together with your solution.

Halogen X reacts with an aqueous solution of another halogen compound KYO_3 according to the equation:

$X_2 + 2\ KYO_3 \rightarrow 2\ KXO_3 + Y_2$

1. The atomic number of halogen X is greater than that of halogen Y. (If you find this answer correct open envelope 1.)
2. The atomic number of halogen X is smaller than that of halogen Y. (If you find this assertion correct open envelope 2.)

Choose the correct answer 1 or 2, open the correct envelope and continue in the solution according to the text in the opened envelope.

Text in envelope 1:

Your answer is correct. Continue.

Compound KXO_3 is oxidised in alkaline solution by halogen Y forming a compound $KX^{VII}O_4$ whereas halogen Y is reduced to halide KY:

$KXO_3 + 2\ KOH + Y_2 \rightarrow KXO_4 + 2\ KY + H_2O$

An aqueous solution of potassium halide KY yields with $AgNO_3$ solution a white precipitate AgY insoluble in water but readily soluble in aqueous ammonia solution.

3. Halogen Y is fluorine (envelope 3).
4. Halogen Y is chlorine (envelope 4).
5. Halogen Y is bromine (envelope 5).

Choose the correct answer 3, 4 or 5, open the corresponding envelope and carry on according to the instructions inside.

Text in envelope 2:

Your answer is incorrect. Choose envelope 1.

Text in envelope 3:

Your answer is incorrect. Choose answers 4 or 5.

Text in envelope 4:

Your answer is correct. Choose the final correct answer by indicating the correct alternative 6 or 7:

6. X = Br; $KXO_4 = KBrO_4$
7. X = I; $KXO_4 = KIO_4$

Text in envelope 5:

Your answer is incorrect. Choose answers 3 or 4.

SOLUTION

The correct answers are as follows: 1, 4, 7.

PROBLEM 2b

The reaction of permanganate ions with hydrogen peroxide in an acidic solution gives Mn(II) salt and at the same time oxygen is released:

$$2\,MnO_4^- + 1\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 3\,O_2 + 4\,H_2O$$

$$2\,MnO_4^- + 3\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 4\,O_2 + 6\,H_2O$$

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O$$

$$2\,MnO_4^- + 7\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 6\,O_2 + 10\,H_2O$$

Problems:

1. The possible ratios of the reactants in the above equations express:
   a) all equations ☐
   b) only some of the equations ☐
   c) only one equation ☐
   d) none ☐

Indicate the correct assertion by a cross in the corresponding square and explain your decision.

2. Which of the reactants is an oxidising agent and which is a reducing one?
3. How much potassium permanganate is needed to release 112 cm^3 of oxygen at STP conditions from an excess of hydrogen peroxide in acidic solution?

SOLUTION

1. Correct is **c**.

   Explanation on the basis of electron balance:

   $Mn^{VII} + 5\,e \rightarrow Mn^{II}$

   $(O_2)^{-II} - 2\,e \rightarrow O_2^0$

   $2\,Mn^{VII} + 5\,(O_2)^{-II} \rightarrow 2\,Mn^{II} + 5\,O_2^0$

2. Oxidising agent: MnO_4^- or Mn^{VII}

   Reducing agent: H_2O_2 or $(O_2)^{-II}$

3. $V(O_2) = 112\ cm^3$

$$n(O_2) = \frac{0.112\ dm^{-3}}{22.4\ dm^3\ mol^{-1}} = 0.005\ mol$$

$$n(KMnO_4) = 0.005\ mol \times \frac{2}{5} = 0.002\ mol$$

$m(KMnO_4) = 0.316\ g$

PROBLEM 3

The letters **A**, **B**, **C**, **D**, and **E** represent isomeric cyclobutane dicarboxylic acid, one of them being a racemic form.

It was shown that:

a) only compound **C** forms a cyclic anhydride easily,

b) **B** yields an cyclic anhydride only at higher temperatures,

c) of all the acids under investigation, only **A** releases carbon dioxide when heated,

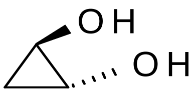
d) **D** and **E** do not change at higher temperatures,

e) 2 moles of diethyl ester of malonic acid when reacted with sodium ethoxide (EtONa), are transformed to sodium salt which by reaction with methylene iodide (CH_2I_2) yields a tetraester $C_{15}H_{24}O_8$. This new ester gives a tetraester $C_{16}H_{24}O_8$ in the reaction with 2 moles of sodium ethoxide and 1 mole of methylene iodide. The last mentioned tetraester is transformed by alkaline hydrolysis and subsequent acidification to a tetracarboxylic acid which when heated, gives a mixture of **B** and **E**.

Problems:

3.1 Give formulas corresponding to the letters **A**, **B**, **C**, **D**, and **E**. Mark the group which is above the plane of the cycle ▬ , that under the plane with ⋯

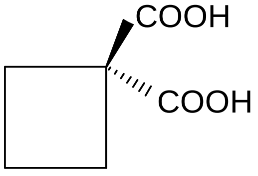
For example:



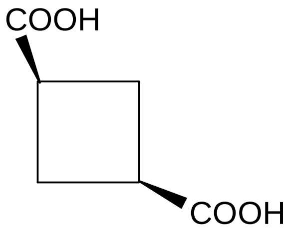
3.2 Express processes a), b), and c) by chemical equations.

SOLUTION

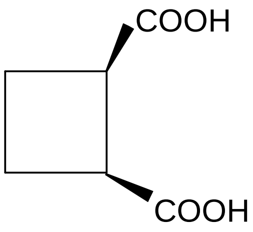
3.1



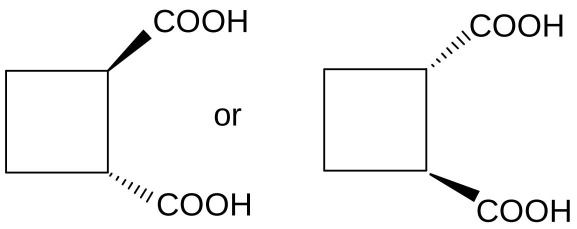
A



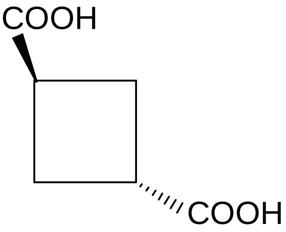
B



C

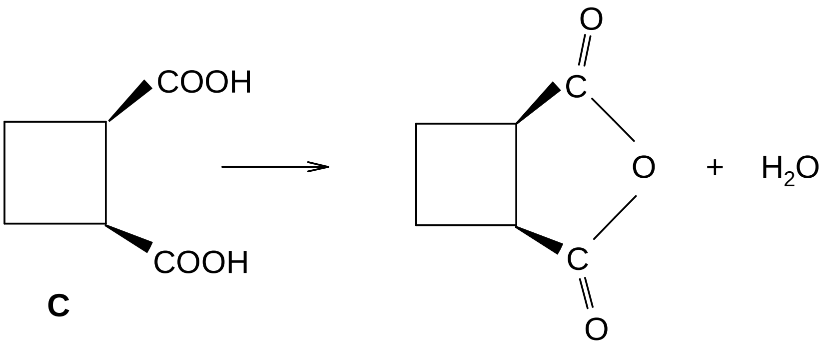

COOH
or
COOH
COOH
COOH

D


COOH
COOH

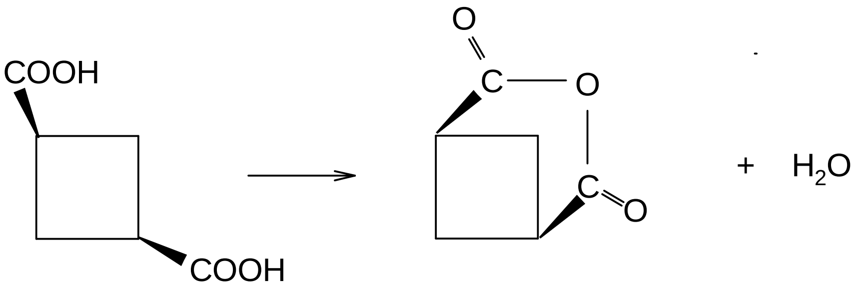
E

3.2 a)


COOH
COOH
O
C
O
C
O
+ H$_2$O

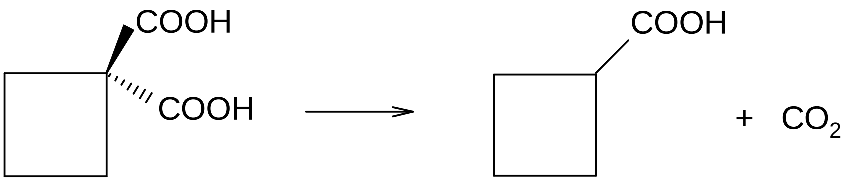
C

b)


COOH
COOH
O
C
O
C
O
+ H$_2$O

B

c)


COOH
COOH
COOH
+ CO$_2$

A

PROBLEM 4a

Note: The International Jury did not choose Task 4a for the competition but the alternative PROBLEM 4b.

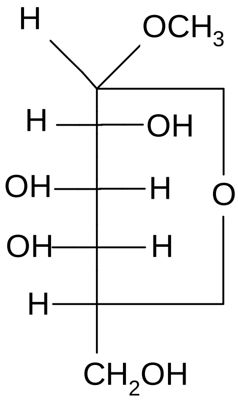
Compounds **A** and **B**, having the same summary formula $C_7H_{14}O_6$ but different physical properties (for example melting point and specific optical rotation), belong to the group of saccharides containing six-member heterocycles. When 1 % solution of sulphuric acid is added to compound A and B respectively, the same compound C containing 40.0 % C and 6.71 % H is obtained at boiling. After reducing compound C (for example catalytically with hydrogen or with hydride $Na[BH_4]$) a crystalline product D was isolated which did not reduce Fehling's reagent and showed no optical activity. Compound C was oxidised with a mild oxidising agent (e. g. with a cold sodium hypobromite solution) yielding a salt of polyhydroxy monocarboxylic acid of D-configuration.

Problems:

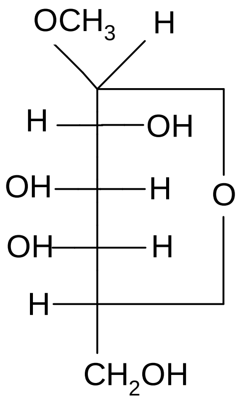
1. Suggest the structure of the compounds A, B, C, and D.
2. If you do not find the task to be unambiguous, explain why.

SOLUTION

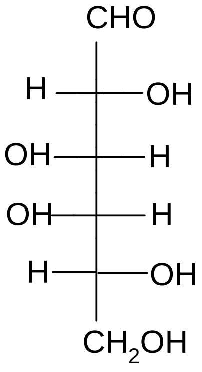
1.



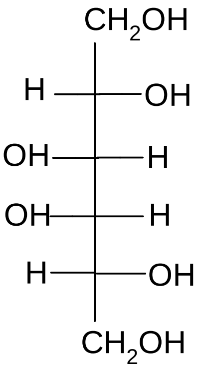
A (or **B**)



B (or **A**)



C



D

2. There is another similar solution in the D-allose series.

PROBLEM 4b

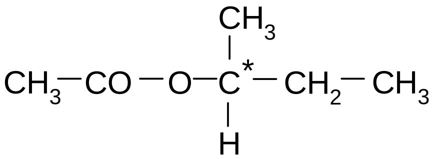
An optically active ester (11.6 g) having the summary formula $C_6H_{12}O_2$, was hydrolysed by heating with an excess of aqueous sodium hydroxide solution. After terminating the hydrolysis the alkaline reaction mixture was several times extracted with ether. The aqueous solution was not optically active. The united ether extracts were dried with anhydrous magnesium sulphate. The ether solution was filtrated, ether was distilled off from it and the residue was redistilled. 7.4 g (100 %) of a liquid boiling at 100 ℃ was obtained.

Problems:

1. Write the structural formula of the ester.
2. What would be the structure of an ester with identical summary formula, i. e. $C_6H_{12}O_2$, if the aqueous solution after the alkaline hydrolysis obtained in the above mentioned way, were optically active?
3. Write down equations for the alkaline hydrolysis of both esters with sodium hydroxide solution.

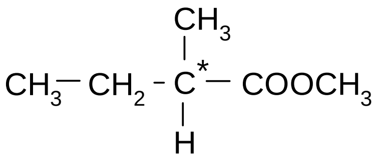
SOLUTION

1.



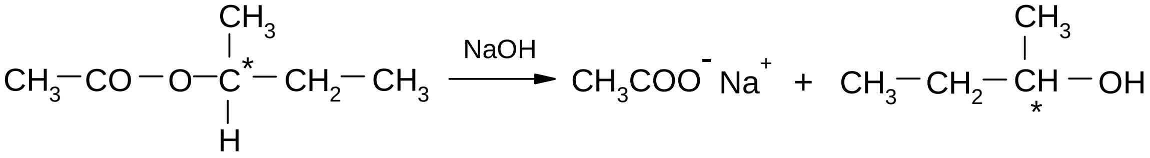
$$CH_3-CO-O-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C^*}}-CH_2-CH_3$$

2.

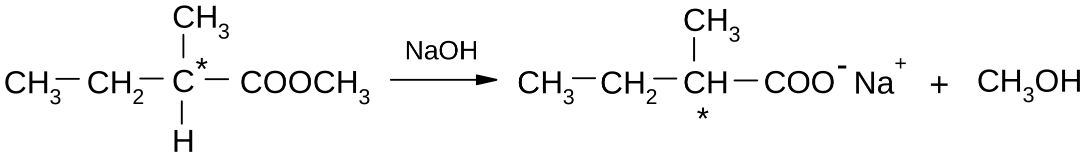


$$CH_3-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C^*}}-COOCH_3$$

3.



$$CH_3-CO-O-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}}-CH_2-CH_3 \xrightarrow{NaOH} CH_3COO^- \, Na^+ + CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{*}{CH}}-OH$$



$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}}-COOCH_3 \xrightarrow{NaOH} CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{*}{CH}}-COO^- \, Na^+ + CH_3OH$$

PROBLEM 5

Two copper(I) salts of the organic acids HA and HB, slightly soluble in water, form a saturated solution in buffer of a given pH.

Problems:

5.1 What will be the concentration of Cu^+ cations in the solution if the solubility products of the two salts are K_s(CuA) and K_s(CuB) and the ionisation constants of the acids are K_a(HA) and K_a(HB)?

SOLUTION

5.1 Equations for the total amounts of substances of the particles A, B, and Cu are as follows:

$a = n(A^-) + n(HA) + n(CuA)$

$b = n(B^-) + n(HB) + n(CuB)$

$m = n(Cu^+) + n(CuA) + n(CuB)$

The amounts of precipitates are eliminated from the equations:

$a + b - m = n(A^-) + n(HA) + n(B^-) + n(HB) - n(Cu^+) = 0$

because, when forming a system of both solid salts, the total number of particles A and B (a + b) must be equal to the total number of cations Cu^+, i. e. to the value of m. When the amounts of substances are divided by the volume of the solution, we get concentrations, and thus:

$$[A^-] + [HA] + [B^-] + [HB] = [Cu^+] \qquad (1)$$

$$K_s(CuA) = [Cu^+][A^-] \quad \Rightarrow \quad [A^-] = \frac{K_s(CuA)}{[Cu^+]} \qquad (2)$$

$$K_s(CuB) = [Cu^+][B^-] \quad \Rightarrow \quad [B^-] = \frac{K_s(CuB)}{[Cu^+]} \qquad (3)$$

$$K_a(HA) = \frac{[H^+][A^-]}{[HA]} \quad \Rightarrow \quad [HA] = \frac{[H^+][A^-]}{K_a(HA)} \qquad (4)$$

$$K_a(\text{HB}) = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} \quad \Rightarrow \; [\text{HB}] = \frac{[\text{H}^+][\text{B}^-]}{K_a(\text{HB})} \qquad (5)$$

By substituting (4) and (5) into (1):

$$[\text{Cu}^+] = [\text{A}^-]\left(1 + \frac{[\text{H}^+]}{K_\text{a}(\text{HA})}\right) + [\text{B}^-]\left(1 + \frac{[\text{H}^+]}{K_\text{a}(\text{HB})}\right) \qquad (6)$$

By substituting (2) and (3) into (6):

$$[\text{Cu}^+] = \frac{K_\text{s}(\text{CuA})}{[\text{Cu}^+]}\left(1 + \frac{[\text{H}^+]}{K_\text{a}(\text{HA})}\right) + \frac{K_\text{s}(\text{CuB})}{[\text{Cu}^+]}\left(1 + \frac{[\text{H}^+]}{K_\text{a}(\text{HB})}\right) \qquad (7)$$

$$[\text{Cu}^+] = \sqrt{K_\text{s}(\text{CuA})\left(1 + \frac{[\text{H}^+]}{K_\text{a}(\text{HA})}\right) + K_\text{s}(\text{CuB})\left(1 + \frac{[\text{H}^+]}{K_\text{a}(\text{HB})}\right)}$$

PROBLEM 6

Amino acids can be determined by measuring the volume of nitrogen released in their reaction with nitrous acid (Van Slyke's method), for example:

$CH_3CH(NH_2)COOH + HNO_2 \rightarrow CH_3CH(OH)COOH + N_2 + H_2O$

Another method consists of the reaction of amino acids with a volumetric solution of perchloric acid, for example:

$CH_3CH(NH_2)COOH + HClO_4 \rightarrow CH_3CH(N^+H_3)COOH + ClO_4^-$

The excess of the perchloric acid is determined then by titration with a volumetric solution of sodium acetate (carried out in a non-aqueous solution).

50.0 cm^3 of a 0.100-normal solution of perchloric acid were added to a sample of glycine in glacial acetic acid. The excess of the perchloric acid was determined after the reaction by titration with 0.150-normal volumetric solution of sodium acetate. The consumption was 16.0 cm^3.

Problem:

6.1 What would be the volume of the nitrogen released at a pressure of 102 658 Pa and a temperature of 20 °C when assumed that the same quantity of sample were analysed by the Van Slyke's method?

SOLUTION

6.1 $n(HClO_4) = V\,c = 0.0500\ dm^3 \times 0.100\ mol\ dm^{-3} = 0.00500\ mol$

$n(NaAc) = 0.0160\ dm^3 \times 0.150\ mol\ dm^{-3} = 0.00240\ mol$

Consumed in the reaction:

$n(HClO_4) = (0.00500 - 0.00240)\ mol = 0.00260\ mol$

$V(HClO_4) = 0.0260\ dm^3$

Since:

$n(HClO_4) = n(glycine) = n(N_2) = 0.0260\ mol$

then:

$$V(N_2) = \frac{n\,R\,T}{p} = \frac{0.0260\ mol \times 8.314\ J mol^{-1} K^{-1} \times 293.1\ K}{102.658\ kPa} = 0.617\ dm^3$$

PROBLEM 7

Photosynthesis by be summarised by the overall equation:

$$CO_2\,(g) + H_2O\,(l) \xrightarrow[\text{chlorophyll}]{\text{light}} C_6H_{12}\,(s) + 6\,O_2\,(g)$$

for which values of Δ*H* and Δ*S* at 25 °C are as follows:

$\Delta H = 2.816 \times 10^6$ J, $\Delta S = -182$ J K^{-1} or

$\Delta H = 2.816 \times 10^6$ J mol^{-1}, $\Delta S = -182$ J K^{-1} mol^{-1} if Δ*H* and Δ*S* values are related to one mole of reaction changes.

Imagine that there have been devised electrodes that would allow selective reduction of oxygen to water and oxidation of glucose to carbon dioxide in a galvanic cell, i. e a reverse process when compared with that of the photosynthetic reaction.

Problems:

7.1 What will be the electromotive force of the cell in which light energy would be transformed to electric energy by means of the photosynthetic reaction?

Note: In the envelope you can find the relation between the electromotive force and the change of free enthalpy of the reaction. (Attention: If you open the envelope you lose some points.)

7.2 In case we would want to quantify the symbol "light" in the equation of photosynthesis, we would ask: how many moles of photons with wavelength for example 500 nm take part in the above reaction? Calculate.

7.3 Calculate, what would be the electric power of a square swimming pool with a side of 10 m containing green algae capable of the photosynthetic reaction if under average illumination a current of 1 mA can be expected from the area of 1 cm^2.

SOLUTION

7.1 Two alternative solutions:

a) By means of quantities related to one mole of reaction changes.	b) By means of quantities related to the given reaction.
For the reaction taking place in the cell it would correspond: $\Delta G = -2.87 \times 10^6$ J mol^{-1}	For the reaction taking place in the cell it would correspond: $\Delta G = -2.87 \times 10^6$ J

Relation between the electromotive force and the change of free enthalpy of the reaction taking place in a cell:

$$-\Delta G = n\,F\,E$$

where n is so-called charge number	where n is the number of moles of charges which passed through the electrode during the reaction.

In our case, n has the value equal to 24 since one molecule of oxygen is reduced according to the equation:

$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$

F (Faraday's constant) = 96 487 C mol^{-1}

Since one voltcoulomb is one joule, then:

$E = \dfrac{-(-2.87\times10^6)\ \text{V C mol}^{-1}}{24 \times 96\,487\ \text{C mol}^{-1}} = 1.24\ \text{V}$	$E = \dfrac{-(-2.87\times10^6)\ \text{V C}}{24\ \text{mol} \times 96\,487\ \text{C mol}^{-1}} = 1.24\ \text{V}$

7.2 Energy of absorbed photons is the only source of energy which enables the course of photosynthesis, and therefore, the number of absorbed photons x multiplied by their energy must be equal to the increase of energy in the system, i. e. to the value of 2.87×10^6 J. Thus:

$$\text{x}\,h\,\nu\,N_A = \text{x}\,h\,\frac{c}{\lambda}\,N_A = 2.87 \times 10^6\ \text{J}$$

$$\text{x} = \frac{2.87 \times 10^6\ \text{J} \times \lambda}{h\,c\,N_A} =$$

$$= \frac{2.87 \times 10^6\ \text{J} \times 500.10^{-9}\ \text{m}}{6.6256.10^{-34}\ \text{J s} \times 2.9979.10^{8}\ \text{m s}^{-1} \times 6.022.10^{23}\ \text{mol}^{-1}} =$$

= 11.99 ≈ 12 mol of photons

7.3 The area of the swimming pool is 100 m^2. Current density at a voltage of 1.24 V is equal to 1. 10^4 mA m^{-2} = 10 A m^{-2}.

The total electric power :

$1.24 \text{ V} \times 10 \text{ A m}^{-2} \times 100 \text{ m}^2 = 1.24 \text{ kW}$

PROBLEM 8a

Note: The International Jury did not choose Task 8a for the 9th IChO but the alternative Task 8b.

Due to the lack of other methods in the middle of the 19th century a chemist determining the molar mass of a new element **X** chose the following procedure:

He succeeded in preparing four compounds **A**, **B**, **C**, and **D** containing the element **X** and determined its content (in mass %) in each of the compounds. At 250 °C all four compounds were in gaseous state. They were individually transferred into previously evacuated flasks until the pressure reached the value of 1.013 .10^5 Pa and then the flasks were weighed. After subtracting the weight of the empty flask, the mass of the gas inside was determined. This procedure was repeated with nitrogen. Thus the following Table of data was obtained:

Gas	Total mass of gas	Content of element X in gas (mass %)
N_2	0.652 g	0
A	0.849 g	97.3
B	2.398 g	68.9
C	4.851 g	85.1
D	3.583 g	92.2

Problem:

8.1 Determine the probable molar mass of element **X**.

SOLUTION

8.1 $$n(N_2) = \frac{m(N_2)}{M(N_2)} = \frac{0.652\ \text{g}}{28\ \text{g mol}^{-1}} = 0.0233\ \text{mol}$$

At a temperature of 250 °C all the substances **A**, **B**, **C**, and **D** are considered to behave as ideal gases and according to Avogadro's law:

$n(N_2) = n(\mathbf{A}) = n(\mathbf{B}) = n(\mathbf{C}) = n(\mathbf{D})$

$$M(\mathbf{A}) = \frac{m(\mathbf{A})}{n(\mathbf{A})}$$

$$M(\mathbf{B}) = \frac{m(\mathbf{B})}{n(\mathbf{B})}$$

$$M(\mathbf{C}) = \frac{m(\mathbf{C})}{n(\mathbf{C})}$$

$$M(\mathbf{D}) = \frac{m(\mathbf{D})}{n(\mathbf{D})}$$

The mass of element **X** in one mole of **A**, **B**, **C** or **D**:

A: $M(\mathbf{A}) \times 0.973 = 35.45$ g mol^{-1}

B: $M(\mathbf{B}) \times 0.689 = 70.91$ g mol^{-1}

C: $M(\mathbf{C}) \times 0.851 = 177.17$ g mol^{-1}

D: $M(\mathbf{D}) \times 0.922 = 141.78$ g mol^{-1}

Because in one molecule of a compound there must be at least one atom **X** or its integer multiple, we must calculate the highest common measure of the molar masses obtained. It is in our case equal to 35.45 g mol^{-1} in average which can be considered as the probable molar mass of element **X**. It is only the most probable value because its integer fraction cannot be excluded.

PROBLEM 8b

Among other factors, deterioration of the environment is manifested also by air pollution with carbon monoxide. Its most powerful source are combustion engines. The toxicity of carbon monoxide is caused by the fact that it forms with the blood dye - haemoglobin (Hb), the compound carbonyl haemoglobin (HbCO):

$\text{Hb} + \text{CO} \rightarrow \text{HbCO}$

The chemical bond in carbonyl haemoglobin is about 200 times stronger than that in oxyhaemoglobin (HbO_2) originating under common conditions. Consequently, haemoglobin cannot be used in oxygen transfer. The lack of oxygen starts to be felt from 50 ppm carbon monoxide in the air, i. e. 10 % carbonyl haemoglobin in blood.

Air oxygen dissolves in blood in the lungs and its concentration under common conditions is kept at 1.6×10^{-6} mol dm^{-3} by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to 8×10^{-6} mol dm^{-3}

Problems:

8.1 Calculate the rate of oxyhaemoglobin formation if the rate constant is $k = 2.1 \times 10^6$ dm^3 mol^{-1} s^{-1} (at 37 °C – normal body temperature).

8.2 In some cases (carbon monoxide poisoning) an increase of the rate of oxyhaemoglobin formation up to 1.1×10^{-4} mol dm^{-3} s^{-1} is needed.

a) Calculate the required concentration of oxygen assuming that the concentration of haemoglobin in blood is constant.

b) Suggest of practical solution on the assumption that the concentration of oxygen in blood is proportional to the pressure of oxygen entering the lungs.

SOLUTION

8.1 $v = k\,[\text{Hb}][O_2]$

$k = 2.1 \times 10^6$ dm^3 mol^{-1} s^{-1}

$[\text{Hb}] = 8 \times 10^{-6}$ mol dm^{-3}

$[O_2] = 1.6 \times 10^{-6}$ mol dm^{-3}

$\underline{v = 2.688 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}}$

Because 1 mole of oxygen (O_2) is needed to form 1 mole of oxyhaemoglobin, the rate of oxygen consumption is the same as the of oxyhaemoglobin formation.

8.2 $[O_2] = \dfrac{v}{k\ [Hb]}$

$v = 1.1 \times 10^{-4}$ mol dm^{-3} s^{-1}

$k = 2.1 \times 10^{6}$ dm^{3} mol^{-1} s^{-1}

$[Hb] = 8 \times 10^{-6}$ mol dm^{-3}

$\underline{[O_2] = 6.5 \times 10^{-6} \text{ mol dm}^{-3}}$

The oxygen concentration must increase up to 6.5×10^{-6} mol dm^{-3}. Oxygen concentration can be affected by elevation of air pressure only partially. The fourfold increase of oxygen concentration would demand an increase of the air pressure four times in comparison with the normal value. This pressure would be harmful for living organisms and therefore, air enriched with oxygen is breathed.

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

You will follow the concentration change of one of the reactants by the method of comparative visual colorimetry. From data obtained experimentally plot graphically the change of the reactant concentration in dependence on time.

Procedure:

1. *Making of the comparative colorimetric scale of bromine solution*

Measure with a syringe into 10 identical test-tubes the following quantities of bromine water (0.01-molar): into the first one – 10.0 cm^3; 2nd – 9.0 cm^3; 3rd – 8.0 cm^3, ... 9th – 2.0 cm^3; into the tenth one – 1.0 cm^3. Then add to all the test-tubes (except the first one) distilled water to reach a total volume of 10.0 cm^3 in each. Seal the test-tubes with stoppers and mix the solutions. Put the test-tubes in a stand with a white background. Finally calculate the concentration (in mol dm^{-3}) of bromine in the solutions in all test-tubes.

2. *Reaction of bromine solution with formic acid*

Carry out the reaction by mixing 100.0 cm^3 of bromine solution with 1.0 cm^3 of 1.00-molar solution of formic acid. Immediately after mixing transfer 10.0 cm^3 of the resulting solution to the test-tube identical with that used for colorimetric scale. By comparing the colour shade of the reaction mixture (in one-minute intervals) with that of the solutions in the scale, investigate changes of bromine concentration in dependence on time.

Put the data in a table containing time (t) and concentration of Br_2.

Task:

Plot the bromine concentration in dependence on time a read the half-time of the reaction from the diagram.

Questions:

1.1 Write the equation for the reaction of bromine with formic acid assuming that the reactants are in stoichiometric amounts.

1.2 In analytical chemistry a volumetric solution of bromine can be prepared by dissolving a mixture of bromate and bromide in acid medium. Explain this mode of preparation by means of a chemical equation in ionic form.

SOLUTION

Questions:

1.1 $HCOOH\ (aq) + Br_2\ (aq) \rightarrow CO_2\ (g) + 2\ H^+\ (aq) + 2\ Br^-\ (aq)$

1.2 $BrO_3^- + 5\ Br^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$

PROBLEM 2 (practical)

By thermometric titration of a hypochlorite solution with a solution of propanone you will find the equivalent amounts of the reactants and consequently, the reaction products.

Procedure:

For the reaction of a hypochlorite solution with a propanone use solutions tempered at laboratory temperature (check). Put 100,0 cm^3 of a hypochlorite solution into a thermobeaker, insert a thermometer and keep adding a 4-molar solution of propanone in 1,0 cm^3 portions from burette, stirring the reaction mixture continuously by means of the thermometer (carefully, do not break!). Stir the reaction mixture thoroughly after each addition and read the highest temperature reached. Keep on adding the propanone solution as long as the temperature rises. Then add three more portions and finish the experiment. Keep the reaction mixture for possible later use.

Problems:

2.1 Draw a titration curve from the data of the temperature changes and consumption of propanone solution. Read the end point of the titration from the curve. Express the equivalent amounts of the reactants in moles.

2.2 Write equation for the chemical reaction and name the product that is formed.

2.3 Suggest a calculation for the approximate value of the reaction heat from the data obtained.

2.4 Consider the procedure of isolation of the product from the reaction mixture and give the method of its identification.

2.5 The exact concentration of a hypochlorite solution can also by determined by measuring the volume of oxygen released after catalytic decomposition of hypochlorite. Illustrate the principle of this method by means of a chemical equation and show schematically the procedure for the calculation.

SOLUTION

2.2 $CH_3COCH_3 + 3\ ClO^- \rightarrow \underset{\text{chloroform}}{CHCl_3} + 2\ OH^- + CH_3COO^-$

2.3 Calculation of heat evolved in the course of the reaction:

$Q = m\,c\,\Delta t$

Q – reaction heat,

m – mass of the solution,

c – specific heat capacity of the solutions taking part in the reaction,

Δt – temperature difference (elevation of temperature)

On the basis of the data obtained in the task, it is possible to calculate Q value per one mole of reactant.

2.4 The mixture contains:

reactants – (excess of about 3 cm^3 of the 4-molar propanone solution),

products – $CHCl_3$, OH^-, CH_3COO^-.

Acetone and chloroform are separated from other substances in the aqueous solution by means of a separatory funnel and a subsequent distillation.

Identification of chloroform: smell, density.

2.5 $2\ ClO^- \rightarrow O_2$

$2\ \text{mol} \rightarrow 1\ \text{mol} = 22.4\ \text{dm}^3$

PROBLEM 3 (practical)

If a known excess of hydroxide solution with a known concentration is added to a weighed sample of ammonium salt and the liberated ammonia is removed by boiling, it is possible to determine the unreacted quantity of hydroxide by titration with a volumetric solution of an acid.

Procedure:

Three samples of an ammonium salt, weighed with accuracy of 0.001 g, are at your disposal. Introduce each of them into a 250 cm^3 Erlenmeyer flask. Add 50.0 cm^3 of a 0.2-normal sodium hydroxide solution to each sample. Put several boiling stones into each mixture and heat the flasks slowly on a small flame till there is no more ammonia in the liberating vapours. After expelling ammonia, cool the solution to the laboratory temperature, add 2 or 3 drops of indicator solution (Bromothymol blue) and titrate with a 0,2-normal volumetric solution of oxalic acid to the first lasting yellow colour of the solution.

Problems:

3.1 Calculate the molar mass of ammonium salt from the experimental data.

3.2 The sample is a salt of a monobasic inorganic acid. Consider which one.

3.3 Calculate the absolute and relative error of your determination.

3.4 Give reactions by means of which ions of the salt can be proved in the solution.

10th

International Chemistry Olympiad

5 theoretical problems
2 practical problems

THE TENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
3–13 JULY 1978, TORUN, POLAND

THEORETICAL PROBLEMS

PROBLEM 1

a) A chromium ore which does not contain water, consists of: $Fe(CrO_2)_2$, $Mg(CrO_2)_2$, $MgCO_3$, and $CaSiO_3$.

b) It was found by analysis the ore contains 45.6 % of Cr_2O_3, 7.98 % of Fe_2O_3, and 16.12 % of MgO.

c) When the ore was treated with a concentrated hydrochloric acid, chromium compounds being present in the ore did not react with the acid.

d) When the reaction was finished, the ore was thoroughly washed with water (till the reaction with Cl^- was negative) and the solid residue was dried to a constant mass.

Problems:

1.1 Write stoichiometric and ionic equations for the reactions taking place when the ore is treated with the hydrochloric acid as given in c).

1.2 Calculate:

- the content of the compounds (in mass %) present in the ore,
- amounts of substances of the compounds present in the ore.

1.3 Calculate the content of Cr_2O_3 (in mass %) in the dried residue obtained according to d).

1.4 A glass tube was filled with a sufficient amount of granulated CaO, the total mass of the filled tube having been 412.02 g. A gas formed by the reaction as given in c), was dried and then transmitted through the glass tube. Calculate the mass of the glass tube with its filling after the reaction was finished.

Relative atomic masses: $A_r(Cr) = 52.01$; $A_r(Fe) = 55.85$; $A_r(Mg) = 24.32$; $A_r(Ca) = 40.08$;
$A_r(Si) = 28.09$; $A_r(C) = 12.01$; $A_r(O) = 16.00$.

SOLUTION

1.1 $MgCO_3 + 2\,HCl \rightarrow MgCl_2 + CO_2 + H_2O$

$MgCO_3 + 2\,H^+ \rightarrow Mg^{2+} + CO_2 + H_2O$

$CaSiO_3 + 2\,HCl \rightarrow CaCl_2 + SiO_2 + H_2O$

$CaSiO_3 + 2\,H^+ \rightarrow Ca^{2+} + SiO_2 + H_2O$

1.2 The total amount of iron is in the form of $Fe(CrO_2)_2$:

Since:

$$Fe_2O_3 \triangleq 2\ Fe(CrO_2)_2$$

$M_r(Fe_2O_3) = 159.70$

$M_r(Fe(CrO_2)_2) = 223.87$ % $Fe_2O_3 = 7.98$

$$\textbf{\% Fe(CrO}_\mathbf{2}\mathbf{)}_\mathbf{2} = \frac{2 \times 223.87}{159.70} \times 7.98 = \mathbf{22.37}$$

The difference between the total amount of Cr_2O_3 and that being contained in $Fe(CrO_2)_2$ corresponds to the amount of Cr_2O_3, having been in the form of $Mg(CrO_2)_2$.

% Cr_2O_3 in $Fe(CrO_2)_2$:

$$\begin{array}{lcc} & Fe(CrO_2)_2 \triangleq & Cr_2O_3 \\ M_r: & 223.87 & 152.02 \end{array}$$

$$\textbf{\% Cr}_\mathbf{2}\textbf{O}_\mathbf{3} = \frac{152.02}{223.87} \times 22.37 = \mathbf{15.19}$$

% Cr_2O_3 in $Mg(CrO_2)_2$: 45.5 – 15.19 = 30.41

Content of $Mg(CrO_2)_2$:

$$\begin{array}{lcc} & Cr_2O_3 \triangleq & Mg(CrO_2)_2 \\ M_r: & 152.02 & 192.34 \end{array}$$

$$\textbf{\% Mg(CrO}_\mathbf{2}\mathbf{)}_\mathbf{2} = \frac{192.34}{152.02} \times 30.41 = \mathbf{38.47}$$

The difference between the total amount of MgO in the ore and that corresponding to $Mg(CrO_2)_2$, is contained in $MgCO_3$. % MgO and % $MgCO_3$ can be calculated analogously as it is given above.

$$\begin{array}{lcc} & Mg(CrO_2)_2 \triangleq & MgO \\ M_r: & 192.34 & 40.32 \end{array}$$

$$\textbf{\% MgO} = \frac{40.32}{192.34} \times 38.47 = \textbf{8.06}$$

$$\begin{array}{lcc} & MgO \triangleq & MgCO_3 \\ M_r: & 40.32 & 84.32 \end{array}$$

$$\textbf{\% MgCO}_\textbf{3} = \frac{84.32}{40.32} \times 8.06 = \textbf{16.86}$$

Content of $CaSiO_3$ is obtained as complementary value to 100 %.

% $CaSiO_3$ = 100 – (22.37 + 38.47 + 16.86) = **22.30**

One kilogram of the ore contains:

223.7 g of $Fe(CrO_2)_2 \triangleq$ 1 mol

384.7 g of $Mg(CrO_2)_2 \triangleq$ 2 mol

168.6 g of $MgCO_3 \triangleq$ 2 mol

223.0 g of $CaSiO_3 \triangleq$ 2 mol

1.3 In order to simplify the problem we can assume that the hydrochloric acid reacts with 1 kg of the ore, i. e. with 168.6 g of $MgCO_3$ and with that CaO which is contained in 223.0 g $CaSiO_3$, i. e. with 107.65 of CaO.

Thus, 276.25 g of the ore (168.6 g + 107.65 g) reacted while 723.75 g remain unreacted.

One kilogram of the ore contains 456 g of Cr_2O_3 (45.6 %) and the same amount remains in the unreacted part that represents:

$$\textbf{\% Cr}_\textbf{2}\textbf{O}_\textbf{3} = \frac{456}{723.75} \times 100 = \textbf{63.0}$$

1.4 The mass of the filling in the tube is increased by the mass of CO_2 formed by decomposition of $MgCO_3$ with hydrochloric acid. From 168.6 g of $MgCO_3$ 87.98 g of CO_2 are formed and thus, the mass of the tube after reaction is 500 g.

PROBLEM 2

A sample of water under investigation had 10° of temporary hardness and 10° of permanent hardness. Hardness of the water was caused by cations Fe^{2+} and Ca^{2+} only.

A volume of 10.00 dm^3 of the water was at disposal. From this volume 100.00 cm^3 were taken for further procedure. The water was oxidised with a H_2O_2 solution and then precipitated with an aqueous ammonia solution. A brown precipitate was dried and after an appropriate heating 0.01432 g of an anhydrous product was obtained.

Problems:

2.1 Calculate the molar ratio of Fe^{2+} : Ca^{2+} in the water under investigation.

2.2 In another experiment, 10.00 dm^3 of the water was used again. The temporary hardness caused by cations Ca^{2+} was removed first and the permanent hardness caused by cations Fe^{2+} was removed by addition of Na_3PO_4. Calculate the mass of the precipitate (in its anhydrous form) on the assumption that only one half of cations Fe^{2+} was oxidised to Fe^{3+} in 10.00 dm^3 of the water analysed. Calculation should be made with an accuracy of one hundredth. Give the molar ratio in integers.

1° of hardness = 10 mg CaO in 1 dm^3 of water.

Relative atomic masses:

$A_r(Ca) = 40.08$; $A_r(Fe) = 55.85$; $A_r(C) = 12.01$;

$A_r(H) = 1.01$; $A_r(P) = 31.00$; $A_r(O) = 16.00$.

SOLUTION

2.1 Anhydrous product: Fe_2O_3

$m(Fe_2O_3) = 0.01432$ g from 100 cm^3 of water, i. e. 1.432 g from 10 dm^3

1 mol Fe_2O_3 $\Leftrightarrow$ 2 mol FeO

$$n(Fe_2O_3) = \frac{1.432\text{ g}}{159.7\text{ g mol}^{-1}} \approx 0.009\text{ mol}$$

$m(FeO) = n\,M = 2 \times 0.009\text{ mol} \times 71.85\text{ g mol}^{-1} \approx 1.293$ g

1° of hardness = 10 mg CaO / dm^3 of water

$$1^\circ \text{ of hardness} = \frac{M(\text{FeO})}{M(\text{CaO})} \times 10 \text{ mg} = 12.81 \text{ mg FeO/dm3 of water}$$

$$\frac{1.293 \text{ g FeO}}{0.1281 \text{ g FeO}} \approx 10^\circ \text{ of hardness}$$

Since the water has totally 20° of hardness, and 10 ° of hardness fall on FeO, the other 10° of hardness are attributed to CaO which corresponds to 1 g of CaO in 10 dm^3 of the water.

Molar ratio:

$$n(\text{FeO}) : n(\text{CaO}) = \frac{m(\text{FeO})}{M(\text{FeO})} : \frac{m(\text{CaO})}{M(\text{CaO})} = \frac{1.289 \text{ g}}{71.85 \text{ g mol}^{-1}} : \frac{1 \text{ g}}{56.08 \text{ g mol}^{-1}} = 1 : 1$$

2.2 A volume of 10.00 dm^3 of the water contains so much iron that corresponds to 1.293 g of FeO. 50 % of iron (0.6445 g of FeO) were oxidised to Fe(III), and therefore $Fe_3(PO_4)_2$ as well as $FePO_4$ are formed at the same time.

3 mol FeO . . . . . . 1 mol $Fe_3(PO_4)_2$

215.55 g . . . . . . 357.55 g

0.6445 g . . . . . . $\underline{1.0699 \text{ g } Fe_3(PO_4)_2}$

1 mol FeO . . . . . . 1 mol $FePO_4$

71.85 g . . . . . . 150.85 g

0.6445 g . . . . . . $\underline{1.3542 \text{ g } FePO_4}$

Mass of the precipitate: 1.0699 g + 1.3542 g = 2.4241 g

PROBLEM 3

Chromium plating is usually made by electrolysis in a solution of chromic acid. The chromium plated objects form the cathode. The anode is an alloy that is inert under given conditions, i. e. it does not react either chemically or electrochemically.

An electrolytic cell was filled with 100.0 dm^3 of an aqueous solution which contained 0.230 kg of chromium acid anhydride in 1 dm^3 of the solution.

In electrolysis a current of 1500 A passed through the electrolyte for 10.0 hours. After electrolysis an increase of the mass of the cathode was 0.679 kg.

The ratio of gas volumes

$$\frac{V_C}{V_A} = 1.603$$

where V_C is a volume of gases evolved at the cathode, whereas that marked as V_A is the volume of gases which are evolved at the anode. Both volumes were measured at the same conditions.

Problems

3.1 What part of the total charge (in %) was used for a deposition of 0.679 kg of chromium?

3.2 Calculate:

a) the volume ratio of both gases (at STP) which are evolved as by-products at the cathode and anode,

b) current efficiency for the corresponding reactions taking place separately at the cathode and anode when the gases are evolved.

If you find any disproportion between the data calculated and those given in the task, try to explain what process would take place in the electrolytic cell which has not been considered till now.

Write the corresponding summary equation for the reactions at electrodes and correct your previous calculations if possible.

SOLUTION

3.1 The total electric charge passed through the electrolyte:

$$Q = \frac{1500 \times 3600 \times 10}{96500} = 559.6\ \text{F}$$

Reaction at the cathode:

$Cr^{VI} + 6\ e^- \rightarrow Cr^0$ or

$CrO_4^{2-} + 8\ H^+ + 6\ e^- \rightarrow Cr + 4\ H_2O$

Deposited:

$$\frac{679\ \text{g}}{51.996\ \text{g mol}^{-1}} = 13.06\ \text{mol of chromium}$$

A charge of 78.36 F was required to deposit the above chromium.

Current efficiency:

$$\frac{78.36\ \text{F}}{559.6\ \text{F}} \times 100 = 14.0\ \%$$

3.2 The simplest assumption: Only hydrogen is evolved at the cathode and at the same time oxygen at the anode. On this assumption the amounts of substances of the evolved oxygen and hydrogen are as follows:

$$n(H_2) = \frac{559.6 \times 0.86}{2} = 240.63\ \text{mol}$$

$$n(O_2) = \frac{559.6}{4} = 139.9\ \text{mol}$$

The molar ratio is:

$$\frac{n(H_2)}{n(O_2)} = \frac{V(H_2)}{V(O_2)} = \frac{240.63\ \text{mol}}{139.9\ \text{mol}} = 1.720$$

This value is different from that given in the task. Thus, beyond the mentioned reactions also other processes take place at the electrodes. The current efficiency may be calculated from the volume ratio of gases evolved, without making any investigation of what kind the processes are.

Balance of the processes:

The main process: $CrO_3 \rightarrow Cr + 3/2\ O_2$

cathode anode

$\eta_1 = 14.0\ \%$

The by process: (electrolysis of water)

$$2\,H_2O \rightarrow \underset{\text{cathode}}{2\,H_2} + \underset{\text{anode}}{O_2}$$

$$\eta_2 = ?$$

The amount of substance of the hydrogen evolved at the cathode is equal to:

$$n(H_2) = \frac{Q\,.\,\eta_2}{2}$$

The amount of substance of the oxygen evolved at the anode is equal to:

$$n(O_2) = \frac{Q\,.\,(\eta_1 + \eta_2)}{4}$$

According to the data given in the task:

$$\frac{V(H_2)}{V(O_2)} = \frac{n(H_2)}{n(O_2)} = \frac{\dfrac{Q\,.\,\eta_2}{2}}{\dfrac{Q\,.\,(\eta_1 + \eta_2)}{4}} = 1.603$$

In solving the equation for η_2 we get a value:

$\eta_2 = 0.565$ (56.5 %)

Volumes of the hydrogen and oxygen evolved:

$$n(H_2) = \frac{559.6 \times 0.565}{2} = 158.1\,\text{mol}$$

$V(H_2) = 22.41\ \text{dm}^3\ \text{mol}^{-1} \times 158.1\ \text{mol} = 3543\ \text{dm}^3$

$$n(O_2) = \frac{559.6 \times (0.140 + 0.565)}{4} = 98.6\ \text{mol}$$

$V(O_2) = 22.41\ \text{dm}^3\ \text{mol}^{-1} \times 98.6\ \text{mol} = 2210\ \text{dm}^3$

The current efficiency when the hydrogen is evolved at the cathode is equal to 56.5 %. The current efficiency when the oxygen is evolved at the anode is equal to 70.5 %.

Thus, 29.5 % of the electric charge is used without an apparent effect. Therefore some cyclic process is taking place in the electrolytic cell which causes that anion CrO_4^{2-} is reduced incompletely. One of the reactions which causes a decrease of the current efficiency value, is the following:

$$CrO_4^{2-} + 8\,H^+ + 3\,e^- \underset{\text{anode}}{\overset{\text{cathode}}{\rightleftarrows}} Cr^{3+} + 4\,H_2O$$

PROBLEM 4

A vessel of a volume of 5.0 dm^3 was filled with ethane at a temperature of 300 K and normal pressure and sealed. The vessel with the gas was then heated and the pressure in it was measured at distinct temperatures. The following data were found:

T (K)	Pressure p, measured (kPa)	Pressure p', calculated (kPa)
300	101.25	
500	169.20	
800	276.11	
1000	500.48	

Problems:

4.1 Calculate the pressure p' of ethane in the vessel according to the ideal gas law equation and fill in the values in a free column in the above table.
(R = 8.314 J mol^{-1} K^{-1})

4.2 Explain the differences between theoretical value p' and those (p) obtained by measurements.

4.3 Write the chemical equation for the reaction which takes place probably in the vessel at higher temperatures.

4.4 Calculate the value for the conversion degree α of ethane and that for equilibrium constant K_p of the reaction that takes place at temperatures of 800 and 1000 K.

4.5 The ratio of equilibrium constant K_p at two different temperatures is according to van't Hoff's equation equal to:

$$\ln\frac{K_1}{K_2} = \frac{\overline{\Delta H}}{R} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(ln = 2.303 log)

Calculate the mean value $\overline{\Delta H}$ for reaction heat in the temperature range of 800 – 1000 K.

4.6 What influence will have an elevation of temperature and pressure on the conversion degree of ethane?

4.7 Calculate the relative error of the calculation.

SOLUTION

4.1 The complete table contains the following data:

T (K)	Pressure p, measured (kPa)	Pressure p', calculated (kPa)
300	101.325	101.325
500	169.820	168.706
800	276.111	269.930
1000	500.748	337.412

4.2 The p values at higher temperatures are greater than those calculated (p'). Hence, the number of molecules (moles) in the system increases. Apparently, there occurs a thermal decomposition of ethane.

4.3 Alkanes are thermally decomposed to produce alkenes and hydrogen:

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

4.4 Clapeyron's equation for the substances undergoing thermal decomposition into two other gaseous substances, has the form:

$$p\,V = n(1 + \alpha)\,R\,T$$

where α is degree of decomposition.

From one mole of C_2H_6:

α moles of C_2H_4 and α moles of H_2 are obtained, and $(1 - \alpha)$ moles of C_2H_6 remain unreacted.

From n moles of C_2H_6:

$n\alpha$ moles of C_2H_4 and $n\alpha$ moles of H_2 are obtained, and $n(1 - \alpha)$ moles of C_2H_6 remain unreacted.

Hence, the total amounts of substances of compounds in the gaseous mixture will be:

$$\Sigma\, n = 2n\alpha + n(1 - \alpha) = n(1 + \alpha)$$

In comparing the theoretical and experimental values of pressure we obtain:

$$p'\,V = n\,R\,T \quad \Rightarrow \quad p' = \frac{n}{V}\,RT$$

$$p\,V = n(1 + \alpha)\,R\,T \Rightarrow p = \frac{n(1+\alpha)}{V}\,R\,T$$

$$\frac{p'}{p} = \frac{n}{n(1+\alpha)} \;\Rightarrow\; \alpha = \frac{p-p'}{p'}$$

$$\alpha_{800} = \frac{276.111 - 269.930}{269.930} = 0.023$$

$$\alpha_{1000} = \frac{500.748 - 337.412}{337.412} = 0.484$$

The reaction takes place in gaseous phase and thus, the equilibrium constant K_p is calculated according to the relation:

$$K_p = \frac{p_{C_2H_4}\ p_{H_2}}{p_{C_2H_6}}$$

$p_{\mathrm{C_2H_4}} = p_{\mathrm{H_2}} = p'\ \alpha$ $\qquad$ $p_{\mathrm{C_2H_6}} = p'\ (1 - \alpha)$

$$K_p = \frac{\alpha^2\ p'}{1-\alpha}$$

T = 800 K $\qquad K_p = \dfrac{0.023^2 \times 269.930}{0.977} = 0.146\ \text{kPa}$

T = 1000 K $\qquad K_p = \dfrac{0.484^2 \times 337.412}{0.516} = 153.18\ \text{kPa}$

4.5 According to van't Hoff's equation:

$$\overline{\Delta H} = \frac{2.303\ \log \dfrac{K_1}{K_2}\ R}{\dfrac{1}{T_2} - \dfrac{1}{T_1}}$$

After substituting the known values:

$\overline{\Delta H}$ = 231.36 kJ mol^{-1}

4.6 The reaction is endothermic and the number of particles has increased in the course of the reaction. Thus, the equilibrium is shifted according to Le Chatelier-Bronw's principle in the sense of forward reaction when the temperature rises and on the contrary, the equilibrium is shifted in the sense of reverse reaction when the pressure is elevated.

4.7 If the correct value is ΔH_1 and ΔH_2 is a calculated one then the relative error is calculated according to the relation:

$$\frac{\Delta H_1 - \Delta H_2}{\Delta H_1} \times 100 \quad (\%)$$

PROBLEM 5

A certain liquid organic compound **X** (being present in coal tar) with a mass of 1.06 g was burned to produce 0.90 g of water and 3.52 g of carbon dioxide. Its vapours were 3.79 times as dense as nitrogen.

The compound **X** was oxidised by a hot mixture of CrO_3 + H_2SO_4. A colourless crystalline substance **A** was isolated from the reaction mixture. It was soluble in an aqueous solution of NaOH or $NaHCO_3$.

Compound **A** when heated loses water and converts to compound **B**. Condensation of compound **B** with phenol in the presence of H_2SO_4 or $ZnCl_2$ yields a substance **Y** which is very often used as an acid-base indicator.

Both compound **A** and compound **B** when heated with an access of 1-butanol (some drops of a concentrated H_2SO_4 solution are added) gives the same liquid compound **C**.

If accepted that a carbon atom shows a tendency to form four bonds in organic compounds, it is possible to write formally two different formulas for the compound **X**. The formulas written in this way do not correspond, however, to the chemical structure of the molecule **X** because up to date nobody has succeeded in the preparation of the two hypothetical isomers.

Haayman and Witbaut carried out in 1941 an ozonisation of the compound **X** in a CH_3Cl solution. After hydrolysis of ozonides, it was found that the water layer contains three different organic compounds in a molar ratio of **D** : **E** : **F** = 3 : 2 : 1. Only two of them formed new compounds **G** and **H** by a mild oxidation, the third one remains unchanged under these conditions but the effect of stronger oxidising agents as H_2O_2 for example, results in forming a well known liquid compound **I** with a characteristic sharp smell.

A sample of a pure anhydrous compound **G** was dissolved in an aqueous 1-molar solution of H_2SO_4 and the resulting solution was titrated with a volumetric 0.05-molar $KMnO_4$ solution. An amount of 0.288 g of substance **G** required 25.6 cm^3 of the $KMnO_4$ solution.

Problems:

5.1 Write the summary formula for the compound **X**.

5.2 Based on the information and data in the task, write chemical equations for the reactions by which products **A**, **B**, and **C** are formed.

5.3 Give the name for compound **Y** and write the equation of its synthesis. Write its structural formula and colour in both acidic and basic solutions.

5.4 Write two formal structural formulas for the compound **X** as well as a more correct structural formula according to the latest findings.

5.5 Write the chemical equation for the ozonolysis of compound **X** by which the fact can be explained why compounds **D**, **E**, and **F** are after hydrolysis of ozonides present in water layer in a molar ration of 3 : 2 : 1.

5.6 Write chemical equations for the reactions of formation of compounds **G**, **H**, and **I**.

5.7 Write both formal structural formulas used before, and the more correct modern structural formula of another liquid organic compound if you know that the compound is also present in coal tar and it is a derivative of compound **X**. What name of a known chemist is connected in the history with the formula of this basic compound? What are the products obtained by its ozonolysis?

5.8 Write the names of the substances **X**, **Y**, **A** – **I** under the corresponding compounds in the equations.

Note:

Use in your calculation:

M(C) = 12 g mol^{-1}; M(O) = 16 g mol^{-1}; M(H) = 1 g mol^{-1}; M(KMnO$_4$) = 158 g mol^{-1}.

SOLUTION

5.1 The empirical formula of the compound **X** can be calculated from the composition of combustion products of this compounds:

$$n(H_2O) = \frac{0.9\ \text{g}}{18\ \text{g mol}^{-1}} = 0.05\ \text{mol} \quad \Rightarrow\ n(H) = 0.1\ \text{mol}$$

$$\%\,H = \frac{0.1\ \text{g}}{1.06\ \text{g}}\,100 = 9.4$$

$$n(CO_2) = \frac{3.52\ \text{g}}{44\ \text{g mol}^{-1}} = 0.08\ \text{mol} \quad \Rightarrow\ n(C) = 0.8\ \text{mol i. e. } 0.96\ \text{g}$$

$$\%\,C = \frac{0.96\ \text{g}}{1.06\ \text{g}} \times 100 = 90.6$$

$$\textbf{X}\text{:}\quad C_xH_y \qquad x : y = \frac{90.6}{12} : \frac{9.4}{1} = 4 : 5$$

Empirical formula: C_4H_5

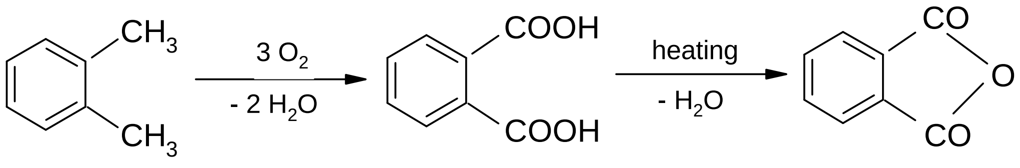
Molecular formula: $(C_4H_5)_n$

Molar mass of **X** is calculated in the following way:

$$M(\mathbf{X}) = M(N_2)\,\frac{\rho(\mathbf{X})}{\rho(N_2)} = 28\ \text{g mol}^{-1} \times 3.79 = 106\ \text{g mol}^{-1}$$

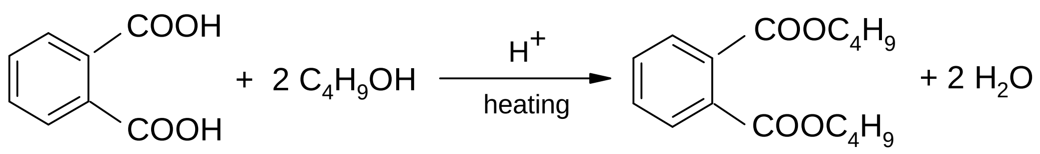
Molecular formula of the compound **X** is C_8H_{10}.

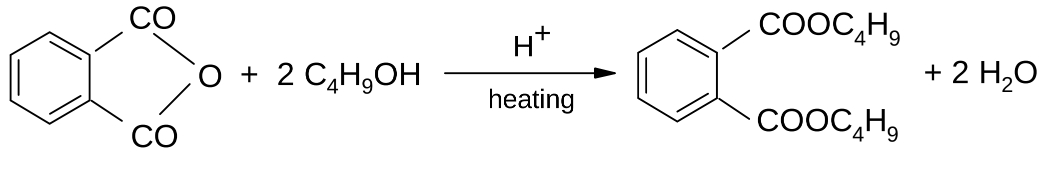
5.2 The information given in the task and concerning compound **X** supports the assumption that compound **X** is o-xylene.



X	**A**	**B**
o-xylene	phthalic acid	phthalic anhydride
1,2-dimetylbenzene	1,2-benzene-dicarboxylic acid	

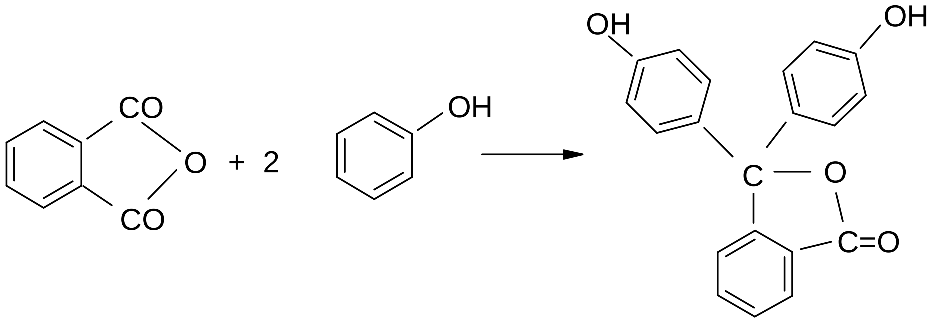
Phthalic acid (**A**) or its anhydride (**B**) when heated with an excess of 1-butanol with addition of a certain amount of mineral acid as a catalyst, yield dibutyl ester of phthalic acid – **C**:





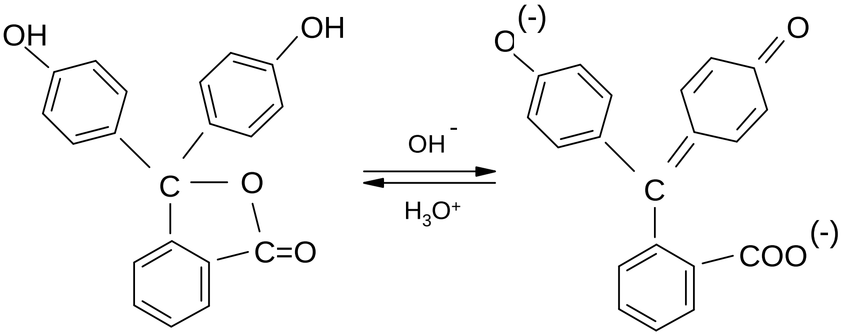
C : dibutyl phthalate

5.3 Condensation of the anhydride of phthalic acid with phenol in the presence of H_2SO_4 or anhydrous $ZnCl_2$:



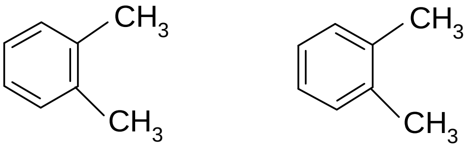
Y : phenolphthalein

Phenolphthalein is used as acid-base indicator which is colourless in an acidic solution but purple red in an alkaline solution.

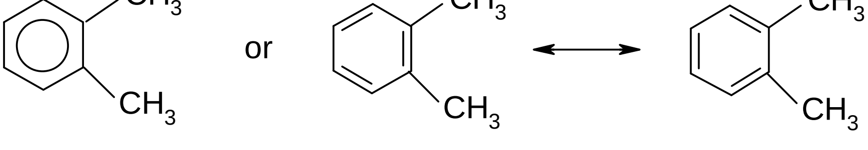


colourless red

5.4 Kekule's formulas for o-xylene:



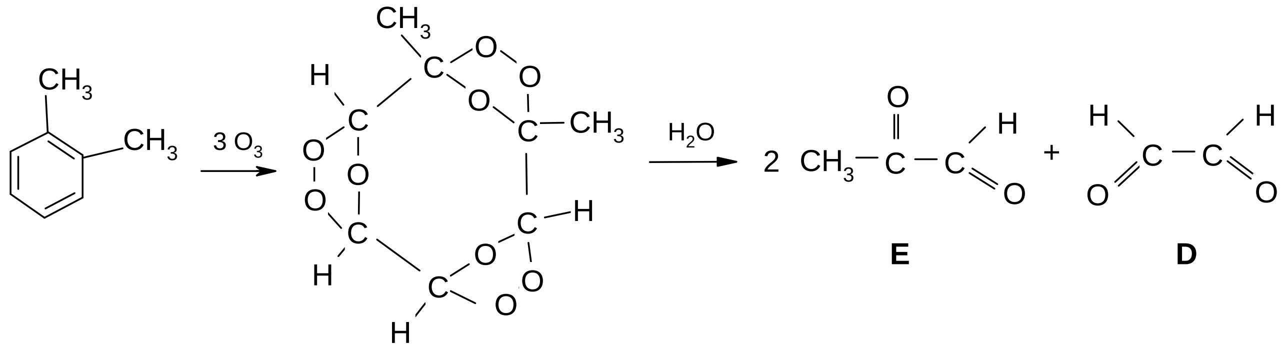
would allow to suggest that this compound does exist in two isomeric forms. Nobody, however, has succeeded in obtaining the two isomers of o-disubstituted benzene. At present it is already known that all bonds C-C as well as C-H in benzene and its derivatives are equivalent. Therefore, the formula for o-xylene can be written in the following way:

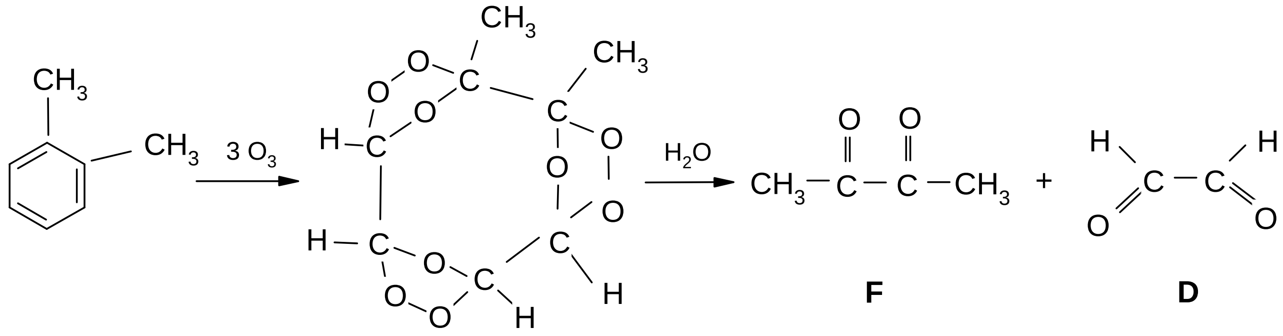


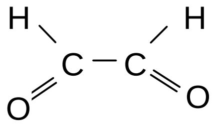
This kind of writing of the formulas expresses that the π-bonds are equally divided on the whole benzene ring. Of course, such formulas no longer support the existence of two isomeric forms of o-xylene.

In 1941 Haayman and Witbaut provided further chemical evidence for the equivalence of the six C-C bonds in the benzene ring. They allowed to react o-xylene with ozone and obtained two different triozonides in a molar ratio of 1 : 1. Products of ozonolysis were decomposed by water to form three different substances:

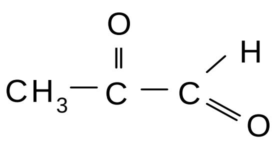
5.5





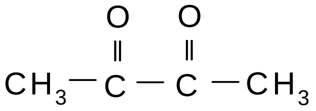


D ethanedial, glyoxal



$CH_3-CO-CHO$

E propanonal, methylglyoxal

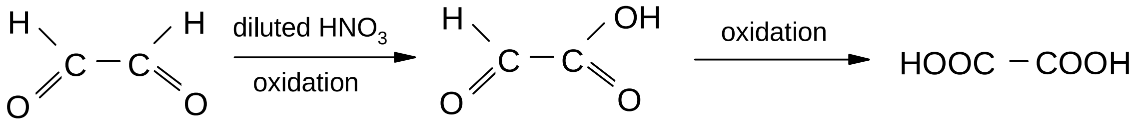


$CH_3-\overset{\overset{\large O}{\|}}{C}-\overset{\overset{\large O}{\|}}{C}-CH_3$

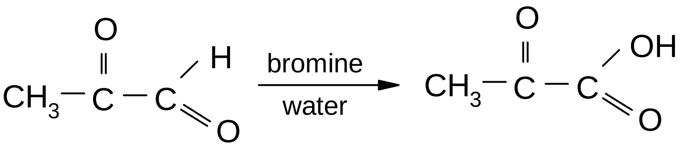
F butanedion, diacetyl

Products in the resulting mixture after hydrolysis of ozonides are in a molar ratio 3 : 2 : 1 and it proves the equivalence of C-C bonds in the benzene ring.

5.6 From the three above obtained compounds **D**, **E**, and **F** only the first two are easily oxidized to the corresponding acids:

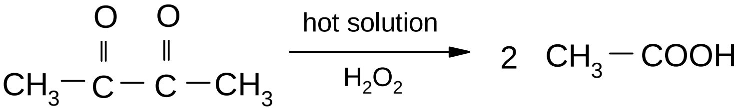


glyoxalic acid   oxalic acid



H pyruvic acid
alpha-ketopropionic acid

Compound **F** requires a stronger oxidising agents, such as aqueous solutions of H_2O_2, HIO_4, etc.



ethanoic acid, acetic acid

Oxalic acid is used as a standard substance in preparation of volumetric $KMnO_4$ solutions:

$2\ KMnO_4 + 5\ (COOH)_2 + 3\ H_2SO_4 \rightarrow 2\ MnSO_4 + K_2SO_4 + 10\ CO_2 + 8\ H_2O$

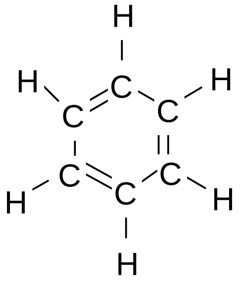
Experimental data on determination of compound **G** by titration with a 0.05-molar $KMnO_4$ solution show that compound **G** is oxalic acid, and thus they do confirm the correctness of the solution.

$n(KMnO_4) = c\,V = 0.05\ \text{mol dm}^{-3} \times 0.0256\ \text{dm}^3 = 0.00128\ \text{mol}$

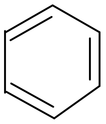
$n((COOH)_2) = 5/2 \times 0.00128\ \text{mol} = 0.0032\ \text{mol}$

It corresponds to 0.288 g of substance **G** what is in agreement with the result given in the task.

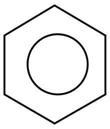
5.7 In 1865 Kekulé suggested a cyclic formula for benzene:



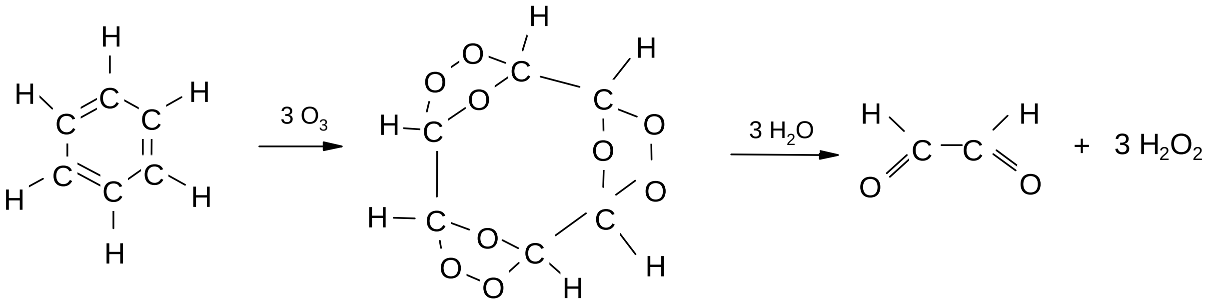
or



It was, however, proved by experiments that all atoms of carbon and hydrogen are in the benzene molecule equivalent. For the same reason as given under 4, the formula of benzene is at present written in the form:



Ozonolysis of benzene yields a triozonide which after hydrolysis gives glyoxal:



PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Four aqueous solutions are available on the laboratory desk. These are solutions of HCl, NaOH, NH_3, and CH_3COOH whose concentrations are approximately 1 mol dm^{-3}. The concentration of HCl solution is the only one that is exactly determined and known.

Using the volumetric solution of HCl, determine the exact concentrations of the other solutions. A burette, pipette, titration flasks and indicators methyl orange and phenolphthalein are at your disposal. Perform twice each titration and calculate the mean value for concentration. The third determination is needed to be carried out only in such a case when the results of the previous two titrations differ more than by 2 %.

Now you will perform the following thermochemical measurements of neutralisation heat evolved in the reactions of the above given solutions of acids and bases:

a) Measure quantitatively exactly 50.0 cm^3 of the hydrochloric acid solution into a beaker. Measure into another equal beaker a volume of NaOH solution that contains such a number of moles of NaOH as that of HCl being present in the first beaker. Then measure the temperatures of both solutions with a precision of 0.2 K. Pour quickly the content of the first beaker into the other using the thermometers as a glass stick and stir the resulting solution with the thermometer. Determine the final highest temperature of the mixture.

b) Perform analogous measurement with the following pairs of acids and bases:
HCl – NH_3, CH_3COOH – NaOH, CH_3COOH – NH_3.

Problems:

1.1 What indicators have been used for the individual determinations? Give approximately pH regions in which the mentioned indicators show colour transitions. Give reasons for the use of the individual indicators using only ionic equations for the reactions which are characteristic of specific properties of salts being formed in the individual neutralisation reactions. Calculate the concentrations of all solutions under investigations.

1.2 Write the calorimetric equation in its general form by means of which the neutralisation heat can be calculated. Calculate the thermal effect for each neutralisation reaction under investigation and give the value in relation to one mole of the water formed.

Densities of the solutions are as follows:

$\rho(HCl) = 1.02\ g\ cm^{-3}$

$\rho(NaOH) = 1.04\ g\ cm^{-3}$

$\rho(NH_3) = 0.99\ g\ cm^{-3}$

$\rho(CH_3COOH) = 1.01\ g\ cm^{-3}$

In the calculations consider the specific heat capacity value for the solutions equal to 4.19 J g^{-1} K^{-1} whereas the heat capacity of glass and thermometer may be neglected.

1.3. Have you obtained equal results in all four cases? If not, order the particular reaction systems according to the decreasing value of reaction heat. What reactions cause the above mentioned differences? Express the reactions by means of chemical equations.

1.4 The exact methods showed that neutralisation heat in the reaction of the strong acid with a strong base (i. e. the reaction heat when 1 mole of water is formed from H^+ and OH^- ions) is equal to 57.57 kJ mol^{-1}. Calculate the relative error of your determination.

SOLUTION

1.1. In titrating a strong acid with a strong base, both phenolphthalein and methyl orange can be used as acid-base indicators. The drop on the titration curve covers the colour changes of both indicators (pH values from 4 – 10).

Only phenolphthalein can be used in the case when a weak acid is titrated with a strong base because the neutralisation occurs at higher pH values (the colour transition of phenolphthalein is in the region of pH = 8 – 10). A salt formed undergoes hydrolysis (more precisely its anion) and the solution exhibits a basic reaction:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

In titrating a strong acid with a weak base or vice versa, methyl orange is used (pH = 3 – 4.5) and due to hydrolysis the resulting solution shows an acidic reaction:

$$NH_4^+ + 2\,H_2O \rightleftharpoons NH_3\,.\,H_2O + H_3O^+$$

The exact concentrations of the aqueous solutions of sodium hydroxide and ammonia are determined by titrations with the volumetric solution of hydrochloric acid. The exact concentration of the acetic acid solution is then determined by a titration with the sodium hydroxide solution.

1.2 When the specific heat capacities of glass and thermometer are neglected the neutralisation heat can be then calculated according to a simple relation:

$\Delta H_{neutr.} = (m_1 + m_2)\, c\, (T_2 - T_1)$

m_1 – mass of the first solution,

m_2 – mass of the second solution,

c – specific heat capacity of the solutions,

T_1 – temperatures of the solutions before mixing,

T_2 – temperatures of the solutions after mixing.

If the temperatures of the solutions before mixing are not equal then T_1 will be the mean temperature of both. Finally, the neutralisation heat value should be related to 1 mole of water formed.

1.3 The results obtained for the neutralisation of a strong base with a weak acid and vice versa, as well as for the reaction of a weak acid with a weak base, are lower than those obtained for the neutralisation of a strong acid with a strong base. A part of the heat is consumed for ionisation of a weak electrolyte:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

A similar equation can be written for $NH_3.H_2O$.

PROBLEM 2 (practical)

The values of standard reduction potentials are given for the following redox systems:

$2\ S_2O_3^{2-} / S_4O_6^{2-}$ $E_1^0 = 0.17$ V

$2\ I^- / I_2$ $E_2^0 = 0.535$ V

$2\ SO_4^{2-} / S_2O_8^{2-}$ $E_3^0 = 2.05$ V

Problems:

2.1 Set in order the oxidation forms of the above given redox systems from the weakest to the strongest oxidising agent (write into Table 1)

In a similar way order the reduction forms from the weakest to the strongest reducing agent.

2.2 In the bellow given equations mark by arrows the expected possible course (direction) of the chemical reaction (Table 1).

$2\ I^- + S_4O_6^{2-} = I_2 + 2\ S_2O_3^{2-}$

$2\ I^- + S_2O_8^{2-} = I_2 + 2\ SO_4^{2-}$

$2\ S_2O_3^{2-} + S_2O_8^{2-} = S_4O_6^{2-} + 2\ SO_4^{2-}$

2.3 On the assumption that solutions of the same concentration are used, is it possible to tell without making any experiment which of the given reactions would run at a higher rate and which ones at a lower rate?

In order to confirm your hypothesis given under 3, perform the following three qualitative experiments:

Experiment 1

Pour 20.0 cm^3 of a 0.10-molar solution of $Na_2S_2O_3$ into an Erlenmeyer flask and quickly add under intense stirring 1.0 cm^3 of a 0.10-molar iodine solution.

Experiment 2

Measure 20.0 cm^3 of a 0.10-molar solution of $(NH_4)_2S_2O_8$ into an Erlenmeyer flask and quickly add under intense stirring 4.0 cm^3 of a 0.10-molar potassium iodide solution.

Experiment 3

Put 20.0 cm^3 of a 0.10-molar solution of $(NH_4)_2S_2O_8$ into an Erlenmeyer flask and then quickly add under intense stirring 2.0 cm^3 of a 0.10-molar sodium thiosulphate solution.

Since both the reactants and reactant products are colourless, the course of the reaction can be followed indirectly. For that purpose, add to the solution after 1 – 2 minutes two or three drops of a 0.10-molar iodine solution. If the result of your experiment is surprising, perform experiment No 3 again but allow solutions of $Na_2S_2O_3$ and $(NH_4)_2S_2O_8$ to react for 10 minutes.

Order the reactions from experiments No 1 – 3 (into Table 3) according to their increasing reaction rate and then answer the question whether it is possible on the basis of known values of the standard reduction potentials to guess, at least qualitatively, the reaction rate for the reaction mixture containing two pairs of redox systems.

Conclusions made on the above experiments make it possible to investigate the influence of concentration of each of the starting substances on the rate of the reaction between I^- and $S_2O_8^{2-}$ ions.

Perform experiment No 4 according to the following instructions:

Experiment 4

a) Measure successively into a 250 cm^3 Erlenmeyer flask: 25.0 cm^3 of a 0.20-molar potassium iodide solution, 10.0 cm^3 of a 0.01-molar sodium thiosulphate solution, 5.0 cm^3 of a starch paste, and stir the content of the flask.

b) Measure 25.0 cm^3 of a 0.20-molar $(NH_4)_2S_2O_8$ solution into a 100 cm^3 beaker. Pour the content of the beaker quickly into the flask, press a stop-watch and stir the content of the flask. Measure the time till the moment when the solution becomes blue.

Perform analogously experiment No 4 three times over, using the bellow given volumes of the 0.20-molar potassium iodide solution, while the volumes of $Na_2S_2O_3$ and $(NH_4)_2S_2O_8$ solutions as well as that of the starch paste remain unchanged. Moreover, add to the solution the bellow given volumes of a 0.20-molar potassium nitrate solution so that the volume of the resulting solution is always the same. Explain the use of potassium nitrate in this case.

4 (ii): 15.0 cm^3 0.20-molar KI + 10.0 cm^3 0.20-molar KNO_3
4 (iii): 10.0 cm^3 0.20-molar KI + 15.0 cm^3 0.20-molar KNO_3
4 (iv): 5.0 cm^3 0.20-molar KI + 20.0 cm^3 0.20-molar KNO_3

2.4 List the results of experiments No 1-4 briefly and clearly in the attached Tables.

Write formulas of the corresponding substances above the arrows in Table 1 (as required under 2.1) and mark the expected course of the mentioned chemical reactions by arrows in the equations.

For a qualitative evaluation of reaction rate (Table 2) use terms such as: very rapid, rapid, slow, very slow.

Fill in Table 3 exactly according to the titles of the columns.

2.5 Calculate the reaction rate according to the formula:

$$v = \frac{\Delta c(S_2O_8^{2-})}{\Delta \tau} \text{ (mol dm}^{-3}\text{ s}^{-1}\text{)}$$

$\Delta c(S_2O_8^{2-})$ - concentration change of $S_2O_8^{2-}$ in a time interval.

Plot (on the attached mm-paper) the dependence of reaction rate on the concentration of I^- anions at a constant concentration of $S_2O_8^{2-}$ anions in the solution.

2.6 Making use of the knowledge gained from the preceding experiment and the solutions which are at your disposal, suggest another experiment which would make it possible to investigate the reaction rate dependence on concentration of $S_2O_8^{2-}$ anions at a constant concentration of I^- anions in the solution.

Considering Table 3, fill in Table 4. Mark the columns in the Table, suggest a plan of the experiment and list experimental results as well as the calculated values. Similarly as before, plot the dependence under investigation on a mm-paper.

2.7 Write a general relation for the reaction rate dependence on the concentration of reactants and then using the diagrams attached, calculate the values for the reaction rate constant for both cases and determine their mean value.

SOLUTION

2.1 $S_4O_6^{2-}$ I_2 $S_2O_8^{2-}$

$$\xrightarrow{\hspace{8cm}}$$

Increase of oxidising properties of oxidised forms

SO_4^{2-} I^- $S_2O_3^{2-}$

$$\xrightarrow{\hspace{8cm}}$$

Increase of reducing properties of reduced forms

2.2 The expected course of the chemical reactions:

$$2\ I^- + S_4O_6^{2-} \leftarrow I_2 + 2\,S_2O_3^{2-} \qquad \text{(a)}$$

$$2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2\,SO_4^{2-} \qquad \text{(b)}$$

$2\ S_2O_3^{2-} + S_2O_8^{2-} \rightarrow S_4O_6^{2-} + 2\ SO_4^{2-}$ (c)

2.3 The formulation of any hypothesis either supporting or neglecting the possibility of predicting the reaction rate, should be accepted as correct.

Results of experiments Nos 1-3:

1 - reaction (a) is very rapid;

2 - reaction (b) is slow;

3 - reaction (c) is very slow, its course can hardly be observed.

Conclusion: The known differences between the values of standard reduction potentials of two pairs of redox systems do not allow to guess even qualitatively the proper relations between the rates of the corresponding reactions.

2.4 You are required to fill in the following data into Table 3:

- volumes of individual solutions,
- the total volume of the solution (65 cm^3),
- calculated values for I^- and $S_2O_8^{2-}$ concentrations,
- reaction time,
- calculated values for the reaction rate.

The addition of 0.20-molar KNO_3 solution is needed to keep the constant ionic strength of the resulting solution.

In plotting the reaction rate in dependence on the values of $[I^-]^2$ (at the constant concentration of $S_2O_8^{2-}$ anions) we get a straight line crossing the beginning of the coordinate system.

Table 4 should be filled in analogously as Table 3 where, moreover, the individual columns should be specified.

Solutions for the experiment are prepared in the same way but the solution of KI (25 cm^3) will form a constant addition, whereas those of $(NH_4)_2S_2O_8$ and $(NH_4)_2SO_4$ will form a changeable addition in the resulting solution and the other conditions are equal. Ammonium sulphate plays the same role in the solution as potassium nitrate in the preceding experiment.

In this case the reaction rate versus the concentration of $S_2O_8^{2-}$ anions is plotted (at a constant concentration of I^- anions) to give also a straight line crossing the beginning of the coordinate system.

2.5 The rate of the reaction:

$v = k\,[S_2O_8^{2-}]\,[I^-]^2$

a) $[I^-]$ = const $\Rightarrow$ $v = k'\,[S_2O_8^{2-}]$

$$k = \frac{k'}{[I^-]^2}$$

k' is the slope of the straight line.

b) $[S_2O_8^{2-}]$ = const $v = k''\,[I^-]^2$

$k'' = k\,[S_2O_8^{2-}]$

$$k = \frac{k''}{[S_2O_8^{2-}]}$$

k'' is the slope of the straight line.

The values of the rate constants obtained from the procedures a) and b) should be theoretically equal. If they partly differ, calculate the mean value of the rate constant.

11th

IChO

International Chemistry Olympiad

6 theoretical problems
2 practical problems

THE ELEVENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
2–11 JULY 1979, LENINGRAD, SOVIET UNION

THEORETICAL PROBLEMS

PROBLEM 1

When carrying out this programmed assignment, encircle those letters which in your opinion correspond to the correct answers to each of the 20 questions.

1. Which element is oxidized in the reaction between ethylene and an aqueous solution of potassium permanganate?

   A) carbon, B) hydrogen, C) potassium, D) manganese, E) oxygen.

2. How many litres of CO_2 will approximately be evolved in the reaction of 18 g of potassium hydrogen carbonate with 65 g of 10 % sulphuric acid?

   A) 1, B) 2, C) 3, D) 4, E) 5.

3. Which of the following hydrocarbons gives the maximum heat yield on complete combustion of 1 litre of the gas:

   A) propane, B) methane, C) acetylene, D) ethylene, E) all give the same yield.

4. How many isomers can have a compound if its formula is C_3H_5Br?

   A) 1, B) 2, C) 3, D) 4, E) 5.

5. Which of the following hydrocarbons will be the best engine fuel?

   A) cyclooctane, B) 2,2-dimethylhexane, C) normal octane, D) 3-ethylhexane, E) 2,2,4-trimethylpentane.

6. With which of the following compounds will an aqueous solution of a higher oxide of element No 33 react?

   A) CO_2, B) K_2SO_4, C) HCl, D) NaOH, E) magnesium.

7. What must be the minimum concentration (% by mass) of 1 kg of a potassium hydroxide solution for a complete neutralisation of 3.57 moles of nitric acid?

   A) 5 %, B) 10 %, C) 15 %, D) 20 %, E) 25 %.

8. How many compounds with the formula C_3H_9N can exist?

   A) 1, B) 2, C) 3, D) 4, E) 5.

9. In which of the following compounds has the nitrogen content (in mass %) a maximum value?

   A) potassium nitrate, B) barium nitrate, C) aluminium nitrate, D) lithium nitrate, E) sodium nitrate.

10. To which carbon atom (indicate the serial number) will chlorine mainly add in the reaction of HCl with penten-2-oic acid?

    A) 1, B) 2, C) 3, D) 4, E) 5.

11. How many moles of water are there per mole of calcium nitrate in a crystallohydrate if the water content is 30.5 % by mass?

    A) 1, B) 2, C) 3, D) 4, E) 5.

12. Which of these organic acids is the strongest?

    A) benzoic, B) 2-chlorobenzoic, C) 4-methylbenzoic, D) 2-aminobenzoic, E) 4-bromobenzoic.

13. Which of these acids has the highest degree of dissociation?

    A) $HClO$, B) $HClO_2$, C) $HClO_3$, D) $HClO_4$, E) all have the same degree.

14. Which of the salts given below do not undergo hydrolysis?

    A) potassium bromide, B) aluminium sulphate, C) sodium carbonate, D) iron(III) nitrate, E) barium sulphate.

15. How many litres of air are approximately required for complete combustion of 1 litre of ammonia?

    A) 1, B) 2, C) 3, D) 4, E) 5.

16. Which element is oxidised in the thermal decomposition of sodium hydrogen carbonate?

    A) sodium, B) hydrogen, C) oxygen, D) carbon, E) none.

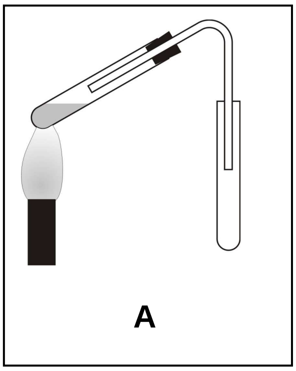
17. Which of the following changes have no effect on the chemical equilibrium in the thermal decomposition of $CaCO_3$?

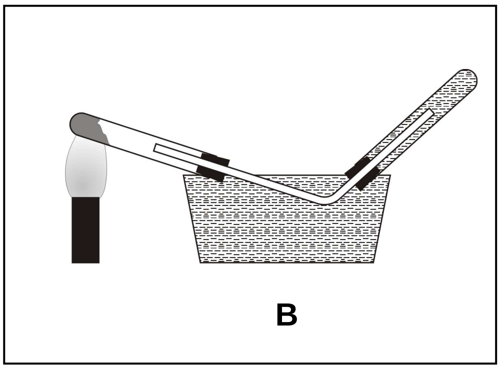
    A) temperature elevation, B) pressure decrease, C) addition of catalyst, D) a change in the CO_2 concentration, E) an increase in the amount of the initial substance.

18. Which of the substances given bellow will be formed at the Pt-anode in the electrolysis of an aqueous solution of aluminium chloride?

    A) aluminium, B) oxygen, C) hydrogen, D) aluminium hydroxide, E) chlorine.

19. The apparatus shown in the figures is intended for preparing ammonia under laboratory conditions. The test tube being heated contains a mixture of NH_4Cl and $Ca(OH)_2$. Which of the figures is correct?


A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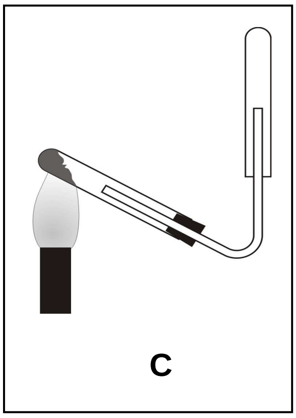
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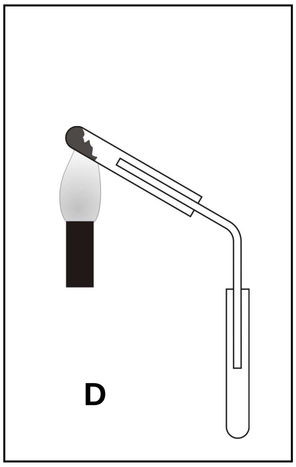
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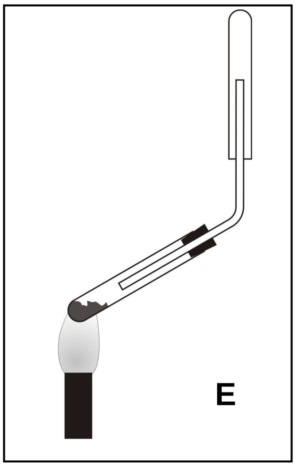
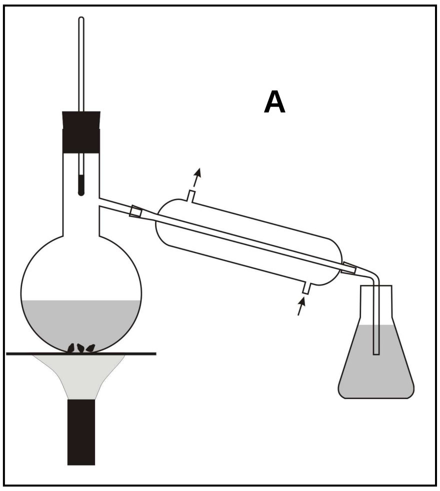
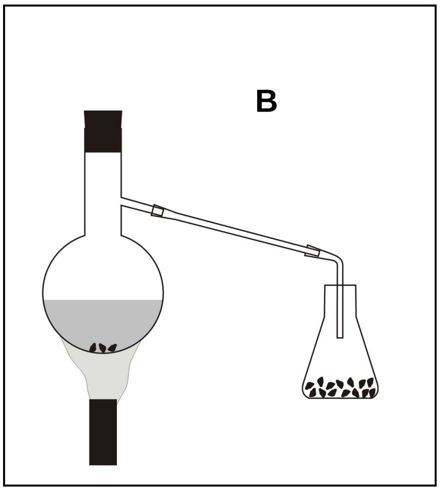

E

20. Which of the apparatuses shown in the figures is the best one for the synthesis of bromethane from potassium bromide, concentrated sulphuric acid and ethanol?


A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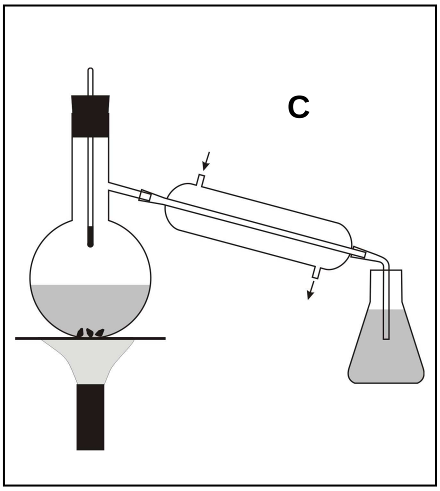
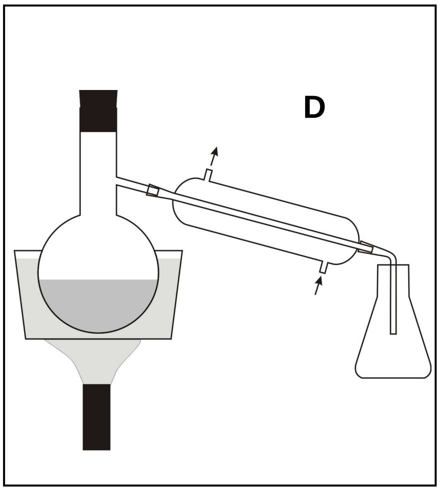
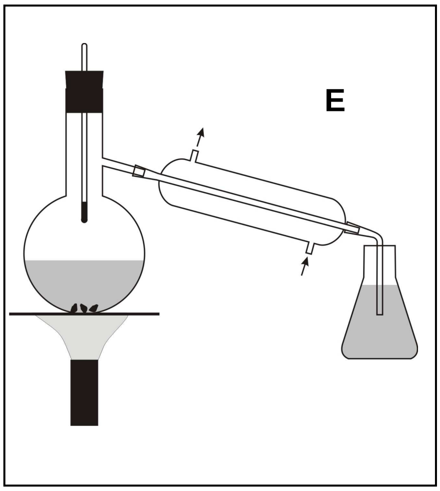






SOLUTION

1 – A
2 – C
3 – A
4 – E
5 – E
6 – D and E
7 – D
8 – D
9 – D
10 – C
11 – D
12 – B
13 – D
14 – A and E
15 – D
16 – E
17 – C and E
18 – B and E
19 – C
20 – A

PROBLEM 2

An alloy comprises the following metals: cadmium, tin, bismuth, and lead. A sample of this alloy weighing 1.2860 g, was treated with a solution of concentrated nitric acid. The individual compound of metal **A** obtained as a precipitate, was separated, thoroughly washed, dried and calcinated. The mass of the precipitate after the calcination to constant mass, was 0.3265 g.

An aqueous ammonia solution was added in excess to the solution obtained after separation of the precipitate. A compound of metal **B** remained in the solution while all the other metals precipitated in the form of sparingly soluble compounds. The solution was first quantitatively separated from the precipitate, and then hydrogen sulphide was passed through the separated solution to saturation. The resulting precipitate containing metal **B** was separated, washed and dried. The mass of the precipitate was 0.6613 g.

The precipitate containing the compounds of metals **C** and **D** was treated with an excess of a NaOH solution. The solution and the precipitate were then quantitatively separated. A solution of HNO_3 was added to the alkaline solution to reach pH 5 – 6, and an excess of K_2CrO_4 solution was added to the resulting transparent solution. The yellow precipitate was separated, washed and quantitatively transferred to a beaker. Finally a dilute H_2SO_4 solution and crystalline KI were added. Iodine produced as a result of the reaction was titrated with sodium thiosulphate solution in the presence of starch as an indicator. 18.46 cm^3 of 0.1512 normal $Na_2S_2O_3$ solution were required.

The last metal contained in the precipitate as a sparingly soluble compound was transformed to an even less soluble phosphate and its mass was found to be 0.4675 g.

2.1 Write all equations of the chemical reactions on which the quantitative analysis of the alloy sample is based. Name metals **A**, **B**, **C**, and **D**. Calculate the mass percentage of the metals in the alloy.

SOLUTION

2.1 The action of nitric acid on the alloy:

$$Sn + 4\,HNO_3 \rightarrow H_2SnO_3 + 4\,NO_2 + H_2O$$

$$Pb + 4\,HNO_3 \rightarrow Pb(NO_3)_2 + 2\,NO_2 + 2\,H_2O$$

$$Bi + 6\,HNO_3 \rightarrow Bi(NO_3)_3 + 3\,NO_2 + 3\,H_2O$$

$Cd + 4\ HNO_3 \rightarrow Cd(NO_3)_2 + 2\ NO_2 + 2\ H_2O$

Weight form of tin determination:

$H_2SnO_3 \rightarrow SnO_2 + H_2O$

Calculation of tin content in the alloy:

M(Sn) = 118.7 g mol^{-1}; M(SnO$_2$) = 150.7 g mol^{-1}

$$\frac{m(\text{Sn})}{m(\text{SnO}_2)} = \frac{M(\text{Sn})}{M(\text{SnO}_2)}; \quad m(\text{Sn}) = \frac{118.7\ \text{g mol}^{-1} \times 0.3265\ \text{g}}{150.7\ \text{g mol}^{-1}} = 0.2571\ \text{g}$$

Mass percentage of tin (metal A) in the alloy:

$$w(\text{Sn}) = \frac{0.2571\ \text{g}}{1.2860\ \text{g}} = 0.1999 = 19.99\ \%$$

The reactions taking place in the excess of aqueous ammonia solution:

$Pb(NO_3)_2 + 2\ NH_4OH \rightarrow Pb(OH)_2\downarrow + 2\ NH_4NO_3$

$Bi(NO_3)_3 + 3\ NH_4OH \rightarrow Bi(OH)_3\downarrow + 3\ NH_4NO_3$

$Cd(NO_3)_2 + 4\ NH_4OH \rightarrow \underset{\text{solution}}{[Cd(NH_3)_4](NO_3)_2} + 4\ H_2O$

Saturating of the solution with hydrogen sulphide:

$[Cd(NH_3)_4](NO_3)_2 + 2\ H_2S \rightarrow CdS\downarrow + 2\ NH_4NO_3 + (NH_4)_2S$

Calculation of the cadmium content in the alloy:

M(Cd) = 112.4 g mol^{-1}; M(CdS) = 144.5 g mol^{-1}

$$m(\text{Cd}) = \frac{112.4\ \text{g mol}^{-1} \times 0.6613\ \text{g}}{144.5\ \text{g mol}^{-1}} = 0.5143\ \text{g}$$

Mass percentage of cadmium (metal B) in the alloy:

$$w(\text{Cd}) = \frac{0.5143\ \text{g}}{1.2860\ \text{g}} = 0.3999 = 39.99\ \%$$

The reactions taking place in the excess of sodium hydroxide solution:

The action of excess sodium hydroxide on lead(II) and bismuth(III) hydroxides:

$Pb(OH)_2 + 2\ NaOH \rightarrow \underset{\text{solution}}{Na_2[Pb(OH)_4]}$

$Bi(OH)_3 + NaOH \rightarrow$ no reaction

Acidification of the solution with nitric acid (pH = 5 – 6):

$Na_2[Pb(OH)_4] + 4\ HNO_3 \rightarrow Pb(NO_3)_2 + 2\ NaNO_3 + 4\ H_2O$

The reaction with K_2CrO_4:

$Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4\downarrow + 2\ KNO_3$

The reactions on which the quantitative determination of lead in $PbCrO_4$ precipitate is based:

$2\ PbCrO_4 + 6\ KI + 8\ H_2SO_4 \rightarrow 3\ I_2 + 2\ PbSO_4 + 3\ K_2SO_4 + Cr_2(SO_4)_3 + 8\ H_2O$

$I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6$

Percentage of lead (metal C) in the alloy:

$$w(\text{Pb}) = \frac{c(\text{Na}_2\text{S}_2\text{O}_3) \times V(\text{Na}_2\text{S}_2\text{O}_3) \times M(\text{Pb})}{m(\text{alloy}) \times 3}$$

(One Pb^{2+} ion corresponds to one CrO_4^{2-} ion which accepts 3 electrons in the redox reaction considered.)

$$w(\text{Pb}) = \frac{0.1512\ \text{mol dm}^{-3} \times\ 0.01846\ \text{dm}^3 \times\ 207.2\ \text{g mol}^{-1}}{1.286\ \text{g} \times 3} = 0.1499 = 14.99\ \%$$

In order to convert bismuth(III) hydroxide to phosphate it is necessary:

a) to dissolve the bismuth(III) hydroxide in an acid:

$Bi(OH)_3 + 3\ HNO_3 \rightarrow Bi(NO_3)_3 + 3\ H_2O$

b) to precipitate Bi^{3+} ions with phosphate ions:

$Bi(NO_3)_3 + K_3PO_4 \rightarrow BiPO_4\downarrow + 3\ KNO_3$

Calculation of the bismuth content in the alloy:

$M(\text{Bi}) = 209\ \text{g mol}^{-1}$; $M(\text{BiPO}_4) = 304\ \text{g mol}^{-1}$

$$m(\text{Bi}) = \frac{209\ \text{g mol}^{-1} \times 0.4676\ \text{g}}{304\ \text{g mol}^{-1}} = 0.3215\ \text{g}$$

Percentage of bismuth (metal D) in the alloy:

$$w(\text{Bi}) = \frac{0.3215\ \text{g}}{1.2860\ \text{g}} = 0.2500 = 25.00\ \%$$

Composition of the alloy: % Cd = 40, % Sn = 20, % Pb = 15, % Bi = 25

PROBLEM 3

Which chemical processes can take place in the interaction of:

a) aluminium ammonium sulphate with baryta water,

b) potassium chromate, ferrous chloride and sulphuric acid,

c) calcinated soda and sodium hydrogen sulphate,

d) 4-bromoethyl benzene and chlorine,

e) n-propyl alcohol, phenol and concentrated sulphuric acid?

Write ionic equations for the reactions that proceed in aqueous solutions. For the other chemical reactions write complete equations and indicate the type of the reaction. Indicate the differences in the reaction conditions for those reactions that may lead to the formation of various substances.

SOLUTION

(a) a-1 $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$

a-2 $NH_4^+ + OH^- \rightarrow NH_3.H_2O \rightarrow NH_3\uparrow + H_2O$

a-3 $Al^{3+} + 3\ OH^- \rightarrow Al(OH)_3\downarrow$

a-4 $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$

a-5 possibly: $Ba^{2+} + 2\ [Al(OH)_4]^- \rightarrow Ba[Al(OH)_4]_2\downarrow$

(b) b-1 $2\ CrO_4^{2-} + 2\ H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

b-2 $6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \rightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$

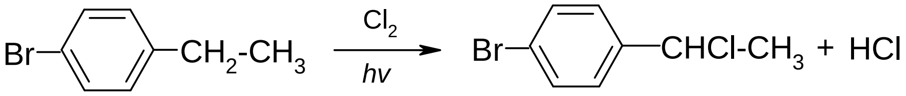
b-3 with high concentrations of Cl^- and H_2SO_4:

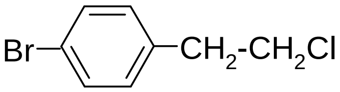
$Cr_2O_7^{2-} + 4\ Cl^- + 6\ H^+ \rightarrow CrO_2Cl_2 + 3\ H_2O$

(c) c-1 with excess of H^+: $CO_3^{2-} + 2\ H^+ \rightarrow H_2O.CO_2 \rightarrow H_2O + CO_2\uparrow$

c-2 with excwss of CO_3^{2-}: $CO_3^{2-} + H^+ \rightarrow HCO_3^-$

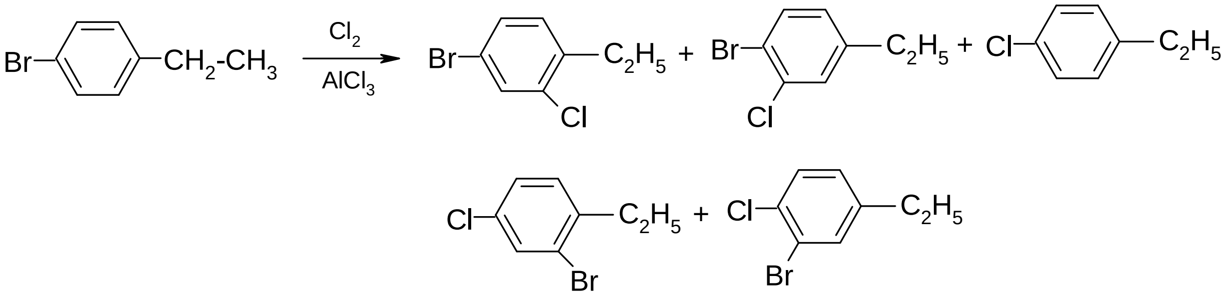
(d) d-1 free radical substitution (upon exposure to light or on heating)



small quantity of  and polychlorination

d-2 in the presence of electrophilic substitution catalysts:

and as side reaction products:



(e) e-1

$$CH_3CH_2CH_2OH + H_2SO_4 \xrightarrow[heat]{-\,H_2O} C_3H_7OSO_3H + H_2O \longrightarrow (C_3H_7O)_2SO_2 + H_2O$$

e-2

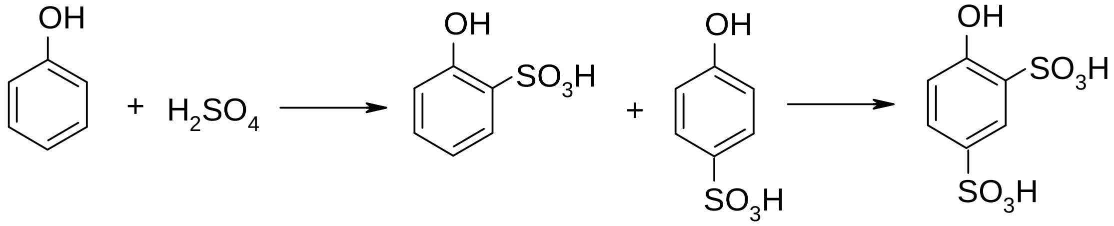
$$2\ C_3H_7OH + H_2SO_4 \xrightarrow[heat]{} C_3H_7OC_3H_7\ (\text{excess of } C_3H_7OH) + H_2O$$

e-3

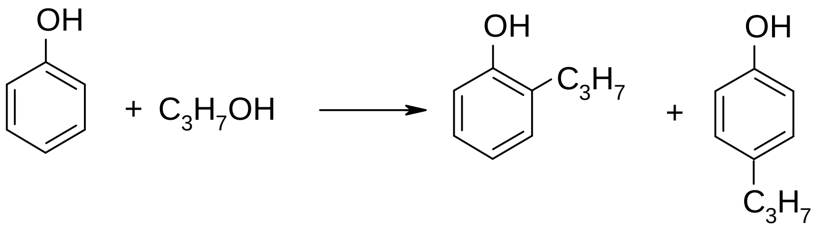
$$3\ CH_3CH_2CH_2OH \xrightarrow[heat]{H_2SO_4} CH_3CH{=}CH_2 \xrightarrow[H_2SO_4]{.H_2O} CH_3CH(OH)CH_3$$

(in e-1 and e-2)

e-4



e-5



polyalkylation n- and iso-

e-6 partial oxidation of C_3H_7OH and C_6H_5OH with subsequent condensation or esterification

PROBLEM 4

Compound **X** contains nitrogen and hydrogen. Strong heating of 3.2 g of **X** leads to its decomposition without the formation of a solid residue. The resulting mixture of gases is partially absorbed by sulphuric acid (the volume of the gaseous mixture decreased by a factor of 2.8). The non-absorbed gas, that is a mixture of hydrogen and nitrogen, occupies under normal conditions a volume of 1.4 dm^3 and has a density of 0.786 g dm^{-3}.

Determine the formula of compound **X**.

SOLUTION

If the density of the mixture of N_2 and H_2 is known, its composition can be determined as

$$0.786 \times 22.4 \times (n + 1) = 28\,n + 2$$

Hence n = 1.5. The mass of the mixture is 0.786 g dm^{-3} × 1.4 ≈ 1.1 g. Consequently, the mixture of gases absorbed by sulphuric acid (these gases could be NH_3 and N_2H_4) had an average molar mass of

$$\frac{3.2\text{ g} - 1.1\text{ g}}{1.4\text{ dm}^3 \times (2.8 - 1)} \times 22.4\text{ dm}^3\text{ mol}^{-1} \cong 18.67\text{ g mol}^{-1}$$

while NH_3 corresponds to 17 g mol^{-1}.

This means that the absorbed gaseous products consist of a mixture of NH_3 and N_2H_4. The composition of the absorbed fraction is

$$\frac{32 + 17\,n}{n + 1} = 18.67$$

n = 8, i. e. 8 NH_3 + N_2H_4.

As a result, the overall ratio of the components of the mixture is as follows:

8 NH_3 + N_2H_4 + 3 N_2 + 2 H_2 which corresponds to a composition of the initial substance X: N : H = (2 + 8 + 6) : (4 + 24 + 4) = 1 : 2.

The initial substance X is hydrazine N_2H_4.

PROBLEM 5

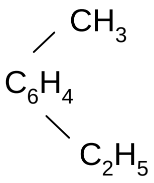
Benzene derivative **X** has the empirical formula C_9H_{12}. Its bromination in the light leads to the formation of two monobromo derivatives in approximately identical yield. Bromination in the dark in the presence of iron also gives two monobromo derivatives. If the reaction is carried out to a higher degree, the formation of four dibromo derivatives may occur.

Suggest the structure for compound **X** and for the bromination products. Write schemes for the reactions.

SOLUTION

The compound with the empirical formula C_9H_{12} can be:

$C_6H_5 – C_3H_7$ I



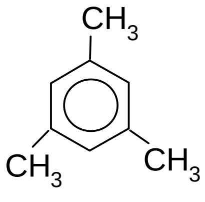
$C_6H_4(CH_3)(C_2H_5)$

II

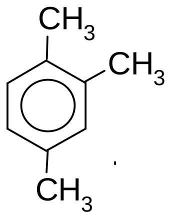
$C_6H_3(CH_3)_3$ III

Under the action of bromine in the light without catalysts, bromination of the aliphatic portion will occur, predominantly on the carbon atoms bonded to the aromatic nucleus. When the reaction is conducted in the dark in presence of iron, the latter is converted to $FeBr_3$ and catalyzes the bromination of the aromatic ring.

Compound **X** cannot be **I** (as then only one monobromo derivative would be formed in the light); it cannot be one of the isomers IIIa, IIIb either.

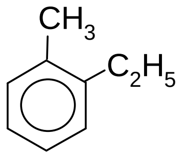


IIIa - Only one monobromo derivative is possible in the bromination of the CH_3 groups.

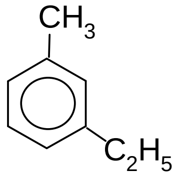


IIIb - Three different monobromo derivatives are possible under the same conditions.

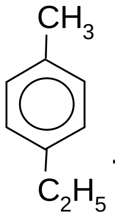
Thus, selection must be made from the following four structures:



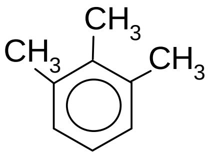
IIa



IIb



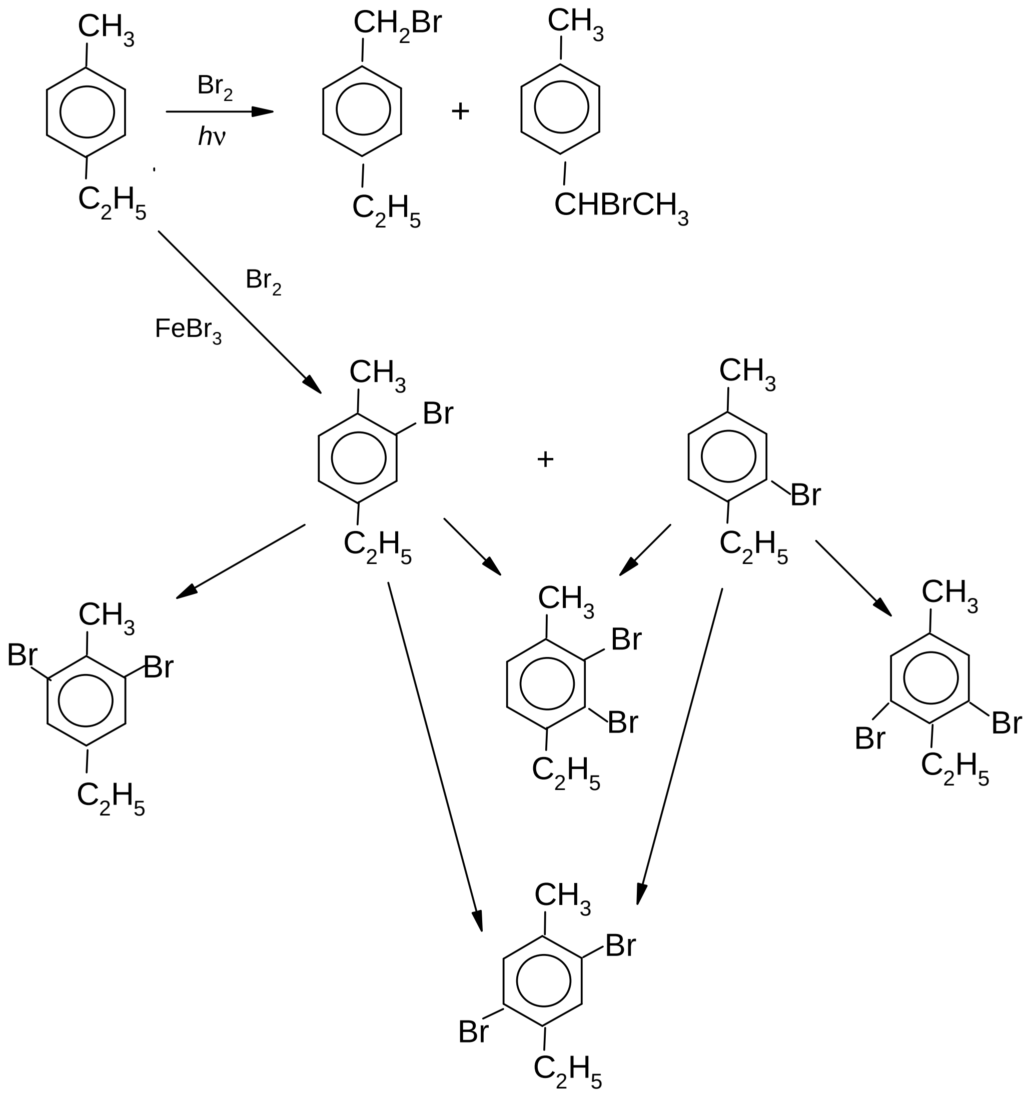
IIc



IIIc

The condition that two monobromo derivatives can be formed in the dark, rules out structures IIa and IIb. The condition of the possibility of four dibromo derivatives rules out structure IIIc. Hence, the only possible structure of compound **X** is IIc.

The scheme of the bromination reaction (next page):


Br2
hν
Br2
FeBr3
+
+

PROBLEM 6

130 g of an unknown metal M were treated with excess of a dilute nitric acid. Excess hot alkaline solution was added to the resulting solution and 1.12 dm^3 of a gas evolved (normal conditions).

What metal M was dissolved in the nitric solution?

SOLUTION

The gas that evolved during the reaction with the alkaline solution was ammonia. Therefore, one of the products resulting from dissolution of the metal M in the acid is ammonium nitrate. Thus, the reaction equations will have the form:

$$8\ M + 10\ n\ HNO_3 \rightarrow 8\ M(NO_3)_n + n\ NH_4NO_3 + 3\ n\ H_2O$$

$$n\ NH_4NO_3 + n\ NaOH \rightarrow n\ NH_3 + n\ H_2O + NaNO_3$$

Hence, the scheme:

$$\begin{array}{lcl} x & & 1.12\ dm^3 \\ 8\ M & \longrightarrow & n\ NH_3 \\ 8\ A_r(M) & & n\ 22,4\ dm^3 \end{array}$$

where n is the valency of the metal (oxidation number of M^{n+}) and $A_r(M)$ is the relative atomic mass of the metal.

$8\ A_r(M) \Rightarrow 22.4 \times n$

$13\ g \Rightarrow 1.12\ dm^3$

$$A_r(M) = \frac{13\ g \times 22.4\ dm^3 \times n}{8\ g \times 1{,}12\ dm^3} = 32.5\ n$$

If	n = 1	then	$A_r(M) = 32.5$	no metal
	n = 2		$A_r(M) = 65$	zinc
	n = 3		$A_r(M) = 97{,}5$	none
	n = 4		$A_r(M) = 130$	none

Answer: The unknown metal is zinc.

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

10 numbered test tubes, 20 cm^3 each, contain 0.1 M solutions of the following substances: barium chloride, sodium sulphate, potassium chloride, magnesium nitrate, sodium orthophosphate, barium hydroxide, lead nitrate, potassium hydroxide, aluminium sulphate, sodium carbonate. Using only these solutions as reagents, determine in which of the numbered test tubes each of the above given substances, is found.

Draw up a plan of the analysis and write equations of the reactions to be carried out. Do not forget to leave at least 2 cm^3 of the solutions in each test tube for checking. If in the course of the analysis an additional quantity of a solution is needed, you may ask the teacher to give it to you but in such case you will lose some points.

SOLUTION

Table:

	$BaCl_2$	Na_2SO_4	KCl	$Mg(NO_3)_2$	Na_3PO_4	$Ba(OH)_2$	$Pb(NO_3)_2$	KOH	$Al_2(SO_4)_3$	Na_2CO_3
$BaCl_2$	▨	↓	—	—	↓	—	↓	—	↓	↓
Na_2SO_4	↓	▨	—	—	—	↓	↓	—	—	—
KCl	—	—	▨	—	—	—	↓	—	—	—
$Mg(NO_3)_2$	—	—	—	▨	↓	↓	—	↓	—	↓
Na_3PO_4	↓	—	—	↓	▨	↓	↓	—	↓	—
$Ba(OH)_2$	—	↓	—	↓	↓	▨	↓	—	↓	↓
$Pb(NO_3)_2$	↓	↓	↓	—	↓	↓	▨	↓	↓	↓
KOH	—	—	—	↓	—	—	↓	▨	↓	—
$Al_2(SO_4)_3$	↓	—	—	—	↓	↓	↓	↓	▨	↓
Na_2CO_3	↓	—	—	↓	—	↓	↓	—	↓	▨

Using the table, the entire problem cannot be solved at once: all the precipitates are white and there are substances that form the same number of precipitates. From the number of precipitates only KCl (1), $Mg(NO_3)_2$ (4), and $Pb(NO_3)_2$ (8) can be determined immediately.

Furthermore, Na_2SO_4 and KOH (giving three precipitates each) can be differentiated via the reaction with $Mg(NO_3)_2$ ($Mg(OH)_2$).

$Ba(OH)_2$ and $Al_2(SO_4)_3$ (giving 6 precipitates each): through the reaction with KOH ($Al(OH)_3$).

$BaCl_2$, Na_3PO_4 and Na_2CO_3 (giving 5 precipitates each): first the reaction with Na_2SO_4 indicates $BaCl_2$. Then the reaction with $BaCl_2$: $Al_2(SO_4)_3$ yields $AlCl_3$ ($BaSO_4$ precipitate is flittered off). Evolution of CO_2 and formation of $Al(OH)_3$ in the reaction with $AlCl_3$ solution indicates Na_2CO_3.

PROBLEM 2 (practical)

Determine the mass of potassium permanganate in the solution you are given. You are provided with hydrochloric acid of a given concentration, a potassium hydroxide solution of an unknown concentration, an oxalic acid solution of an unknown concentration, and a sulphuric acid solution (2 N).

Equipment and reagents:
A burette for titration, indicators (methyl orange, lithmus, phenolphthalein), pipettes (volumes 10, and 15 or 20 cm^3), 2 volumetric flasks (250 cm^3), 2 titration flasks (100 – 150 cm^3).

12th

IChO

International Chemistry Olympiad

6 theoretical problems
3 practical problems

THE TWELFTH
INTERNATIONAL CHEMISTRY OLYMPIAD
13–23 JULY 1980, LINZ, AUSTRIA

THEORETICAL PROBLEMS

PROBLEM 1

The dissociation of (molecular) chlorine is an endothermic process, ΔH = 243.6 kJ mol^{-1}. The dissociation can also be attained by the effect of light.

1.1 At what wavelength can the dissociating effect of light be expected?

1.2 Can this effect also be obtained with light whose wavelength is smaller or larger than the calculated critical wavelength?

1.3 What is the energy of the photon with the critical wavelength?

When light that can effect the chlorine dissociation is incident on a mixture of gaseous chlorine and hydrogen, hydrogen chloride is formed. The mixture is irradiated with a mercury UV-lamp (λ = 253.6 nm). The lamp has a power input of 10 W. An amount of 2 % of the energy supplied is absorbed by the gas mixture (in a 10 litre vessel). Within 2.5 seconds of irradiation 65 millimoles of HCl are formed.

1.4 How large is the quantum yield (= the number of product molecules per absorbed photons)?

1.5 How can the value obtained be (qualitatively) explained? Describe the reaction mechanism.

SOLUTION

1.1 $\lambda_1 = \frac{c}{\nu_1}$ from $\Delta H = N_A\, h\, \nu_1$ it follows that

$$\lambda_1 = \frac{c\, N_A\, h}{\Delta H} = \frac{3\,.\,10^8 \times 6.02\,.\,10^{23} \times 6.6\,.\,10^{-34}}{2.436\,.\,10^5} = 4.91\,.\,10^{-7}\ \text{m} = 491\,\text{nm}$$

1.2 Short-wave light is effective, as its photons have a greater energy than required whereas the photons of longer-wavelength light are too poor in energy to affect the dissociation.

1.3 $E_1 = h\,\nu_1 = \dfrac{h\,c}{\lambda_1} = \dfrac{6.6\times10^{-34}\times 3\,.\,10^{8}}{4.91\,.\,10^{-7}} = 4.03\,.\,10^{-19}$ J

1.4 The quantum yield $Ø = \dfrac{\text{the number of HCl molecules formed}}{\text{the number of absorbed photons}}$

$$Ø = \frac{n(\text{HCl})\times N_A}{\dfrac{E_{tot}}{\dfrac{h\,c}{\lambda_2}}} = \frac{6.5\times10^{-2}\times 6.02\times10^{23}}{\dfrac{0.2\times 2.5}{\dfrac{6.6\times10^{-34}\times 3\times10^{8}}{2.536\times10^{-7}}}} = 6.1\times10^{4}$$

The energy input = 10 × 0.02 = 0.2 W

1.5 The observed quantum yield is based on a chain mechanism.

The start of reaction chain: $Cl_2 + h\nu \rightarrow 2\,Cl\bullet$

The propagation of the chain: $2\,Cl\bullet + H_2 \rightarrow HCl + 2\,H\bullet$

$H\bullet + Cl_2 \rightarrow HCl + Cl\bullet$

The chain termination mainly by: $2\,H\bullet \rightarrow H_2$

$2\,Cl\bullet \rightarrow Cl_2$

$H\bullet + Cl\bullet \rightarrow HCl$

PROBLEM 2

Water gas equilibrium

The homogeneous gas reaction

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$

is termed the water gas reaction.

Problems:

2.1 Calculate the Gibbs reaction energy, ΔG^0_{1000}, for the water gas reaction at 1000 K from the reaction enthalpy: $\Delta H^0_{1000} = 35040 \text{ J mol}^{-1}$
and the reaction entropy: $\Delta S^0_{1000} = 32.11 \text{ J mol}^{-1} K^{-1}$.

2.2 What is the value of the equilibrium constant K_p of the water gas reaction at 1000 K?

2.3 What are the values of the equilibrium constants K_x and K_c (x: mole fraction, c: concentration in mol dm^{-3} at the same temperature (1000 K)? (Note: The gas behaves ideally.)

2.4 A mixture of gases containing 35 vol. % of H_2, 45 vol. % of CO and 20 vol. % of H_2O vapours is heated to 1000 K. What is the composition of the mixture after the establishment of the water gas equilibrium?

2.5 Calculate the reaction enthalpy value, ΔH^0_{1400}, at 1400 K from the reaction enthalpy value, ΔH^0_{1000}, and the values of the molar heat, c^0_p, (valid in the temperature range 1000 K to 1400 K)

$\Delta H^0_{1000} = 35040 \text{ J mol}^{-1}$

$c^0_p(CO_2) = 42.31 + 10.09\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$

$c^0_p(H_2) = 27.40 + 3.20\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$

$c^0_p(CO) = 28.34 + 4.14\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$

$c^0_p(H_2O) = 30.09 + 10.67\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$

(It holds that $\int_a^b (c_1 + c_2 x)dx = c_1(b-a) + 0.5\,c_2(b^2 - a^2)$)

2.6 What can you say on the basis of the above findings on ΔH^0 about the shift in the water gas equilibrium with increasing temperature?

SOLUTION

2.1 ΔH^0_{1000} = 35040 J

ΔS^0_{1000} = 32.11 J mol^{-1} K^{-1}

$\Delta G^0_{1000} = \Delta H^0_{1000} - T\,\Delta S^0_{1000} = 35040 - 1000 \times 32.11 = 2930$ J

2.2 $\Delta G^0 = -RT \ln K_p$

$$\ln Kp = -\frac{\Delta G^0}{RT} = -\frac{2930}{8314} = -0.352418$$

$K_p = 0.7030$

2.3 As the numbers of moles do not change in the reaction, the reaction is independent on the concentration and pressure and therefore, $K_x = K_p = K_c$ (dimensionless). Volume fraction and mole fraction are identical in an ideal gas.

2.4 The original composition of the gas:

$x_{0,CO} = 0.45; \quad x_{0,H_2} = 0.35; \quad x_{0,H_2O} = 0.20; \quad x_{0,CO_2} = 0.00;$

If the mole fraction of the CO_2 formed at the equilibrium is denoted as x then the equilibrium concentrations can be obtained from:

$CO: \quad x_{0,CO} - x$

$CO_2: \quad x$

$H_2O: \quad x_{0,H_2O} - x$

$H_2: \quad x_{0,H_2} + x$

$$K_p = K_x = \frac{x_{CO}\ x_{H_2O}}{x_{CO_2}\ x_{H_2}} = \frac{(x_{0,CO} - x)(x_{0,H_2O} - x)}{x\,(x_{0,H_2} + x)} = 0.703$$

$$(x_{0,CO} - x)(x_{0,H_2O} - x) = K\,(x_{0,H_2} + x)\,x$$

$$x_{0,CO}\ x_{0,H_2O} - x(x_{0,H_2O} + x_{0,CO}) + x^2 = K\,x\,x_{0,H_2} + K\,x^2$$

where $K = K_x$

$$x^2\,(1 - K) - x\,(x_{0,H_2O} + x_{0,CO} + K\,x_{0,H_2}) + x_{0,CO}\ x_{0,H_2O} = 0$$

On substitution of the numerical values,

x^2 (1 – 0.703) – x (0.20 + 0.45 + 0.703 × 0.35) + 0.45 × 0.20 = 0

$0.297\,x^2 - 0.89605\,x + 0.09 = 0$

$x^2 - 3.01703\,x + 0.303030 = 0$

$$x_{1,2} = 1.508515 \pm \sqrt{2.275618 - 0.303030} = 1.508515 \pm \sqrt{1.972588}$$

$x = 1.508515 \pm 1.404488 = 0.104027$

(The plus sign leads to a solution that has no physical significance, $x > 1$.)

$x = 0.104$

$x_{CO} = 0.346$; $x_{H_2} = 0.454$; $x_{H_2O} = 0.096$; $x_{CO_2} = 0.104$;

2.5 $\Delta C_p^0 = C_p^0(CO) + C_p^0(H_2O) - C_p^0(CO_2) - C_p^0(H_2)$

$= -11.28 + 1.52 \times 10^{-3}\ T\ J\ K^{-1}\ mol^{-1}$

$$\Delta H_{1400}^0 = \Delta H_{1000}^0 + \int_{1000}^{1400} C_p^0\, dT = \Delta H_{1000}^0 + \int_{1000}^{1400} (c_1 + c_2 T)\, dT$$

$$= \Delta H_{1000}^0 + c_1 (1400 - 1000) + 0.5\, c_2\, (1.96 \times 10^6 - 1 \times 10^6) =$$

$$= \Delta H_{1000}^0 - 11.28 \times 400 + (1.52 \times 10^{-3} \times 4.8 \times 10^5) =$$

$$= \Delta H_{1000}^0 - 4512 + 729.6 =$$

$$= 35040 - 4512 + 729.6 = 31258\ J$$

On the basis of the van't Hoff reaction isobar

$$\frac{\partial \ln K_p}{\partial T} = \frac{\Delta H}{RT^2}$$

2.6 $\ln K_p$ increases with increasing temperature for positive (endothermic) heat of reaction, i.e. the equilibrium shifts with increasing temperature in favour of the reaction products, CO and H_2O.

PROBLEM 3

(Chemistry of ions, stoichiometry, redox reactions)

A white crystalline solid compound **A** exhibits the following reactions:

1) The flame of a Bunsen burner is intensively yellow coloured.
2) An aqueous solution of **A** is neutral. Dropwise addition of sulphurous acid (an SO_2 solution) leads to a deep brown solution that is discoloured in the presence of excess of sulphurous acid.
3) If an $AgNO_3$ solution is added to the discoloured solution obtained by 2) and acidified with HNO_3, a yellow precipitate is obtained that is insoluble on addition of NH_3, but can be readily dissolved by adding CN^- or $S_2O_3^{2-}$.
4) If an aqueous solution of **A** is treated with KI and dilute H_2SO_4 a deep brown solution is formed that can be discoloured by addition of sulphurous acid or a $Na_2S_2O_3$ solution.
5) An amount of 0.1000 g of **A** is dissolved in water, then 0.5 g KI and a few cm^3 of dilute H_2SO_4 are added. The deep brown solution formed is titrated with 0.1000 M $Na_2S_2O_3$ solution until the solution is completely discoloured. The consumption is 37.40 cm^3.

Problems:

3.1 What elements are contained in the compound **A**?

3.2 What compounds can be considered as present on the basis of reactions 1) to 4)? Calculate their molar masses.

3.3 Formulate the reactions corresponding to 2) to 4) for the compounds considered and write the corresponding equations in the ionic form.

3.4 Decide on the basis of 5) which compound is present.

SOLUTION

3.1 The solid must contain Na and I. The yellow colouration of the flame of the Bunsen burner indicates the presence of Na. A yellow silver salt that is dissolved only by strong complexing agents such as CN^- or $S_2O_3^{2-}$, must be AgI.

3.2 Reactions 1) to 4) indicate an Na salt of an oxygen containing acid of iodine:

Both SO_2 and I^- are oxidised. While in the first case I^- is formed with an intermediate of I_2 (or I_3^-, brown solution), in the second I_2 (or I_3^-) is formed.

As the solution of **A** is neutral, $NaIO_3$ and $NaIO_4$ come into consideration.

$M(NaIO_3) = 22.99 + 126.905 + 3 \times 16.000 = 197.895 = 197.90\ g\ mol^{-1}$

$M(NaIO_4) = 22.99 + 126.905 + 4 \times 16.000 = 213.895 = 213.90\ g\ mol^{-1}$

3.3 $2\ IO_3^- + 4\ H_2O + 5\ SO_2 = 5\ HSO_4^- + 3\ H^+ + I_2$

$I_2 + SO_2 + 2\ H_2O = HSO_4^- + 3\ H^+ + 2\ I^-$

$IO_4^- + 7\ I^- + 8\ H^+ = 4\ I_2 + 4\ H_2O$

$IO_3^- + 5\ I^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$

$I_2 + 2\ S_2O_3^{2-} = 2\ I^- + S_4O_6^{2-}$

3.4 Experiment: 0.1000 g of the compound **A** ...... 3.740×10^{-3} moles $S_2O_3^{2-}$

1st hypothesis: The compound is $NaIO_3$.

1 mole $NaIO_3$ . . . . 197.90 g $NaIO_3$ . . . . 6 moles $S_2O_3^{2-}$

0.1000 g $NaIO_3$ . . . . $\dfrac{0.1000 \times 6}{197.90} = 3.032 \times 10^{-3}$ moles $S_2O_3^{2-}$

The hypothesis is false.

2nd hypothesis: The compound is $NaIO_4$.

mole $NaIO_4$ . . . . 213.90 g $NaIO_4$ . . . . 8 moles $S_2O_3^{2-}$

0.1000 g $NaIO_4$ . . . . $\dfrac{0.1000 \times 8}{213.90} = 3.740 \times 10^{-3}$ moles $S_2O_3^{2-}$

The compound **A** is $NaIO_4$.

PROBLEM 4

(Organic chemistry, stereochemistry)

Carbonic acid **A** with an overall formula of $C_5H_8O_2$ yields two geometric isomers, cis (**A'**) and trans (**A"**). On hydrogenation with Pt/H_2 the same racemic carboxyl acid **B** is obtained from <u>both</u> stereoisomers that can be separated into enantiomers (+)-**B** and (-)-**B**. **A'** and **A"** rapidly react with one mole of bromine in CCl_4 in the dark at 20 °C to yield **C**.

Problems:

4.1 What is the constitution of **A** and **B**?

4.2 Write the stereo formulae for **A'** and **A"** and the Fischer projection formulae for the enantiomer **B** (not considering the signs (+) or (-)).

4.3 How many stereo isomers of **C** are simultaneously formed when **A'** and **A"** are treated with bromine?

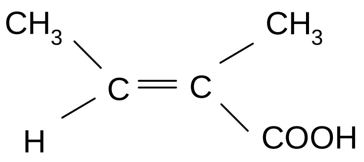
4.4 Briefly, give reasons for your answer to c).

4.5 Write the Fischer projection formulae and one Newman projection formula (conformation) for all the stereoisomers of **C**. Denote those that are mutually enantiomeric and diastereoisomeric.

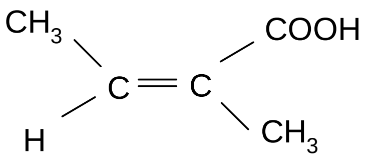
SOLUTION

4.1 **A**: $CH_3\text{-}CH\text{=}C(CH_3)\text{-}COOH$; **B**: $CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}COOH$

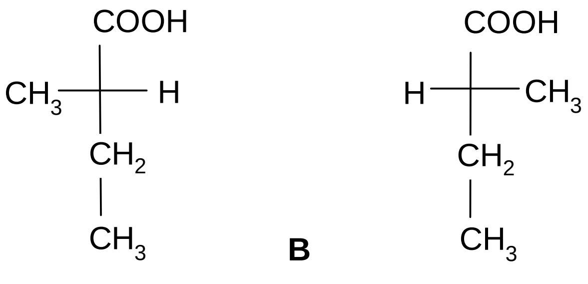
4.2



A'



A"

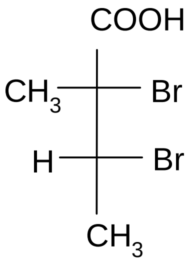


B

4.3 Always two (see e): 1 to 4

4.4 The addition of bromine to the alkene gives trans compound under the given conditions. On the addition, two (non-identical) asymmetrical **C** atoms (chirality centres) are formed yielding together $2^2 = 4$ stereo isomers of which always two are mutually enantiomeric.

4.5 from **A'**:



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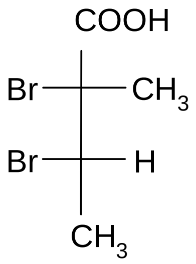
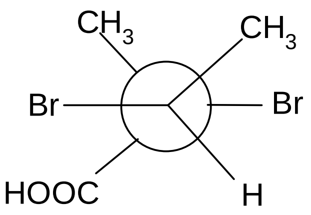
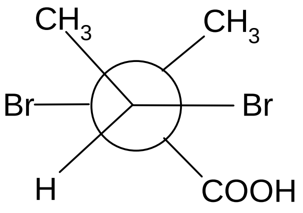
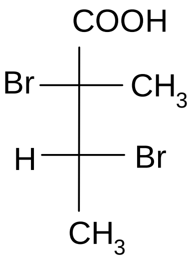






from **A"**:



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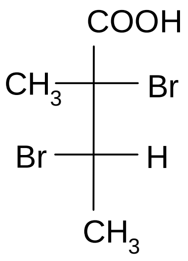
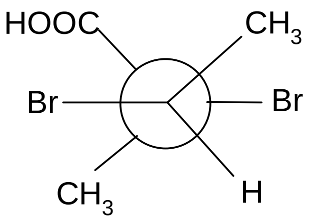
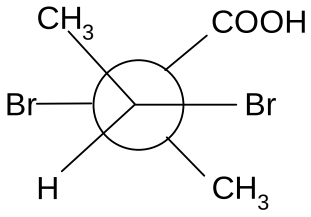






1 and 2 or 3 and 4 are enantiomeric. 1 to 3 and 4, and 2 to 3 and 4 are diastereomeric

PROBLEM 5

(Inorganic chemistry)

From 20 mg of partially methylated disilane, $Si_2H_{6-x}(CH_3)_x$, 27.8 cm^3 of hydrogen are evolved during alkaline hydrolysis at 294 K and 97400 Pa.

5.1 Why the Si-Si bond of the disilane reacts during hydrolysis?

5.2 Why the Si-H bonds of the disilane react during hydrolysis?

5.3 Calculate the degree of substitution x of the methylated disilane.

5.4 Write the complete reaction equation for the hydrolysis.

5.5 How many isomers can form the calculated compound? Give the structural formula for each isomer.

SOLUTION

5.1 The Si-Si bond is coordination unsaturated and thus, has a tendency to react with nucleophilic reagents with the bond breakage.

5.2 Similar to all compounds with negatively polarised hydrogen, this bond also reacts with protons from water with formation of elemental hydrogen.

5.3 $(CH_3)_xSi_2H_{6-x}$

Molecular mass:	2 Si	2×28.086
	(6-x) H	$(6-x) \times 1.008$
	x CH_3	$x \times 15.035$

$$56.172 + 1.008\,(6 - x) + 15.035\,x = 62.22 + 14.027\,x$$

Sample mass**:** 20 mg $\Rightarrow \dfrac{20}{62.22 + 14.027\,x}$ mmol

Hydrogen evolved: $n = \dfrac{pV}{RT}$ mmol H_2 (V in cm^3)

$$n = \frac{0.974 \times 27.8}{0.08314 \times 294} \text{ mmol}$$

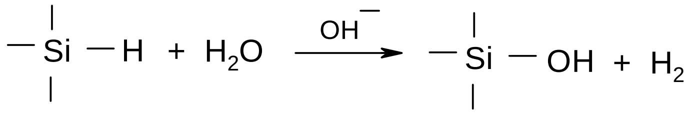
(SiH) (SiSi)

$$(6 - x + 1) \times \frac{20}{62.22 + 14.027\,x} = \frac{0.974 \times 27.8}{0.08314 \times 294}$$

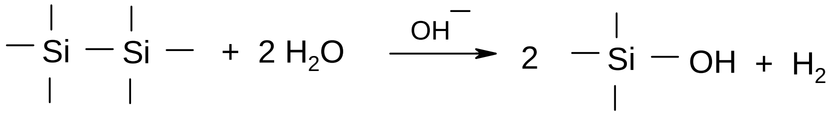
x = 1.9999

Hence, the degree of substitution = 2

5.4



$$-\overset{|}{\underset{|}{Si}}-H + H_2O \xrightarrow{OH^-} -\overset{|}{\underset{|}{Si}}-OH + H_2$$



$$-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{Si}}- + 2\ H_2O \xrightarrow{OH^-} 2\ -\overset{|}{\underset{|}{Si}}-OH + H_2$$

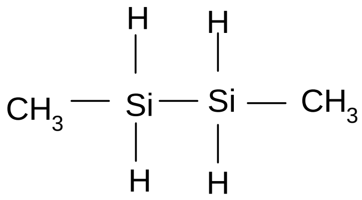
Hence (for a symmetrical isomer):

$Si_2H_4(CH_3)_2 + 6\ H_2O \rightarrow 2\ Si(OH)_3CH_3 + 5\ H_2$ / n

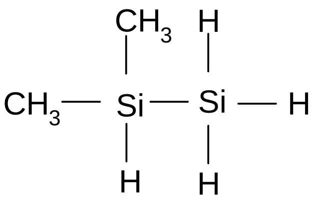
$2\ n\ Si(OH)_3CH_3 \rightarrow [Si_2O_3(CH_3)_2]_n + 3\ n\ H_2O$

$n\ Si_2H_4(CH_3)_2 + 3\ n\ H_2O \rightarrow [Si_2O_3(CH_3)_2]_n + 5\ n\ H_2$

5.5 Two:



$$CH_3-\overset{H}{\underset{H}{Si}}-\overset{H}{\underset{H}{Si}}-CH_3$$



$$CH_3-\overset{CH_3}{\underset{H}{Si}}-\overset{H}{\underset{H}{Si}}-H$$

PROBLEM 6

(Organic chemistry, syntheses)

Benzaldehyde and malonic acid reacted in pyridine at 80 °C yielding (among others) CO_2 and compound **A** in a yield of ca. 80 % of the theoretical value. Catalytic hydrogenation of 1.48 g **A** on Pt at room temperature and normal pressure yielded **B** with a consumption of 0.25 litre of hydrogen. On reaction of **B** with a polyphosphoric acid (the Friedel-Crafts' conditions) compound **C** can be isolated accompanied by two acidic, isomeric side products. The side products **Da** and **Db** can be formed in a greater amount at a high concentration of **B** in the reaction medium, and can be suppressed by dilution.

The elemental analysis of **C** yields 81.8 % of carbon and 6.1 % of hydrogen. The corresponding values for **Da** and **Db,** identical within the experimental error, are 76.6 % and 6.4 %, respectively. An amount of 2.82 g **Da**, as well as **Db** requires ca. 100 cm^3 0.1 N potassium hydroxide solution for its neutralization. **C** can be purified by distillation (b. p. 243 – 245 °C) and then exhibits a melting point of 40 ° C and density of 1.09 g/cm^3. The relative molecular mass can be obtained by mass spectrometry and its value is 132.

Using this information solve the following problems:

6.1 The structural formula of **A**.

6.2 The structural formula of **B**.

6.3 The structural formula of **C**.

6.4 The structural formulae of **Da** and **Db**.

6.5 Give an alternative pathway for the synthesis of **A** using the simplest possible starting materials and forming at least one C–C bond.

6.6 Give an alternative pathway for the synthesis of **B** using the simplest possible starting materials and forming at least one C–C bond.

6.7 Give structural formulae for the products of the following reactions:

a) **C** + hydroxylamine (with acid catalysis) →

b) **C** + phenylmagnesium bromide (C_6H_5MgBr) and subsequent treatment under acidic conditions →

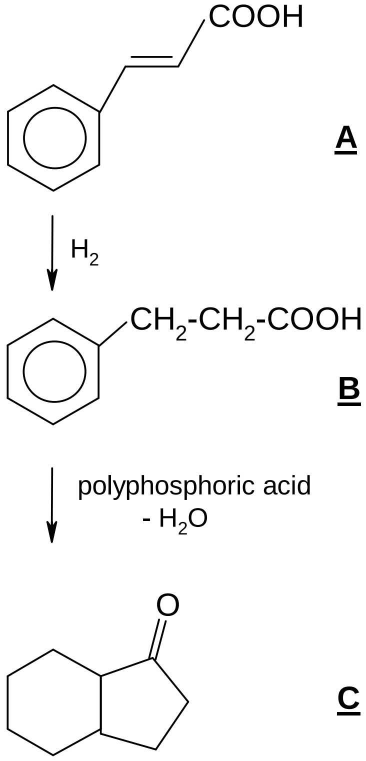
c) **C** + benzaldehyde + $C_2H_5O^-$ Na^+ →

SOLUTION

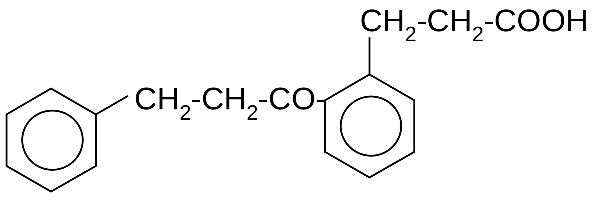
6.1 Condensation

6.2 Hydrogenation

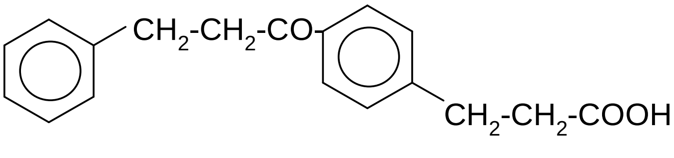
6.3 Intramolecular cyclization



6.4 In addition to **C** two positional isomers **Da** and **Db** are formed.

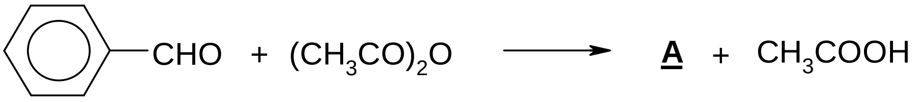


Da

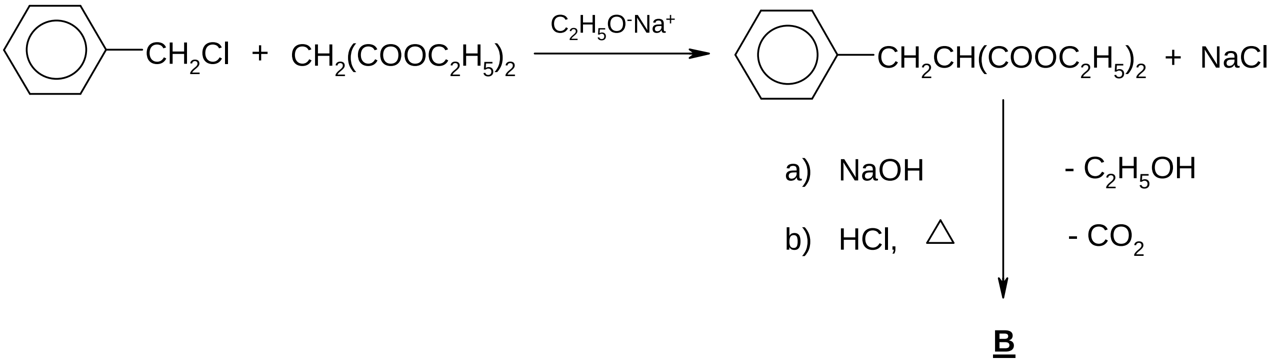


Db

6.5 For example, Perkin reaction: Treatment of benzaldehyde with acetic acid anhydride:

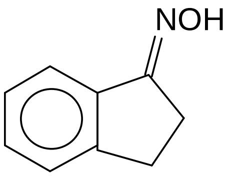


6.6 For example, by malonic ester synthesis

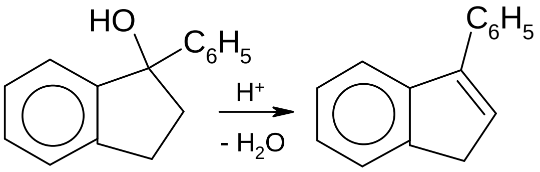


6.7 Reactions a), b), and c) are typical reactions of the carbonyl group.

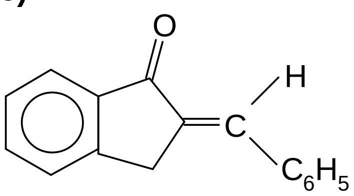
a)



b)



c)



(**E**)

two stereoisomers
(syn and anti)

two stereoisomers

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Qualitative organic analysis

Four different substances that all occur in the nature, are present in 4 test tubes. Find two substances that form basic components of fodders and human foodstuff. Only these two substances are to be identified. Propose the names and structural formulae for those two substances on the basis of combustion tests, solubility experiments, identification of the functional groups and the determination of the melting point.

As an aid the following can be used:

A table of melting points, the Thiele apparatus for melting point determination, a solubility scheme and the following reagents:

diethyl ether, $NaHCO_3$ (5 %), NaOH (2 M), HCl (2 M), H_2SO_4 conc., H_3PO_4 conc., ethanol, Tollens' reagents, (an ammoniac Ag solution), Fehling's solution I and II, phenylhydrazine hydrochloride, β-naphthol, $NaNO_2$ (solid) $Ca(OH)_2$ sat., $FeCl_3$ (5 %), ice, 2,4-dinitrophenylhydrazine, ninhydrine solution (1 % alk.), Seliwanoff's reagent (resorcinol/HCl), phloroglucine.

The requirements: An exact description of the experiments, reaction equations (or reaction schemes where the equation cannot be given) for the reaction required for the identification, the names and the structural formulae of the two test substances.

APPENDIX 1

Determination of the melting point by the Thiele apparatus

A finely pulverized sample is placed in a capillary that is sealed at one side, to a height of 2 – 4 mm. To fill the capillary, it is immersed in the sample. The sample is cautiously wiped off the capillary walls and the content of the capillary is brought to the bottom by cautious tapping. Then the capillary is placed in the opening so that the sample is at the height of the mercury bead of the thermometer. As the heat transmitter, suitable high-boiling silicone oil is used in this apparatus.

To determine the melting point of an unknown organic substance, an approximate melting range is sought first. Thus the heating is carried out according to the figure at about 5 °C/min. For an exact determination another sample is brought about 10 °C below the determined melting range at about 5 °C/min and then the temperature is very slowly, 1 – 2 °C/min., brought to complete melting. The temperature, at which the substance is clearly melted, is taken as the melting point.

APPENDIX 2

Tables of melting points (MP, in °C) and boiling points (BP, in °C)

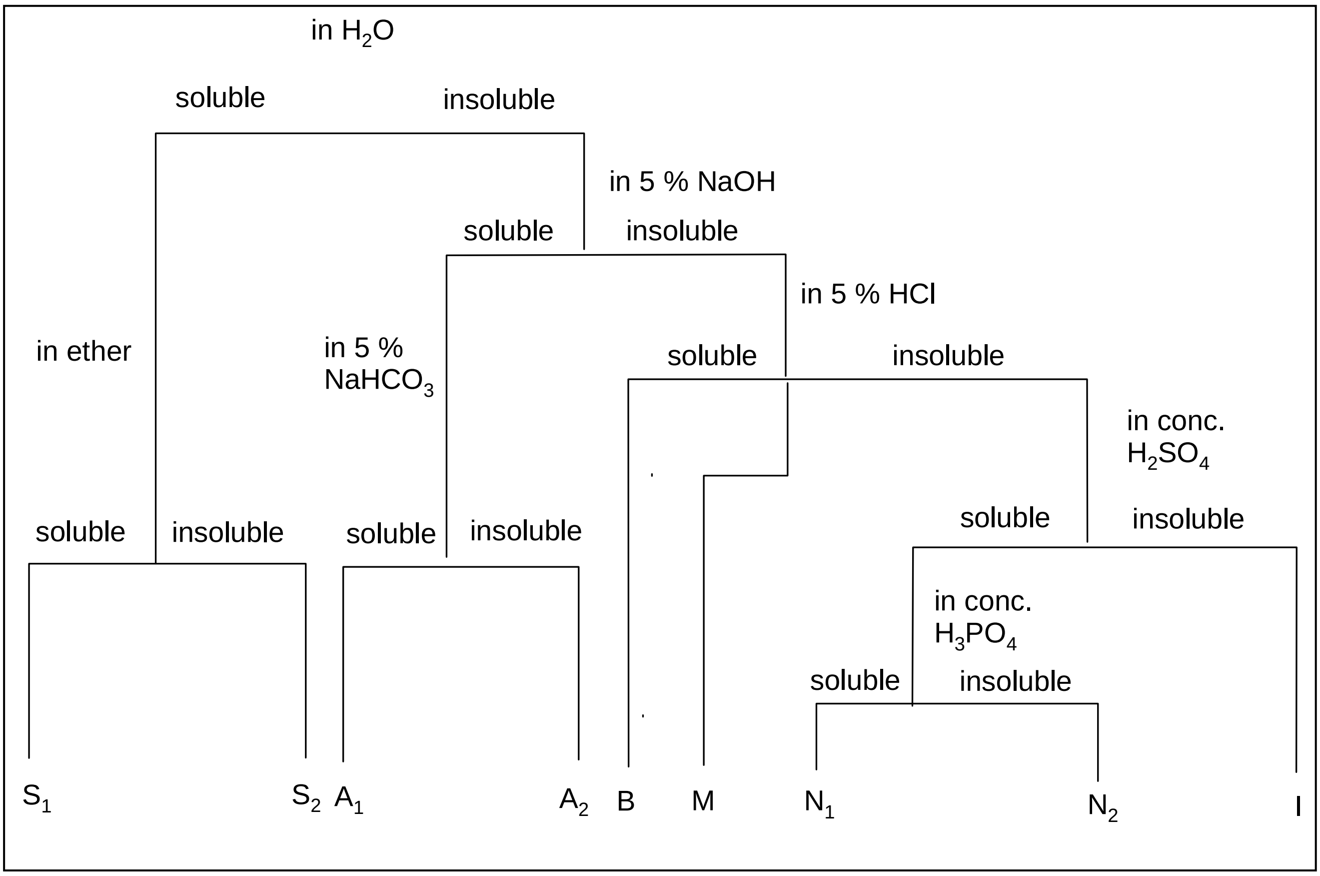
Compound	MP	BP	Compound	MP	BP
ALDEHYDES					
Pentanal	-	103	Acrolein	-	52
Benzaldehyde	-	179	Furfurol	-	161
Salicylaldehyde	-	196	o-Chlorobenzaldehyde	11	214
o-Nitrobenzaldehyde	44	-	α-Naphthaldehyde	34	-
p-Dimetylamino-bemzaldehyde	74	-	Vanillin	81	-
ALCOHOLS					
terc.-Butanol	25	82	Propanol-1	-	97
n-Pentanol	-	136	Ethyleneglycol	-	197
Cyclohexylalcohol	-	160	Butanediol-1,4	-	230
Triphenylcarbinol	165	-	Glycerine	-	290
AMINES					
Diethylamide	-	56	Morpholine	-	130
Cyclohexylamine	-	134	α-Naphthylamine	50	300
Aniline	-	184	p-Bromoaniline	66	-
Diphenylamine	54	-	m-Nitraniline	114	-
o-Phenylenediamine	102	-	p-Aminophenol	186 D	-
ACIDS					
Palmitic acid	63	-	n-Valeric acid	-	186
Stearic acid	70	-	Oleic acid	14	222
Oxalic acid (. 2 H_2O)	101	-	Mandelic acid	118	-
Acetylsalicylic acid	135	-	Benzoic acid	122	-
Phthalic acid	203	-	Malonic acid	135	-
Anthranilic acid	146	-	S-Naphthoic acid	185	-
Glycine	232 D	-	p-Hydroxybenzoic acid	215	-

HALOGENDERIVATIVES					
n-Butyl bromide	-	100	p-Dichlorobenzene	53	-
Cyclohexyl iodide	-	179	p-Bromotoluene	28	185
Trichloroethylene	-	67	Hexachlorobenzene	230	-
KETONES					
Diethyl ketone	-	102	Methylisobutyl ketone	-	118
Cyclohexanone	-	156	Acetophenone	20	202
Benzophenone	49	-	p-Bromoacetophenone	51	-
Benzil	95	-	dl-Camphor	178	-
CARBOHYDRATES					
d-Ribose	95 D	-	β-Maltose	165	-
α-d-Glucose	146	D	β-d-Fructose		
Saccharose	180	-	α-Lactose		
HYDROCARBONS					
n-Heptane	-	99	Pentene-2	-	36
cis-Decaline	-	194	Cyclohexene	-	84
Cumol	-	216	Diphenyl	70	-
Anthracene	216	-	Styrene	-	146
MERCAPTANS – THIOPHENOLS					
n-Amylmercaptan	-	126	p-Thiocresol	-	200
Thiophenol	-	169	p-Bromothiophenol	74	-
PHENOLS					
p-Cresol	36	200	o-Nitrophenol	45	-
α-Naphthol	94	-	Resorcinol	110	-
Pyrocatechol	105	-	β-Naphthol	123	-
Picric acid	122	-	Phloroglucine	218	-
ACID DERIVATIVES					
Acetyl bromide	-	77	Acetamide	82	-
Butyric acid chloride	-	102	N-Methylacetanilide	102	-
4-Nitrobenzoylchloride	73	-	Urea	132	-
Butyric acid ethylester	-	121	Sodium formate	255	-
Malonic acid diethylester	-	199	Al-Acetate	200 – 320 D	-
Palmitic acid cetylester	54	-	Ba-Propionate	ca. 300	-

D after the number denotes decomposition.

APPENDIX 3

Solubility scheme



S_1: Substances with higher volatility;
All low molecular alcohols, aldehydes, ketones, acids, amines, nitriles and acid chlorides.

S_2: Substances with low volatility, often distillable without decomposition: polyols, salts, hydroxyaldehydes and hydroxyketones, carbohydrates, amino- and hydroxyl acids.

A_1: Substances with low volatility: higher molecular acids, nitrophenols.

A_2: Substances with high boiling points: Phenols, primary and secondary nitro compounds, sulfonamides, weak acids.

B: Substances with high boiling points, distillable with water vapour: Basic compounds, amines (with maximum of a few aryl groups), hydrazine.

M: Low volatility substances:
Neutral compounds, tertiary nitro compounds, nitroaniline, azo- and azoxy compounds, nitrito-, nitrato-, sulphuric-, and phosphoric acid esters.

N_1: Substances with small volatility:
Alcohols, aldehydes, methyl ketones and esters with less than 9 C atoms, neutral compounds, ethers, olephins.

N_2: Substances with a very low volatility:
Alcohols, aldehydes, ketones, esters and thioalcohols with more than 9 C atoms, neutral compounds, ethers, olephins.

I: Substances with low boiling point:
Inert compounds, hydrocarbons, halogenoalkanes.

APPENDIX 4

Preparation of the reagents

Tollen's reagent

Mix 0.5 cm^3 2 M NaOH + 1 cm^3 0.1 M $AgNO_3$ in 2 M NH_3.

Fehling's reagent

I: 1.73 g $CuSO_4 . 5 H_2O$ in 25 cm^3 of water
II: 8.5 g Seignette salt + 2.5 g NaOH in 25 cm^3 H_2O

Seliwanoff's reagent

125 g resorcinol is dissolved in 250 cm^3 of diluted HCl (83 cm^3 conc. HCl + 167 cm^3 H_2O), preparing only a necessary amount.

Phenylhydrazine solution

0.5 g of phenylhydrazine hydrochloride + 0.5 cm^3 glacial acetic acid in 2 cm^3 H_2O are shaken until a clear solution is obtained.

2,4-dinitrophenylhydrazine solution,

2 cm^3 of conc. H_2SO_4 are added to 0.4 g of 2,4-dinitrophenylhydrazine and then, with stirring and shaking, 3 cm^3 of H_2O are added. To the warm solution, 10 cm^3 of 95 % ethanol are added.

SOLUTION

In the four test tubes, pure sodium chloride, D-fructose, palmitic acid (hexadecanoic acid), and vanillin were present. D-fructose, as a building block of cane sugar, and palmitic acid, as the building block of most animal and plant fats, were identified.

a) *Fructose*

Melting range: 102 – 105 °C

Combustion test: Carbonizes during combustion with caramel smell.

Solubility: Readily soluble in water, insoluble in diethyl ether.

Identification of the functional groups:

Aldehydic group:

1. With Fehling's reagent

   The oxidation of the carbonyl group with simultaneous reduction of Cu(II) to Cu(I).

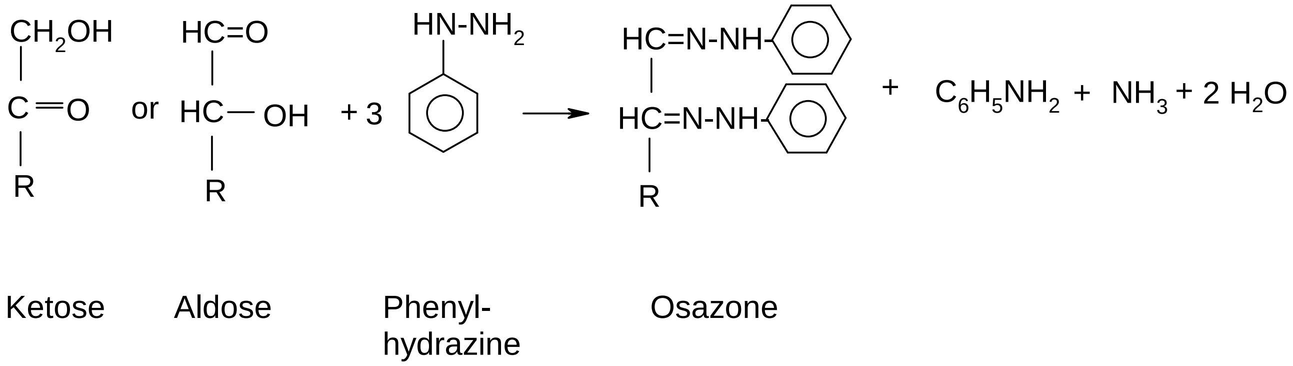
   $$–CHO + 2\,[Cu(C_4H_4O_6)_2]^{2-} + 5\,OH^- \rightarrow –COOH + Cu_2O\downarrow + 3\,H_2O + 4\,C_4H_4O_6^{2-}$$

2. With Tollen's reagent

   The oxidation to the carboxyl group with simultaneous reduction of Ag(I) to Ag.

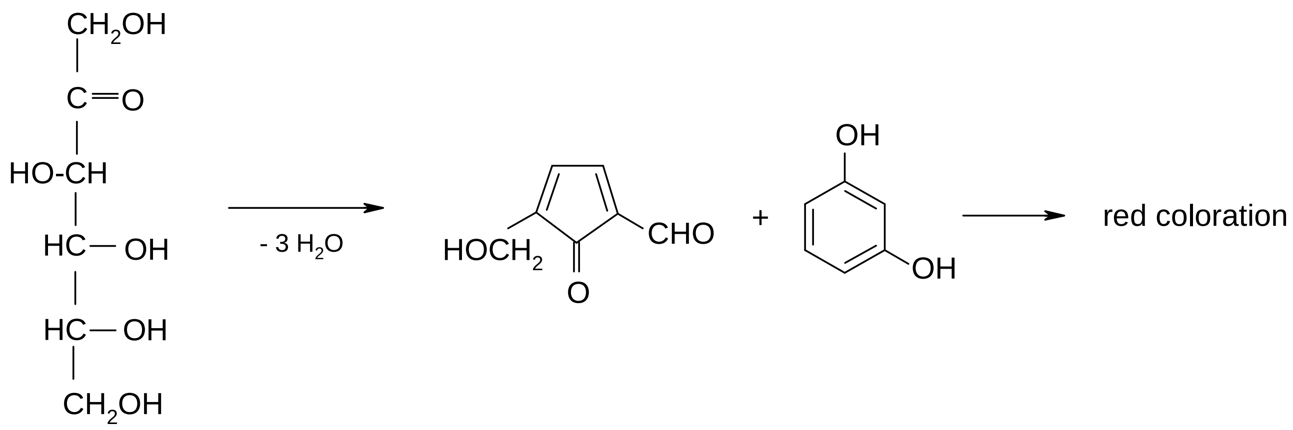
   $$–CHO + 2\,[Ag(NH_3)_2]^+ + 2\,OH^- \rightarrow –COOH + 2\,Ag + 4\,NH_3 + H_2O$$

Osazone formation (indication of monoses)



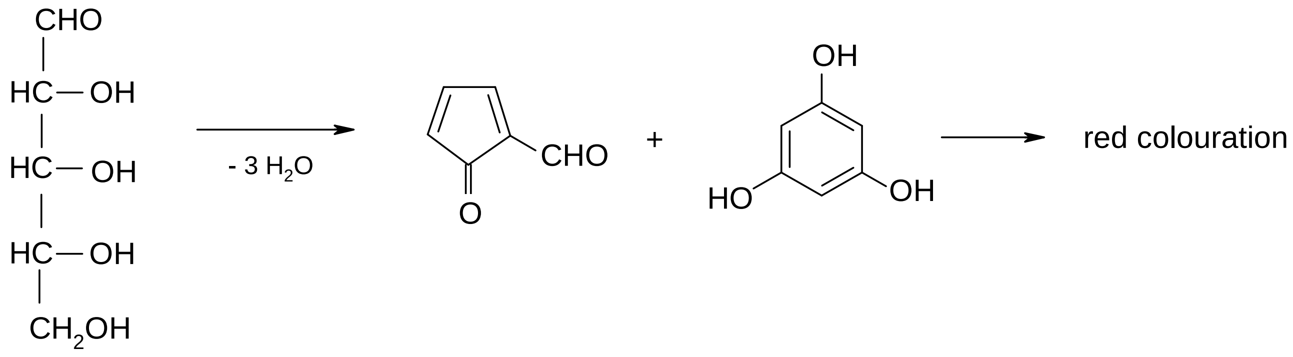
Test for ketohexoses (Saliwanoff's reaction)

Ketohexoses form, with heating in acidic solution, 5-hydroxy-methylfurfural that condenses with resorcinol to red-coloured substances.

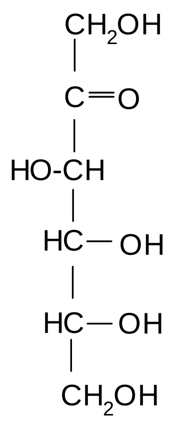


Test for pentoses (Tollens test)

Pentoses, in contrast to hexoses, form furfural in acidic solution that condenses with phloroglucine to give red coloured substances.



Name: The above reactions, the solubility behaviour and the melting range indicate that this substance is D-fructose, a building block of cane sugar.



When giving the configuration, use the Fischer projection.

b) *Palmitic acid*

Melting range: 60 – 63 °C

Combustion test: Burns with yellowish, slightly smoking flame.

Solubility: Insoluble in water, very well soluble in 2 M NaOH, less soluble in 5 % $NaHCO_3$.

Identification of the functional groups:

From alkaline solution a colourless substance is precipitated by Ca^{2+}:

$2\ R\text{-}COO^- + Ca^{2+} \rightarrow (R\text{-}COO)_2Ca$

On the basis of flammability the solubility behaviour and the precipitation of the calcium salt from alkaline solution one can conclude that the substance is an organic carboxyl acid. The melting range indicates palmitic acid = hexadecanoic acid.

$CH_3\text{-}(CH_2)_{14}\text{-}COOH$

PROBLEM 2 (practical)

In 10 reagent bottles are 10 different pure metal samples. By evaluating the solubility and by the following identification, only the six following elements are to be specified by their sample numbers:

calcium, iron, aluminium, zinc, magnesium, tin.

It is expected to specify:

a) the symbol of the identified metal and the corresponding bottle number,

b) a reaction equation for dissolution of each of the six metals,

c) an unambiguous verbal proof or a proof in the form of a chemical equation.

The following chemicals are at disposal:

HCl conc., HCl (2 M), H_2SO_4 (2 M), CH_3COOH (2 M), NaOH (2 M), NH_3 (2 M), NH_4SCN (0.2 M), CH_3COONa (conc.), 3 % H_2O_2, Na_2CO_3 (0.2 M), H_2S (0.1 M), Na_2HPO_4 (0.2 M), $K_4Fe(CN)_6$ (0.2 M), $K_3Fe(CN)_6$ (0.2 M), morin (in CH_3OH), quinalizarine (in C_2H_5OH), urotropine (20 %), dithizone (in CCl_4), $(NH_4)_2C_2O_4$ (0.2 M), distilled water.

SOLUTION

a) See the list at the end.

b) $Ca + 2\ H_2O \rightarrow Ca(OH)_2 + H_2$

$Ca + 2\ H_3O^+ \rightarrow Ca^{2+} + H_2 + 2\ H_2O$

$Fe + 2\ H_3O^+ \rightarrow Fe^{2+} + H_2 + 2\ H_2O$

$Al + 3\ H_3O^+ \rightarrow Al^{3+} + 3/2\ H_2 + 3\ H_2O$

$Al + NaOH + 3\ H_2O \rightarrow Na^+ + [Al(OH)_4]^- + 3/2\ H_2$

$Zn + 2\ H_3O^+ \rightarrow Zn^{2+} + H_2 + 2\ H_2O$

$Zn + 2\ NaOH + 2\ H_2O \rightarrow 2\ Na^+ + [Zn(OH)_4]^{2-} + H_2$

$Mg + 2\ H_2O \rightarrow Mg(OH)_2 + H_2$

$Mg + 2\ H_3O^+ \rightarrow Mg^{2+} + H_2 + 2\ H_2O$

$Sn + 2\ H_3O^+ \rightarrow Sn^{2+} + H_2 + 2\ H_2O$

$Sn + 2\ NaOH + 2\ H_2O \rightarrow 2\ Na^+ + [Sn(OH)_4]^{2-} + H_2$

c) Ca^{2+}: white precipitate with $(NH_4)_2C_2O_4$;

Fe^{2+}: blue with $K_3[Fe(CN)_6]$
or after oxidation with H_2O_2: blue with $K_4[Fe(CN)_6]$ or red with NH_4SCN, or brown precipitate with NaOH;

Al^{3+}: green fluorescence with morine (in dilute acetic acid);

Zn^{2+}: white precipitate with H_2S (in acetic acid),
with dithizone red coloration of the organic phase;

Mg^{2+}: with quinalizarine light blue lacquer (alkali solution);

Sn^{2+}: with H_2S deep brown precipitate (weakly acidic solution),
blue fluorescence of the outer wall of a glass bottle filled with cold water that was immersed in an Sn^{2+} solution (acidified with HCl),
in the flame of a Bunsen burner ("light test").

PROBLEM 3 (practical)

Titrimetric determination of potassium peroxodisulfate ($K_2S_2O_8$)

A) *Principle*

To the sample ($K_2S_2O_8$) a measured amount of a Fe(II) solution is added in an excess. The excess of the Fe(II) is determined using a standard $KMnO_4$ solution.

B) *Procedures*

1) Determination of the concentration of the Fe(II) solution, $[Fe(NH_4)_2(SO_4)_2]$

To a titration vessel, 25.0 cm^3 Fe(II) solution, 10 cm^3 H_3PO_4 (ca. 3.7 mol dm^{-3}) and 10 cm^3 H_2SO_4 (ca. 1 mol dm^{-3}) are added and titrated with the $KMnO_4$ solution to a pink colouration. The concentration of $KMnO_4$ in the solution is exactly 0.02 mol dm^{-3}. Two titrations are carried out and the consumption of the $KMnO_4$ solution is recorded. The mean value (= V_1) is to be given.

2) Determination of peroxodisulfate in the same solution

a) The dissolved sample is diluted with distilled water to 100 cm^3 in a standard flask and mixed.

b) 25.0 cm^3 of this solution are transferred to a titration vessel and mixed with 10 cm^3 H_3PO_4 (ca. 3.7 mol dm^{-3}), 10 cm^3 H_2SO_4 (ca. 1 mol dm^{-3}) and 25.0 cm^3 of the Fe(II) solution. The mixture is allowed to stand for 5 minutes and titrated with the $KMnO_4$ solution (0.02 mol dm^{-3}) to a pink colourization. Two titrations are carried out and the consumption of the $KMnO_4$ solution is recorded. The mean value (= V_2) is to be given.

C) *Calculation and evaluation*

I) Reaction equations: To be given:

Partial equations with electron balance

Overall equations

1) Reaction of peroxodisulfate with Fe(II):

Partial:

a) $S_2O_8^{2-}$ . . . .

b) Fe^{2+} . . . .

c) Overall reaction:

2) Reaction of Fe(II) with permanganate:

Partial:

a) Fe^{2+} . . . .

b) MnO_4^- . . . .

c) Overall reaction:

II) The concentration of the Fe(II) solution

1) Give the consumption of the $KMnO_4$ solution (cm^3) for 25.0 cm^3 of the Fe(II) solution (= V_1); See Procedure 1.
2) Calculate the concentration of the Fe(II) solution in mol dm^{-3}.

III) Determination of $K_2S_2O_8$

1) Give the consumption of the $KMnO_4$ solution in the back-titration of the excess Fe(II) solution in cm^3 (= V_2); See Procedure 2.
2) How many mg $K_2S_2O_8$:
3) Calculate the concentration of $K_2S_2O_8$ in the sample solution in mol dm^{-3}.

SOLUTION

I/1/a $S_2O_8^{2-} + 2\,e^- \rightarrow 2\,SO_4^{2-}$

b) $Fe^{2+} \rightarrow Fe^{3+} + e^-$ /. 2

c) $S_2O_8^{2-} + 2\,Fe^{2+} \rightarrow 2\,SO_4^{2-} + 2\,Fe^{3+}$

I/2/a $Fe^{2+} \rightarrow Fe^{3+} + e^-$ /. 2

$MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$

$5\,Fe^{2+} + MnO_4^- \rightarrow 5\,Fe^{3+} + Mn2^+ + 4\,H_2O$

II/1 V_1 cm^3 $KMnO_4$ (0.02 mol dm^{-3}) / 25 cm^3 Fe(II)

2. $c(Fe^{2+}) = \dfrac{V_1 \times 0.02 \times 5}{25} = \ldots\ldots\text{ mol/l}$

III/1 V_2 cm^3 $KMnO_4$ solution (0.02 mol dm^{-3}) for the back titration

2.

$$\alpha)\quad \frac{(V_1 - V_2)\times 0.02\times 5}{1000}\times\frac{270.33}{2} = \ldots\ldots\text{ mg } K_2S_2O_8$$

$$\beta)\quad \frac{25\times c(\text{Fe}^{2+}) - V_2\times 0.02\times 5}{1000}\times\frac{270.33}{2} = \ldots\ldots\text{ mg } K_2S_2O_8$$

3.

$$\alpha)\quad \frac{(V_1 - V_2)\times 0.02\times 5}{1000}\times\frac{40}{2} = \ldots\ldots\text{ mol } K_2S_2O_8\,/\,\text{dm}^3$$

$$\beta)\quad \frac{25\times c(\text{Fe}^{2+}) - V_2\times 0.02\times 5}{1000}\times\frac{40}{2} = \ldots\ldots\text{ mol / dm}^3$$

13th

International Chemistry Olympiad

6 theoretical problems
3 practical problems

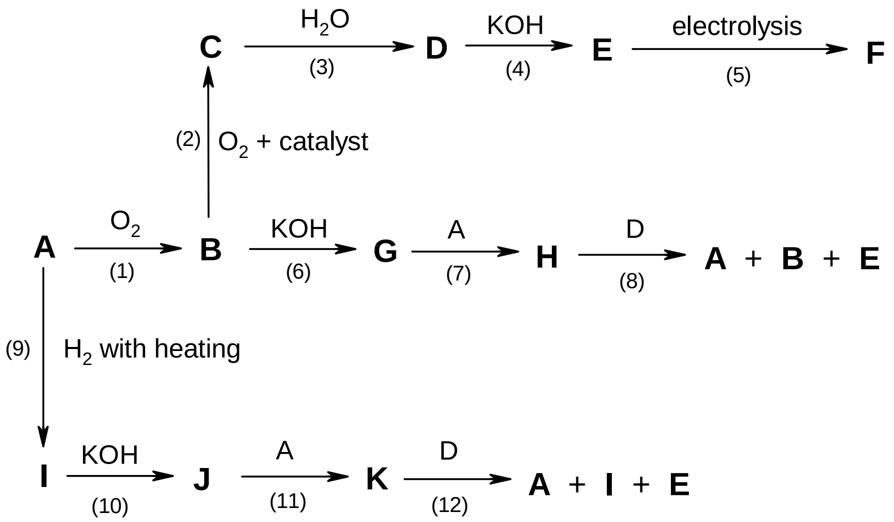
THE THIRTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
13–23 JULY 1981, BURGAS, BULGARIA

THEORETICAL PROBLEMS

PROBLEM 1

The sample **A** participates in the transformations in scheme 1. Only the products containing **A** are shown in the scheme 1.

Scheme 1



a) Substance **A** is a solid and is insoluble in water.

b) Substances **B** and **I** are gases soluble in water.

c) Substances **E**, **F**, **J** and **K** are solid and soluble in water.

d) Aqueous solutions of **B**, **G**, **H**, **I**, **J** and **K** react with **F**, the products in all cases being **E** and **D**.

e) The following transformations occur during the interaction with an aqueous solution of iodine:

$$\mathbf{B} \xrightarrow{(19)} \mathbf{D} \qquad \mathbf{G} \xrightarrow{(20)} \mathbf{E} \qquad \mathbf{H} \xrightarrow{(21)} \mathbf{L}$$

$$\mathbf{I} \xrightarrow[(22)]{} \mathbf{A} \qquad \mathbf{J} \xrightarrow[(23)]{} \mathbf{A} \qquad \mathbf{K} \xrightarrow[(24)]{} \mathbf{A}$$

Write the chemical equations for the above interactions and balance them.

SOLUTION

Schéma:

(1) $S + O_2 \rightarrow SO_2$

(2) $2\ SO_2 + O_2 \rightarrow 2\ SO_3$

(3) $SO_3 + H_2O \rightarrow H_2SO_4$

(4) $2\ KOH + H_2SO_4 \rightarrow K_2SO_4 + 2\ H_2O$

(5) $2\ SO_4^{2-} - 2\ e- \rightarrow S_2O_8^{2-}$

(6) $SO_2 + 2\ KOH \rightarrow K_2SO_3 + H_2O$

(7) $K_2SO_3 + S \rightarrow K_2S_2O_3$

(8) $K_2S_2O_3 + H_2SO_4 \rightarrow K_2SO_4 + S + SO_2 + H_2O$

(9) $H_2 + S \rightarrow H_2S$

(10) $H_2S + 2\ KOH \rightarrow K_2S + 2\ H_2O$

(11) $K_2S + x\ S \rightarrow K_2S_{(x+1)}$

(12) $K_2S_{(x+1)} + H_2SO_4 \rightarrow K_2SO_4 + x\ S + H_2S$

d)

(13) $SO_2 + 2\ H_2O + K_2S_2O_8 \rightarrow K_2SO_4 + 2\ H_2SO_4$

(14) $K_2SO_3 + H_2O + K_2S_2O_8 \rightarrow 2\ K_2SO_4 + H_2SO_4$

(15) $K_2S_2O_3 + 5\ H_2O + 4\ K_2S_2O_8 \rightarrow 5\ H_2SO_4 + 5\ K_2SO_4$

(16) $H_2S + 4\ H_2O + 4\ K_2S_2O_8 \rightarrow 5\ H_2SO_4 + 4\ K_2SO_4$

(17) $K_2S + 4\ H_2O + 4\ K_2S_2O_8 \rightarrow 4\ H_2SO_4 + 5\ K_2SO_4$

(18) $K_2S_{(x+1)} + (4x + 1)\ H_2O + 4\ x\ K_2S_2O_8 \rightarrow 5\ x\ H_2SO_4 + (4x + 1)\ K_2SO_4$ (+S)

e)

(19) $SO_2 + 2\ H_2O + I_2 \rightarrow H_2SO_4 + 2\ HI$

(20) $K_2SO_3 + H_2O + I_2 \rightarrow K_2SO_4 + 2\ HI$

(21) $2\ K_2S_2O_3 + I_2 \rightarrow 2\ KI + K_2S_4O_6$

(22) $H_2S + I_2 \rightarrow 2\ HI + S$

(23) $K_2S + I_2 \rightarrow 2\ KI + S$

(24) $K_2S_x + I_2 \rightarrow 2\ KI + x\ S$

A: S **B**: SO_2 **C**: SO_3 **D**: H_2SO_4
E: K_2SO_4 **F**: $K_2S_2O_8$ **G**: K_2SO_3 **H**: $K_2S_2O_3$
I: H_2S **J**: K_2S **K**: K_2S_x **L**: $K_2S_4O_6$

PROBLEM 2

Maleic acid (H_2A) is a weak dibasic acid. The correlation between the relative quantities of H_2A, HA^-, A^{2-}:

$$\alpha_0 = \frac{c(H_2A)}{c} \qquad \alpha_1 = \frac{c(HA^-)}{c} \qquad \alpha_2 = \frac{c(A^{2-})}{c}$$

and pH values of the solution show that:

a) $\alpha_0 = \alpha_1$ for pH = 1.92

b) $\alpha_1 = \alpha_2$ for pH = 6.22

Find:

2.1 The values of the dissociation constants of maleic acid for the first (K_1) and the second (K_2) degree of dissociation.

2.2 The values of α_0, α_1, and α_2 for pH = 1.92 and pH = 6.22.

2.3 What is the value of pH when α_1 attains a maximum value? Find the maximum value of α.

2.4 Which of the acid-base indicators in the table are suitable for titration of a 0.1 M solution of maleic acid (as a monobasic and as a dibasic acid) with 0.1 M NaOH?

Fill in the table 1 with the correct answers.

All the activity coefficients should be considered equal to 1.

Indicator	pH interval
Methyl green	0.1 – 2.0
Tropeolin 00	1.4 – 3.2
β-Dinitrophenol	2.4 – 4.0
Bromphenol blue	3.0 – 4.6
Congo red	3.0 – 5.2
Methyl red	4.4 – 6.2
Bromphenol red	5.0 – 6.8
Bromthymol blue	6.0 – 7.6
Phenol red	6.8 – 8.0
Cresol red	7.2 – 8.8

Thymol blue	8.0 – 9.6
Phenolphthalein	8.2 – 10.0
Alizarine yellow	10.1 – 12.1
Tropeolin 0	11.0 – 13.0
1,3,5-Trinitrobenzene	12.2 – 14.0

Table 1

2.1		K_1 =
		K_2 =
2.2	pH = 1.92	α_0 =
		α_1 =
		α_2 =
	pH = 6.22	α_0 =
		α_1 =
		α_2 =
2.3		pH =
		α_1 =
2.4	First indicator equivalence point	pH =
		1. 2. 3. 4.
	Second indicator equivalence point	pH =
		1. 2. 3. 4.

SOLUTION

2.1 $\alpha_0 = \alpha_1$

$K_1 = c_{H^+} = 10^{-pH} = 10^{-1.92} = 1.20 \times 10^{-2}$

$\alpha_1 = \alpha_2$

$K_2 = c_{H^+} = 10^{-pH} = 10^{-6.22} = 6.02 \times 10^{-7}$

2.2 $F = c_{H^+}^2 + K_1\, c_{H^+} + K_1\, K_2$

pH = 1.92; $c_{H^+} = 10^{-1.92} = 1.20 \times 10^{-2}$; $F = 2.88 \times 10^{-4}$

$$\alpha_0 = \alpha_1 = \frac{c_{H^+}^2}{F} = \frac{(1.20\,.\,10^{-2})^2}{2.88\,.\,10^{-4}} = 0.500$$

$$\alpha_2 = \frac{K_1\,K_2}{F} = \frac{1.20\,.\,10^{-2} \times 6.02\ .\ 10^{-7}}{2.88\,.\,10^{-4}} = 2.51 \times 10^{-5}$$

pH = 6.22; $c_{H^+} = 10^{-6.22} = 6.02 \times 10^{-7}$; $F = 1.445 \times 10^{-8}$

$$\alpha_0 = \frac{c_{H^+}^2}{F} = \frac{(6.02 \times 10^{-7})^2}{1.445 \times 10^{-8}} = 2.51 \times 10^{-5}$$

$$\alpha_1 = \alpha_2 = \frac{K_1\,K_2}{F} = \frac{1.20 \times 10^{-2} \times 6.02 \times 10^{-7}}{1.445 \times 10^{-8}} = 0.500$$

2.3 $$(\alpha)'_{c_{H^+}} = \frac{\left[K_1 F - K_1\, c_{H^+}\,(2c_{H^+} + K_1\right]}{F^2} = 0$$

$c_{H^+}^2 = K_1 K_2$

$c_{H^+} = \sqrt{(1.20 \times 10^{-2} \times 6.02 \times 10^{-7}} = 8.50 \times 10^{-5}$ mol dm^{-3}

$F = 1.034 \times 10^{-6}$ pH = 4.07

$$\alpha_1 = \frac{K_1\, c_{H^+}}{F} = \frac{1.20 \times 10^{-2} \times 8.50 \times 10^{-5}}{1.034 \times 10^{-6}} = 0.986$$

The pH and the maximum value of α_1 can be estimated either by calculating α_1 for a set of values of c_{H^+} in the interval $1 \times 10^{-5} - 1 \times 10^{-3}$ mol dm^{-3} or from the condition that α_1 can reach a maximum value only when $\alpha_0 = \alpha_2$

2.4 The first equivalence point is found in the region of the α_1 maximum at pH = 4.07 where $c_{HA^-} = c_{NaHA} = \dfrac{0.1}{2} = 0.05\ \text{mol dm}^{-3}$.

The second equivalence point is found in the alkaline region, where:

$$c_{OH^-} = c_{HA^-} \qquad c_{A^{2-}} = \frac{0.1}{3} - c_{OH^-} = 0.0333$$

$$c_{H+}^2 = \frac{K_2\, c_{HA^-}}{c_{A^{2-}}} = \frac{K_2\, c_{OH^-}}{c_{A^{2-}}} = \frac{K_2\, K_w}{c_{H^+}\, c_{A^{2-}}}$$

$$c_{H^+} = \sqrt{\frac{K_2\, K_w}{c_{A^{2-}}}} = \sqrt{\frac{6.02\times10^{-7} \times 1\times10^{-14}}{0.0333}} = 4.25\times10^{-10}\ \text{mol dm}^{-3}$$

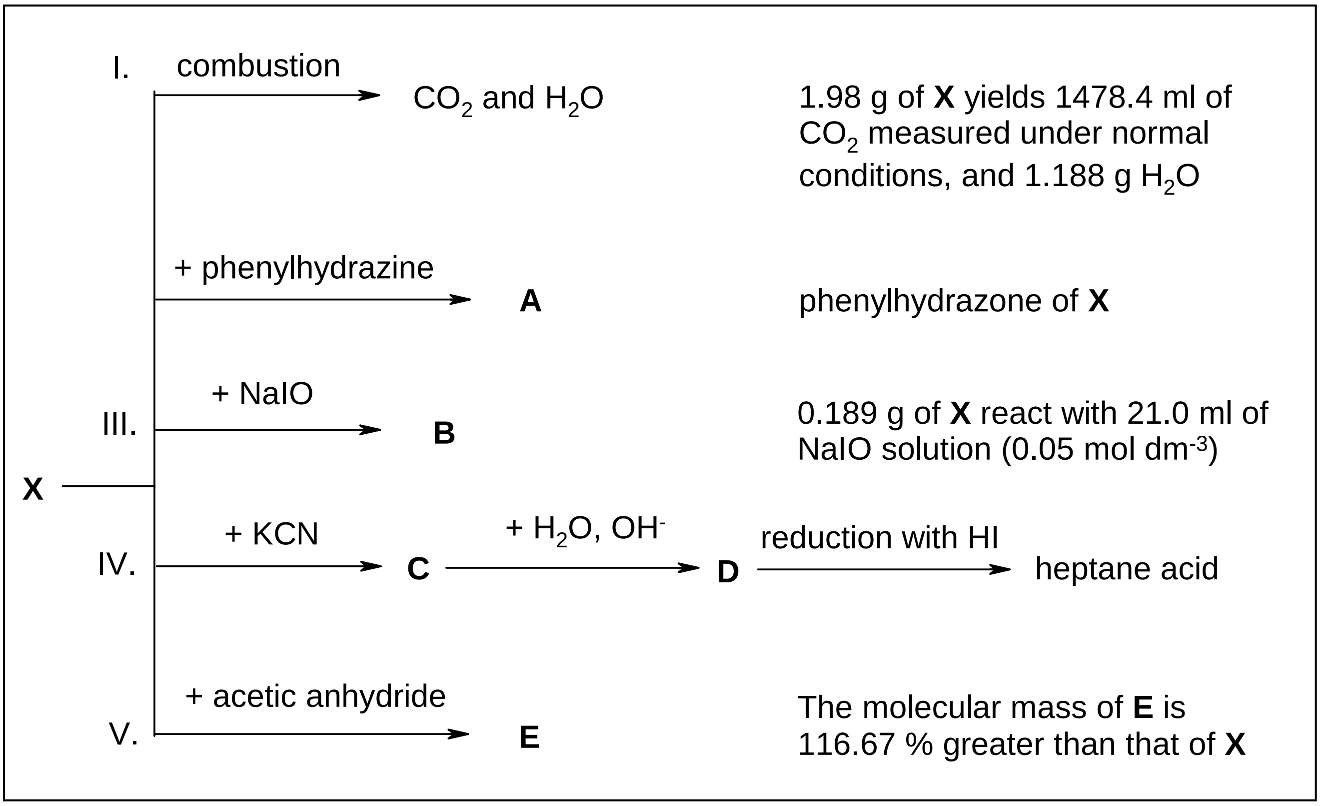
pH = 9.37

Indicators:

Bromphenol blue, Congo red, thymol blue, phenolphthalein.

PROBLEM 3

Compound **X** has been isolated from a neutral product. Different reagents have been used to establish the structure of X. The following results were obtained:



1.98 g of **X** yields 1478.4 ml of CO_2 measured under normal conditions, and 1.188 g H_2O

phenylhydrazone of **X**

0.189 g of **X** react with 21.0 ml of NaIO solution (0.05 mol dm^{-3})

The molecular mass of **E** is 116.67 % greater than that of **X**

3.1 What conclusions can be drawn on the composition and the structure of **X** on the basis of the data obtained from each of the above interactions. The conclusions should be formulated in the most concise and clear way. Fill in the table without describing how you reached your conclusions.

I. …………………………………
II. …………………………………
III. …………………………………
IV. …………………………………
V. …………………………………

3.2 Write the formula of substance **X** on the basis of the data about the composition and structure obtained in point 1.

3.3 Write the formulae of substances **A**, **B**, **C**, **D**, and **E** and the formula for heptane acid.

3.4 To what natural substances could this structure correspond? Write the name of the substance and draw the structural formula which best describes its structure properties.

3.5 Give three properties of this compound that do not correspond to the structure found in point 2.

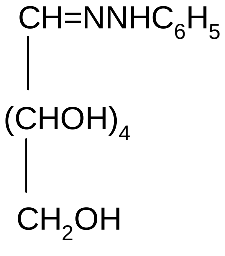
SOLUTION

3.1

Reaction	Yielding
I	The simplest empirical formula, CH_2O
II	Presence of a C=O group
III	Presence of a –CHO group *M*, calculated for a single CHO- 180/n (n – number of CHO groups)
IV	Continuous chain of 6 C atoms 1 CHO, $C_6H_{12}O_6$ (M = 180)
V	5 OH groups

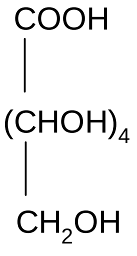
3.2 $HOCH_2(CHOH)_4CHO$

3.3



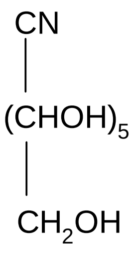
$$\begin{array}{l} CH=NNHC_6H_5 \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

A



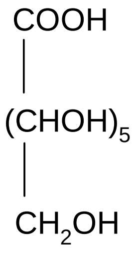
$$\begin{array}{l} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

B



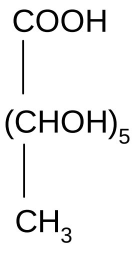
$$\begin{array}{l} CN \\ | \\ (CHOH)_5 \\ | \\ CH_2OH \end{array}$$

C



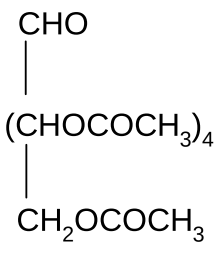
$$\begin{array}{l} COOH \\ | \\ (CHOH)_5 \\ | \\ CH_2OH \end{array}$$

D



$$\begin{array}{l} COOH \\ | \\ (CHOH)_5 \\ | \\ CH_3 \end{array}$$

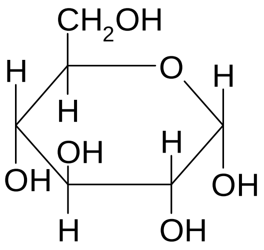
heptane acid



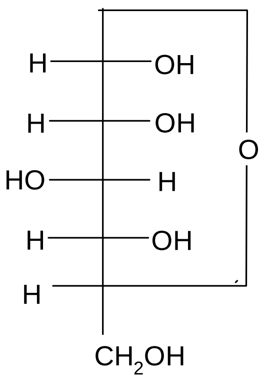
$$\begin{array}{l} CHO \\ | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \end{array}$$

E

3.4 D – (+) – glucose



or



3.5 – does not participate in some reactions typical for aldehydes (e. g. with $NaHSO_3$ or Schiff's reagent),

– the mutarotation phenomenon,

– a stronger reactivity of one of the five OH groups (displayed for example in the interaction with CH_3OH and HCl leading to the methylation of only one OH group).

PROBLEM 4

The thermal decomposition of water

$H_2O \rightleftharpoons H_2 + ½\,O_2$

can be traced ($\alpha = 10^{-3}$) at temperature above 1700 K. This process can be realized at temperatures 800 – 900 K as well as through subsequent stages carried out in a cycle. Suggest such a process on the basis of the reactions:

$CuO(s) + MgCl_2(s) + H_2O(g) \xrightarrow{840\ K} CuCl(s) + MgO(s) + HCl(g) + O_2(g)$

and

$Ag(s) + HCl(g) \xrightarrow{430\ K} AgCl(s) + H_2(g)$

satisfying the following requirements:

a) Only water should be consumed during the process.

b) Oxygen and hydrogen alone should be the end products of the process.

c) In addition to the above substances, a 25 % ammonia solution is needed for the cycle.

d) The temperature for each step in the cycle should not exceed 840 K.

SOLUTION

1. $2\ CuO + 2\ MgCl_2 + H_2O \xrightarrow{840\ K} 2\ CuCl + 2\ MgO + 2\ HCl + 0.5\ O_2$
2. $Ag + 2\ HCl \xrightarrow{430\ K} 2\ AgCl + H_2$
3. $2\ CuCl + 4\ NH_3 \longrightarrow 2\ [Cu(NH_3)_2]^+ + 2\ Cl^-$
4. $2\ AgCl + 4\ NH_3 \longrightarrow 2\ [Ag(NH_3)_2]^+ + 2\ Cl^-$
5. $2\ [Cu(NH_3)_2]^+ + 2\ [Ag(NH_3)_2]^+ \longrightarrow 2\ Ag\downarrow + 2\ [Cu(NH_3)_4]^{2+}$
6. $2\ [Cu(NH_3)_4]^{2+} + 2\ MgO \xrightarrow{boiling} 2\ CuO\downarrow + 2\ Mg^{2+} + 8\ NH_3\uparrow$
7. $2\ Mg^{2+} + 4\ Cl^- \xrightarrow{evaporation} 2\ MgCl_2$
8. $H_2O \longrightarrow H_2 + 0.5\ O_2$

PROBLEM 5

Compounds **B** and **C** are structural isomers. They can be obtained when hydrocarbon **A** interacts with chlorine. Hydrocarbon **A** is a basic product of an industrial organic synthesis. It can react with ozone, yielding an ozonide.

Isomer **B** can be used for the technical production of compounds **D** and **E** that are the initial compounds in the production of the fibre nylon:

6,6-$H–[NH(CH_2)_6NHCO(CH_2)_4CO]_n– OH$.

Compound **D** is soluble in bases, **E** in acids.

The reaction between isomer **C** and an alcohol solution of an alkaline base yields monomer **F** which is used for the production of chloroprene (neoprene) rubber

$–[–CH_2CCl = CHCH_2–]_n$.

This method has a technical application.

5.1 Write down the structural formulae of **A**, **B**, **C**, **D**, **E**, **F** and their names in the IUPAC nomenclature.

5.2 Write down the mechanism of the reaction between hydrocarbon **A** and chlorine. What type of reaction is it in terms of its mechanism? Which of the two isomers is obtained in larger quantities under ordinary conditions?

5.3 Write down the equations for:

- the production of **D** and **E** from isomer **B**,
- the production of monomer **F** from isomer **C**,
- the ozonolysis of hydrocarbon **A** and hydrolysis of the ozonide.

5.4 Write down the chemical scheme for an industrial production of hydrocarbon **A** from the hydrocarbon which is main component of natural gas.

5.5 For chloroprene rubber, write down the formulae of the possible steric forms of the elementary unit.

SOLUTION

5.1 **A**: $CH_2=CH-CH=CH_2$

1,3-butadiene

B: $ClCH_2-CH=CH-CH_2Cl$

1,4-dichloro-2-butene

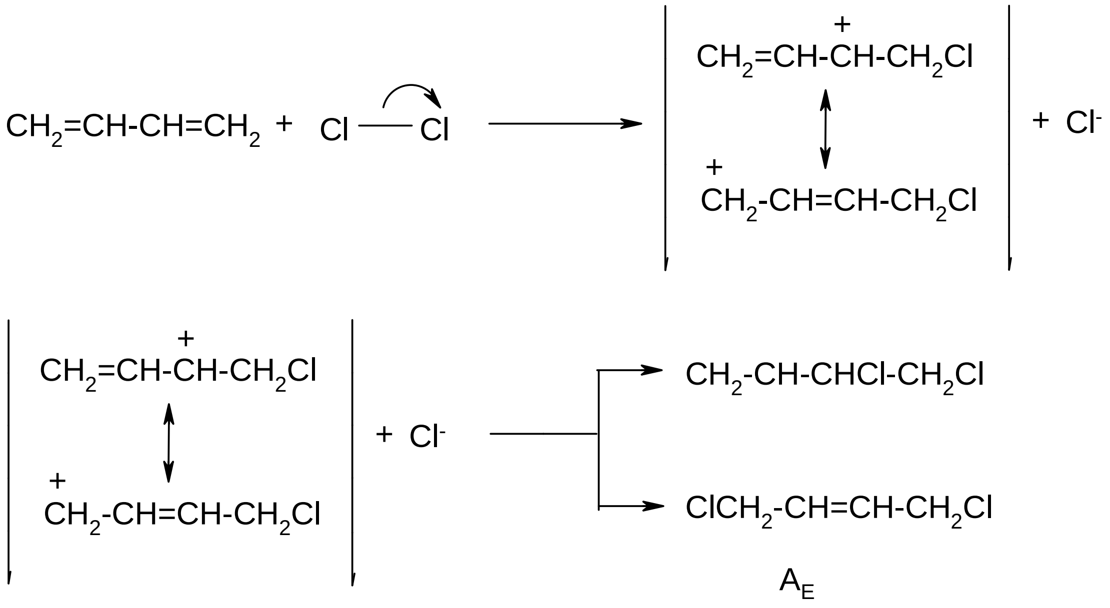
C: $CH_2=CH-CHCl-CH_2Cl$
3,4-dichloro-1-butene

D: $HOOC(CH_2)_4COOH$
hexanedioic acid

E: $H_2N(CH_2)_6NH_2$
1,6-hexandiamine

F: $CH_2=CCl-CH=CH_2$
2-chloro-1,3-butadiene

5.2



1,4-dichloro-2-butene

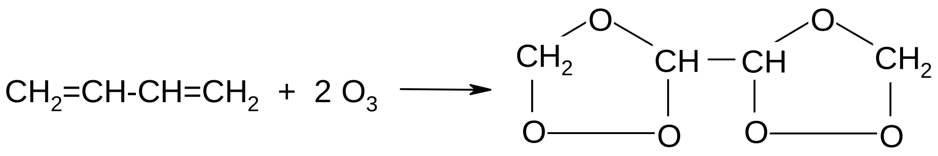
5.3 $ClCH_2CH=CHCH_2Cl + 2\ KCN \longrightarrow NCCH_2CH=CHCH_2CN + 2\ KCl$

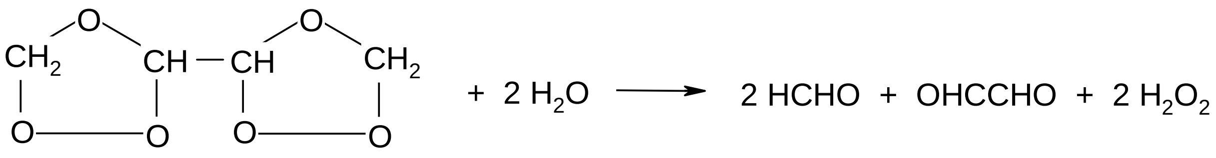
$$NCCH_2CH=CHCH_2CN + H_2 \xrightarrow{\text{cat.}} NCCH_2CH_2CH_2CH_2CN$$

$$NC(CH_2)_4CN + 4\ H_2O \xrightarrow[\text{(HO}^- \text{ or H}^+)]{\text{cat.}} HOOC(CH_2)_4COOH + 2\ NH_3$$

$$NC(CH_2)_4CN + 4\ H_2 \longrightarrow H_2N(CH_2)_6NH_2$$

$$CH_2=CHCHClCH_2Cl + OH^- \longrightarrow CH_2=CH–CCl=CH_2 + Cl^- + H_2O$$





5.4

$$CH_4 \xrightarrow[\triangle]{-\ H_2} CH\equiv CH \xrightarrow[Hg^{2+}]{+\ H_2O} CH_3CHO \xrightarrow[OH^-]{+\ CH_3CHO} CH_3CH(OH)CH_2CHO \longrightarrow$$

$$\xrightarrow[Ni]{+\ H_2} CH_3CH(OH)CH_2CH_2OH \xrightarrow{-\ H_2O} CH_2{=}CH\text{-}CH{=}CH_2$$

or

$$CH_4 \xrightarrow[\triangle]{-\ H_2} CH\equiv CH \xrightarrow[OH-]{+\ HCHO} HOCH_2\text{-}C\equiv C\text{-}CH_2OH \longrightarrow$$

$$\xrightarrow[Ni]{+\ H_2} HO(CH_2)_4OH \xrightarrow{-\ H_2O} CH_2{=}CH\text{-}CH{=}CH_2$$

or

$$CH_4 \xrightarrow[\triangle]{-\ H_2} CH\equiv CH \xrightarrow[Cu_2Cl_2\ .\ 2\ NH_4Cl]{+\ HC\equiv CH} CH_2{=}CH\equiv CH \longrightarrow$$

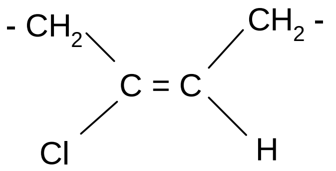
$$\xrightarrow[Zn\ +\ NaOH]{[H]} CH_2{=}CH\text{-}CH{=}CH_2$$

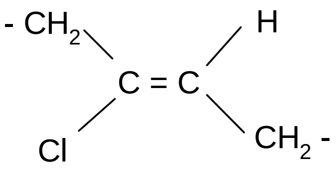
or

$$CH_4 \xrightarrow[\triangle]{-\ H_2} CH\equiv CH \xrightarrow[Hg^{2+}]{+\ H_2O} CH_3CHO \xrightarrow[Ni]{+\ H_2} CH_3CH_2OH \longrightarrow$$

$$\xrightarrow[cat.]{-\ H_2,+\ H_2O} CH_2=CH\text{-}CH=CH_2$$

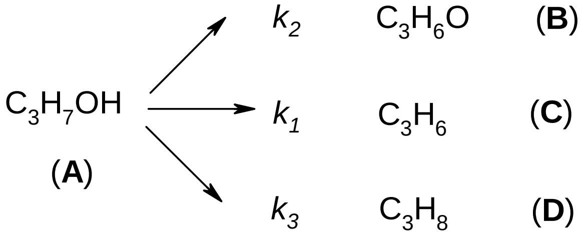
5.5





PROBLEM 6

The catalytic decomposition of isopropanol on the surface of a V_2O_5 catalyst, leading to the products in the scheme, satisfies a first order kinetic equation.



Five seconds after initiation of the reaction at 590 K, the concentrations of the components in the reaction mixture are:

c_A = 28.2 mmol dm^{-3}

c_B = 7.8 mmol dm^{-3}

c_C = 8.3 mmol dm^{-3}

c_D = 1.8 mmol dm^{-3}

6.1 What is the initial concentration c_0 of C_3H_7OH in the system?

6.2 What is the value of the rate constant k for the process:

$$C_3H_7OH \xrightarrow{k} \text{products ?}$$

6.3 What is the interval of time ($\tau_{1/2}$) in which the concentration of C_3H_7OH will reach the value $c = c_0/2$?

6.4 What are the values of rate constants k_1, k_2, and k_3?

6.5 What are the values of concentrations c_B, c_C, c_D at $t = \tau_{1/2}$?

The equation describing the concentration changes of **A** with time t for the first order reaction has the form:

$c_A = c_0 \exp(-k\, t)$

or

$\log (c_0 / c_A) = 0.4343\, k\, t$

or

$\ln (c_0 / c_A) = k\, t$

Fill in the table with the answers obtained.

1	c_0 =
2	k =
3	$\tau_{1/2}$
4	k_1 =
	k_2 =
	k_3 =
5	c_B =
	c_C =
	c_D =

SOLUTION

6.1 $c_0 = c_A + c_B + c_C + c_D = 28.2 + 7.8 + 8.3 + 1.8 = 46.1 \text{ mmol dm}^{-3}$

6.2 $$k = \frac{1}{0.4343\,t}\log\left(\frac{c_0}{c_A}\right) = \frac{1}{0.4343\times 5}\log\left(\frac{46.1}{28.2}\right) = 0.0983\,s^{-1}$$

6.3 $$t = \tau_{1/2} = \frac{1}{0.4343\,k}\log\frac{\frac{c_0}{2}}{c_0} = \frac{1}{0.4343\times 0.0983}\log 2 = 7.05\text{ s}$$

6.4

$$v_1 = \frac{\Delta c_B}{\Delta t} = k_1\,c_A$$

$$v_2 = \frac{\Delta c_C}{\Delta t} = k_2\,c_A$$

$$v_3 = \frac{\Delta c_D}{\Delta t} = k_3\,c_A$$

$v = v_1 + v_2 + v_3 = k\,c_A$

(1) $k_1 + k_2 + k_3 = k = 0.0983 \text{ s}^{-1}$

(2) $$\frac{\Delta c_B}{\Delta c_C} = \frac{c_B - 0}{c_C - 0} = \frac{c_B}{c_C} = \frac{k_1}{k_2} = \frac{7.8}{8.3} = 0.940$$

(3) $$\frac{\Delta c_B}{\Delta c_D} = \frac{c_B - 0}{c_D - 0} = \frac{c_B}{c_D} = \frac{k_1}{k_3} = \frac{7.8}{1.8} = 4.33$$

From equations (1) – (3):

$k_1 = 0.0428\ s^{-1}$

$k_2 = 0.0455\ s^{-1}$

$k_3 = 0.00988\ s^{-1}$

6.5 At $t = \tau_{1/2} = 7.05$ s

(4) $$c_A = \frac{c_0}{2} = c_B + c_C + c_D = 23.05\ \text{mmol dm}^{-3}$$

From equations (2) – (4):

$c_B = 10.0\ \text{mmol dm}^{-3}$

$c_C = 10.7\ \text{mmol dm}^{-3}$

$c_D = 2.32\ \text{mmol dm}^{-3}$

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Fourteen numbered test tubes contain solutions of pure inorganic substances. Each test tube contains only one substance. The samples contain the following ions:

cations K^+, Na^+, Hg_2^{2+}, Ag^+, NH_4^+, Ba^{2+}, Sr^{2+}, Fe^{3+};

anions $OH^–$, NO_3^-, $Cl^–$, $SCN^–$, $I^–$, CO_3^{2-}, $Cr_2O_7^{2-}$, CrO_4^{2-}, $Fe(CN)_6^{4-}$, $Co(NO_2)_6^{3-}$.

Determine the contents of the test tubes. In addition to reactions between samples, the only other possible reagent is a solution of hydrochloric acid with a concentration of 2 mol dm^{-3}.

Fill in the following information on the sheet provided:

1. The chemical formulae of the individual samples and the numbers of the corresponding test tubes.
2. The chemical formulae in ionic form on the basis of which you demonstrated the presence of individual cations present in the samples.

PROBLEM 2 (practical)

Determine the samples in the test tubes using the following reagents:
$FeCl_3$ (2.5 % aqueous solution), water, 2,4-dinitrophenylhydrazine, Lucas' reagent ($ZnCl_2$ – HCl), NaOH (5 % aqueous solution), $NaHCO_3$ (5 % aqueous solution), HCl (conc.), Fehling's solution (an alkaline aqueous solution containing Cu^{2+} ions; this is prepared immediately prior to use by mixing identical volumes of Fehling's solutions I and II), Tollen's reagent (prepared immediately prior to use by mixing identical volumes of 10 % solution of $AgNO_3$ and an NaOH solution with a concentration 2 mol dm^{-3}. Finally, ammonia is added dropwise to complete dissolution of silver dioxide.

Write the results of your observations during testing the unknown substances with the reagents into the table provided.

Write the (IUPAC) names and structural formulae for the substances in the test tubes.

Write the chemical equations for the reactions on the basis of which the individual substances were identified. Write only a reaction scheme where this not possible.

PROBLEM 3 (practical)

Volumetric determination of sodium carbonate and sodium hydrogen carbonate simultaneously.

A) *Procedure:*

1. Determination of the precise concentration of an HCl solution (0.1 mol dm^{-3}) using borax $Na_2B_4O_7 . 10 H_2O$ as a standard.

   Principle:

   An aqueous solution of sodium tetraborate reacts with hydrochloric acid to form trihydrogenboric acid.

   Procedure:

   25.00 cm^3 of a standard borax solution with a concentration of about 0.05 mol dm^{-3} (the exact borax concentration is written on the label on the volumetric flask; the solution needs not be diluted with water to a volume of 100 cm^{-3}) is transferred into a titration flask, 1 to 2 drops of methyl red are added and the solution is titrated to the first orange coloration of the yellow solution. The titration should be carried out at least twice. The consumption of hydrochloric acid should be designated by symbol V_1.

2. Volumetric determination of Na_2CO_3 and $NaHCO_3$ simultaneously.

   Procedure:

   The sample in a volumetric flask (250 cm^3) should be diluted to the mark with distilled water from which the carbon dioxide has been removed by boiling, and mix.

   a) Part of the solution (25 cm^3) is titrated with an HCl solution using methyl orange (2 drops) to the first red coloration of the originally yellow solution. The sample is boiled 2 to 3 minutes to release carbon dioxide. Then the solution is cooled and the titration is continued to a clear red coloration of the solution. The titration should be carried out at least twice. The consumption of hydrochloric acid should be designated as V_2 (average of titration values).

   b) A further part of the sample (25.00 cm^3) is transferred to an Erlenmeyer flask and mixed with 25.00 cm^3 of the NaOH solution with a concentration of 0.1 mol dm^{-3}. Add 10 cm^3 of a 10 % solution of $BaCl_2$ and 2 drops of phenolphthalein. Excess hydroxide should be titrated immediately in the presence of a white precipitate formed, using an HCl solution whose precise concentration has been determined

c) in part 1. The consumption of hydrochloric acid should be denoted as V_3 (average values of at least two titrations).

d) Carry out the same titration as in part b) without the sample (blank). The consumption of HCl is designated as V_4 (average of two titrations).

Use the results of the above experiments to calculate the amounts of Na_2CO_3 and $NaHCO_3$ in the sample.

B) Results

The results should be written into the form provided in which you should note the following:

a) The ionic equation for the reaction according to which the concentration of the HCl solution was determined.

b) The ionic equation for the reaction used in the determination of Na_2CO_3 and $NaHCO_3$ simultaneously.

c) The volume of hydrochloric acid consumed in the titration of 25.00 cm^3 of borax solution.

d) Calculation of the HCl concentration (in mol dm^{-3}).

e) Consumption of the HCl solution – V_2, V_3, and V_4.

f) Mass amounts of Na_2CO_3 and $NaHCO_3$ in the sample in grams.

$M(Na_2CO_3) = 105.989 \text{ g mol}^{-1}$

$M(NaHCO_3) = 84.007 \text{ g mol}^{-1}$

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International Chemistry Olympiad

7 theoretical problems
3 practical problems

THE FOURTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
3–12 JULY 1982, STOCKHOLM, SWEDEN

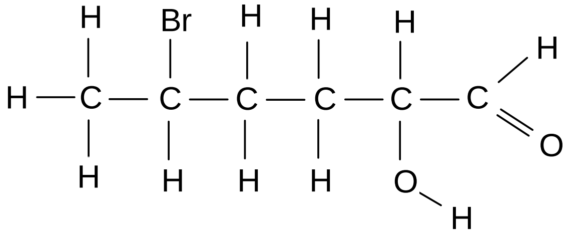
THEORETICAL PROBLEMS

PROBLEM 1

A. The IUPAC name of the compound $[Co(NH_3)_6]Cl_2$ is

- a) cobalt(II) hexaammonia dichlorine,
- b) cobalt(II) hexaammonia dichloride,
- c) hexaamminecobalt(II) chloride.
- d) hexaamminedichlorocobalt(II)
- e) cobalt(II) chloride-hexaammonia

B. The IUPAC name of the compound



is:

- a) 5-bromo-1-hexanoic acid
- b) 5-bromo-2-hydroxy-1-hexanal
- c) 2-bromo-5-hydroxy-6-hexanal
- d) 2-bromo-2-hydroxy-1-hexanal
- e) 5-bromo-2-hydroxy-1-hexanone

C. Which of the following acid-base pairs is most suitable for keeping the pH constant at 9 in an aqueous solution?

- a) CH_3COOH — CH_3COO^-
- b) NH_4^+ — NH_3
- c) H_2CO_3 — HCO_3^-

d) $H_2PO_4^- — HPO_4^{2-}$

e) $H_2C_2O_4 — HC_2O_4^-$

D. One of the following statements cannot be correct. State which one.

a) A water-soluble solid contains Mg^{2+}, Cr^{3+}, and $Br^–$.

b) A solid soluble in a sodium hydroxide solution contains Al^{3+}, K^+, and SO_4^{2-}.

c) A solid soluble in aqueous ammonia solution contains Ag^+, Cu^{2+}, and $Cl^–$.

d) A solid soluble in nitric acid contains Ba^{2+}, Fe^{2+}, and CO_3^{2-}.

e) A solution neutral to litmus contains Na+, Ca^{2+}, and PO_4^{3-}.

E. Complete the following equation:

$H_3AsO_4 + Zn \rightarrow AsH_3 + Zn^{2+}$

The reaction is carried out in an acid solution. Fill in the missing particles and balance the reaction equation.

F. State the degree of protolysis of acetic acid with concentration of 0.25 mol dm^{-3}.

$K_a(HAc) = 1.8 \times 10^{-5}$.

a) 0.021 %; b) 0.21 %; c) 0.84 %; d) 1.3 %; e) 8.4 %

G. A solution with a volume of 1.00 dm^3 is saturated with lead iodide, PbI_2. The concentration of iodide ions is 2.7 mol dm^{-3}. Determine the solubility product of PbI_2.

a) 3.6×10^{-6}; b) 2.0×10^{-8}; c) 9.8×10^{-9}; d) 2.5×10^{-9}; e) 4.9×10^{-9}.

H. The following standard enthalpies of formation are given:

Compound	ΔH^0
Acetic acid	- 0.50 MJ mol^{-1}
Carbon dioxide	- 0.40 MJ mol^{-1}
Water	- 0.30 MJ mol^{-1}

The ΔH^0 of combustion of acetic acid is:

a) 0.90 MJ mol^{-1}; b) - 0.90 MJ mol^{-1}; c) - 0.20 MJ mol^{-1};

d) - 2.1 MJ mol^{-1}; e) 0.20 MJ mol^{-1}

I. $COCl_2(g)$ is introduced in an empty vessel at a pressure of *a*. It dissociates and the following equilibrium is established at constant temperature:

$2\ COCl_2(g) \rightleftharpoons C(graphite) + CO_2(g) + 2\ Cl_2(g)$

If x represents the partial pressure of $CO_2(g)$ at equilibrium, what is the equilibrium expression?

a) $\frac{4x^3}{(a-2x)^2} = K_p$ b) $\frac{2x^4}{(a-2x)^2} = K_p$ c) $\frac{2x^3}{(a-x)^2} = K_p$

d) $\frac{4x^3}{(a-x)^2} = K_p$ e) $\frac{x^3}{(a-3x)^2} = K_p$

K. For a metal M the following redox data are known:

E^0 = - 0.60 V for $M^{2+}(aq) + e^- \rightarrow M^+(aq)$

E^0 = 0.40 V for $M^{4+}(aq) + 2\,e^- \rightarrow M^{2+}(aq)$

The E^0 for $M^{4+}(aq) + 3\,e^- \rightarrow M^+(aq)$ is then:

a) - 0.20 V b) - 1.00 V c) 1.00 V d) 0.07 V e) - 0.07 V

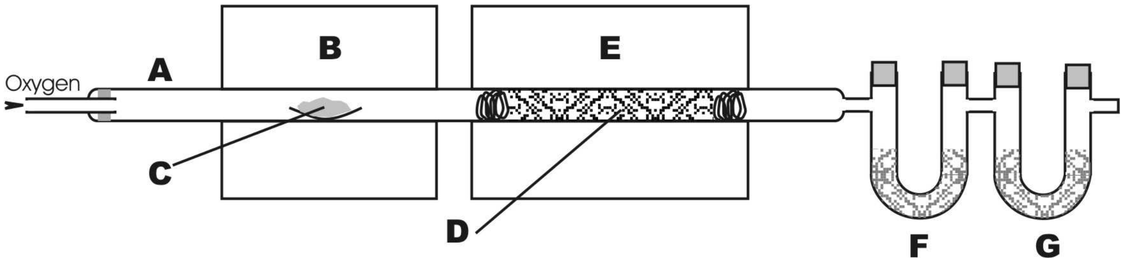
SOLUTION

A. c) B. b) C. b) D. e)

E. $H_3AsO_4 + 4\,Zn + 8\,H^+ \rightarrow AsH_3 + 4\,Zn^{2+} + 4\,H_2O$

F. c) G. c) H. b) I. a) K. d)

PROBLEM 2



Quantitative analysis for carbon and hydrogen was originally carried out using a technique and apparatus (see figure) originally developed in 1831 by the famous chemist Justus Liebig. A carefully weighed sample of organic compound (C) is placed in a combustion tube (A) and vaporized by heating in a furnace (B). The vapours are swept by a stream of oxygen through a heated copper oxide packing (D) and through another furnace (E), which ensures the quantitative oxidation of carbon and hydrogen to carbon dioxide and water. The water vapour is absorbed in a weighed tube (F) containing magnesium perchlorate and the carbon dioxide in another weighed tube (G) containing asbestos impregnated with sodium hydroxide.

A pure liquid sample containing only carbon, hydrogen and oxygen is placed in a 0.57148 g platinum boat, which on reweighing weights 0.61227 g. The sample is ignited and the previously weighed absorption tubes are reweighed. The mass of the water absorption tube has increased from 6.47002 g to 6.50359 g, and the mass of the carbon dioxide tube has increased from 5.46311 g to 5.54466 g.

2.1 Calculate the mass composition of the compound.

2.2 Give the empirical formula of the compound.

To estimate the molar mass of the compound, 1.0045 g was gasified. The volume, measured at a temperature of 350 K and a pressure of 35.0 kPa, was 0.95 dm^3.

2.3 Give the molar mass and the molecular formula of the compound.

2.4 Draw possible structures corresponding to the molecular formula excluding cyclic structures, stereo isomers, peroxides and unsaturated compounds. There are about 15 possibilities. Give 10 of them.

When the compound is heated with a sodium hydroxide solution, two products are formed. Fractional distillation of the reaction mixture yields one of the substances. The other substance is purified by distillation after acidification and appears to be an acid.

2.5 What structures are possible for compound C?

0.1005 g of the acid are dissolved in water and titrated with a sodium hydroxide solution with a concentration of 0.1000 mol dm^{-3}. The indicator changes colour on addition of 16.75 cm^3 of hydroxide solution.

2.6 What was the original substance C?

SOLUTION

2.1 Mass percentage composition: 54.56 % C; 9.21 % H; 36.23 % O

2.2 Empirical formula: C_2H_4O

2.3 Molar mass: 88 g mol^{-1}

Molecular formula: $C_4H_8O_2$

2.4 Possible structures:

1. CH_3-CH_2-CH_2-COOH
2. CH_3-CH(CH_3)-COOH
3. CH_3-O-CO-CH_2-CH_3
4. CH_3-CH_2-O-CO-CH_3
5. CH_3-CH_2-CH_2-O-CO-H
6. CH_3-CH(CH_3)-O-CO-H
7. CH_3-CH_2-CH(OH)-CHO
8. CH_3-CH(OH)-CH_2-CHO
9. CH_2(OH)-CH_2-CH_2-CHO
10. CH_3-C(OH)(CH_3)-CHO
11. CH_2(OH)-CH(CH_3)-CHO
12. CH_3-O-CH_2-CH_2-CHO
13. CH_3-CH_2-O-CH_2-CHO
14. CH_3-O-CH(CH_3)-CHO
15. CH_3-CH_2-CO-CH_2-OH
16. CH_3-CH(OH)-CO-CH_3
17. CH_2(OH)-CH_2-CO-CH_3
18. CH_3-O-CH_2-CO-CH_3

2.5 The possible structures are 3, 4, 5, 6.

2.6 The structure of the compound C is CH_3-CH_2-O-CO-CH_3.

PROBLEM 3

In a chemical factory in which formaldehyde is produced by oxidation of methanol, aqueous solutions containing methanol and formaldehyde are to be analyzed. In order to test the method, experiments are first carried out with known amounts of both methanol and formaldehyde. The following aqueous solutions are used:

Methanol, 5.00 g dm^{-3}
Formaldehyde, 5.00 g dm^{-3}
Potassium dichromate, 3.000×10^{-2} mol dm^{-3}
Ammonium iron(II) sulphate, 0.2000 mol dm^{-3}
Iodine, 0.1000 mol dm^{-3}
Sodium thiosulphate, 0.2000 mol dm^{-3}.

I. 10.00 cm^3 methanol solution and 100.00 cm^3 potassium dichromate solution are mixed, approximately 100 cm^3 concentrated sulphuric acid is added and the solution is allowed to stand for about 30 minutes. Excess dichromate ions are then titrated with iron(II) ions with diphenylamine sulphonic acid as a redox indicator (colour change from red-violet to pale green). The volume of the iron(II) solution consumed is 43.5 cm^3.

II. 10.00 cm^3 of formaldehyde solution and 50.00 cm^3 of iodine solution are mixed. Sodium hydroxide solution is added to alkaline reaction and the mixture is left standing for about 10 minutes. Hydrochloric acid is then added to a neutral reaction, and the excess iodine is determined by titration with thiosulphate, with starch as an indicator. The volume of the thiosulphate solution required is 33.3 cm^{-3}.

3.1 Using the analysis data in I and II calculate the reacting amounts and the molar ratios of methanol/dichromate ions and formaldehyde/iodine.

3.2 Write balanced equations for all reactions described in experiments I and II.

III. It is checked that iodine does not react with methanol. From a solution containing both methanol and formaldehyde, two 10.00 cm^3 samples are taken.

One sample is mixed with 100.00 cm^3 of potassium dichromate solution and concentrated sulphuric acid as in I. Excess dichromate ions consume 4.8 cm^3 of iron(II) solution.

The other sample is mixed with 50.00 cm^3 of iodine solution and treated as in II. Excess iodine consumes 16.50 cm^3 of thiosulphate solution.

3.3 Give balanced equations for the reactions and calculate the contents of methanol and formaldehyde in the solution. Give your answer in g dm^{-3}.

SOLUTION

3.1 Amounts of substance:

methanol	1.56 mol
dichromate ions	3.00 mol
iron(II) ions	8.70 mol

Molar ratio methanol/dichromate: 1 mol $CH_3OH \Rightarrow$ 1 mol $Cr_2O_7^{2-}$

Amounts of substance:

formaldehyde	1.67 mol
iodine	5.00 mol
thiosulphate ions	6.66 mol

Molar ratio formaldehyde/iodine: 1 mol HCHO $\Rightarrow$ 1 mol I_2

3.2 Chemical equations:

$CH_3OH + Cr_2O_7^{2-} + 8\ H^+ \rightarrow CO_2 + 2\ Cr^{3+} + 6\ H_2O$

$Cr_2O_7^{2-} + 6\ Fe^{2+} + 14\ H^+ \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$

$I_2 + 2\ OH^- \rightarrow IO^- + I^- + H_2O$

$HCHO + IO^- + OH^- \rightarrow HCOO^- + I^- + H_2O$

$IO^- + I^- + 2\ H^+ \rightarrow I_2 + H_2O$

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

In (3), (5), and (6), I_3^- may participate instead of I_2.

As an alternative to (4)

$HCHO + I_2 + 2\ OH^- \rightarrow HCOO^- + 2\ I^- + H_2O$ is acceptable.

3.3 Chemical equations

To the chemical equations above is added

$3\ HCHO + 2\ Cr_2O_7^{2-} + 16\ H^+ \rightarrow 3\ CO_2 + 4\ Cr^{3+} + 11\ H_2O$

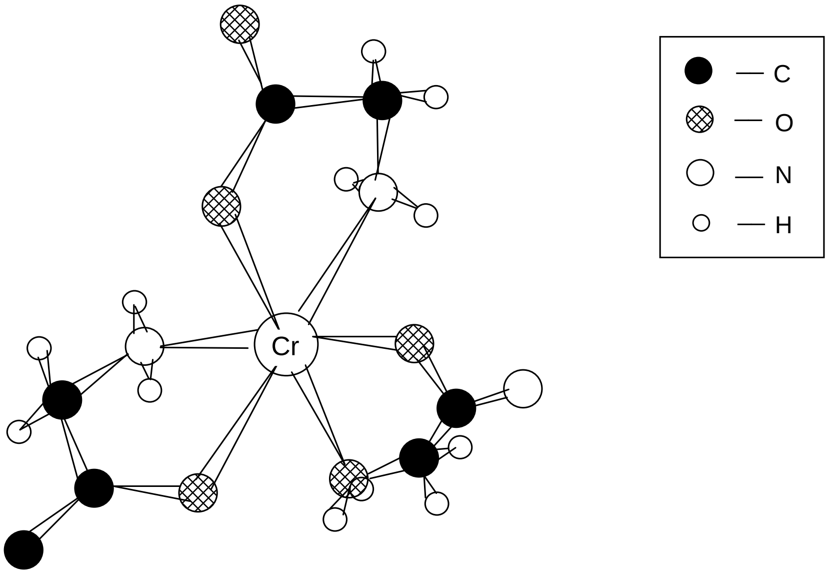
Content of methanol: 1.9 g dm^{-3}

Content of formaldehyde: 10.1 g dm^{-3}

PROBLEM 4

A transition metal atom or ion may be directly bonded to a number of atoms or molecules that surround it (ligands), forming a characteristic pattern. This is the essential structural feature of an important class of so-called coordination or complex compounds. If two or more atoms from one individual ligand form bonds to the same central atom then the ligand is said to form a chelate (Greek chele = crab' claw).

The glycinate ion, $NH_2–CH_2–COO^-$, is a bidentate chelate ligand which can form, for instance, tris-glycinato-chromium(III) complexes. The figure shows one possible structure of such a complex. Oxygen and nitrogen are forced to coordinate to adjacent octahedral positions, as the N – C – C – O chain is too short to "embrace" the chromium ion.



4.1 How many different configurational isomers of the complex are possible, not counting optical isomers?

4.2 Which of these isomers can be further resolved into optical isomers?

Another coordination compound of chromium was analyzed and found to have the following mass composition: 19.5 % Cr, 40.0 % Cl, 4.5 % H, and 36.0 % O. A 0.533 g sample of the compound was dissolved in 100 cm^3 of water, and 10 cm^3 of nitric acid (2 mol dm^{-3}) was added. Excess of silver nitrate solution was then added and the precipitate formed was then filtered, washed, dried and weighed. Its mass was found to be 0.287 g.

When a 1.06 g sample was gently heated to 100 ℃ in a stream of dry air, 0.144 of water was driven off.

The freezing point of a solution prepared from 1.33 g of the compound and 100 cm^3 of water, was found to be –0.18 ℃. (Molar freezing point depression of water is 1.82 K kg mol^{-1}).

Use all the experimental information to solve the following problems:

4.3 Derive the empirical formula of the compound.

4.4 Deduce formula for the compound showing the ligands of the chromium ion. Give molar ratios to support your result.

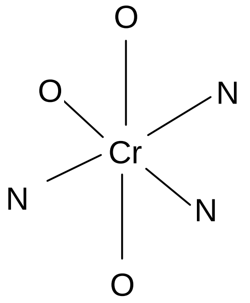
4.5 Sketch all possible steric arrangements of the ligands about the chromium ion.

SOLUTION

4.1 Two geometrical isomers of the complex are possible:

i) the facial, which is the one illustrating the problem,

ii) the meridional, with oxygen and nitrogen positions as shown:



4.2 It is clearly seen that any complex with three bidentate ligands attached octahedrally as shown, lacks mirror symmetry. Hence, both stereoisomers are further resolvable into optical isomers.

4.3 The empirical formula is $CrCl_3H_{12}O_6$.

4.4 The reaction with silver ions indicates that

1 mol $CrCl_3H_{12}O_6 \;\widehat{=}\;$ 1 mol Cl^-

Gentle heating gives

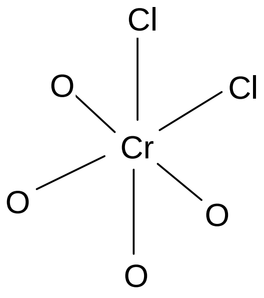
1 mol $CrCl_3H_{12}O_6 \;\widehat{=}\;$ 2 mol H_2O

These results support the coordination $[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O$.

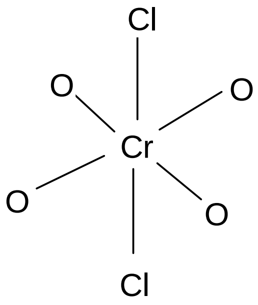
This formula is supported by the freezing point experiment showing that

1 mol $CrCl_3H_{12}O_6 \;\widehat{=}\;$ 2 mol ions in solution

4.5 Possible steric arrangements of the ligands about the chromium atom:



cis-form



trans-form

PROBLEM 5

Iodine is soluble to a certain extent in pure water. It is, however, more soluble in solutions containing iodide ions. By studying the total solubility of iodine as a function of iodide concentration, the equilibrium constants of the following reactions can be determined:

Equation			Equilibrium constants	
$I_2(s)$	$\rightleftharpoons$	$I_2(aq)$	k_1	(1)
$I_2(s) + I^-(aq)$	$\rightleftharpoons$	$I_3^-(aq)$	k_2	(2)
$I_2(aq) + I^-(aq)$	$\rightleftharpoons$	$I_3^-(aq)$	k_3	(3)

5.1 Give the equilibrium equations for (1) – (3).

Solutions of known potassium iodide concentration $[I^-]_{tot}$ were equilibrated with solid iodine. Subsequent titration with sodium thiosulphate solution served to determine the total solubility of iodine $[I_2]_{tot}$.

The experiments yielded the following results:

$[I^-]_{tot}$ / mmol dm^{-3}	10.00	20.00	30.00	40.00	50.00
$[I^-]_{tot}$ / mmol dm^{-3}	5.85	10.53	15.11	19.96	24.82

5.2 Plot $[I_2]_{tot}$ versus $[I^-]_{tot}$ in a diagram.

5.3 Derive a suitable algebraic expression relating $[I_2]_{tot}$ and $[I^-]_{tot}$.

5.4 Use the graph to determine values of the equilibrium constants k_1, k_2, and k_3.

SOLUTION

5.1 Equilibrium equations

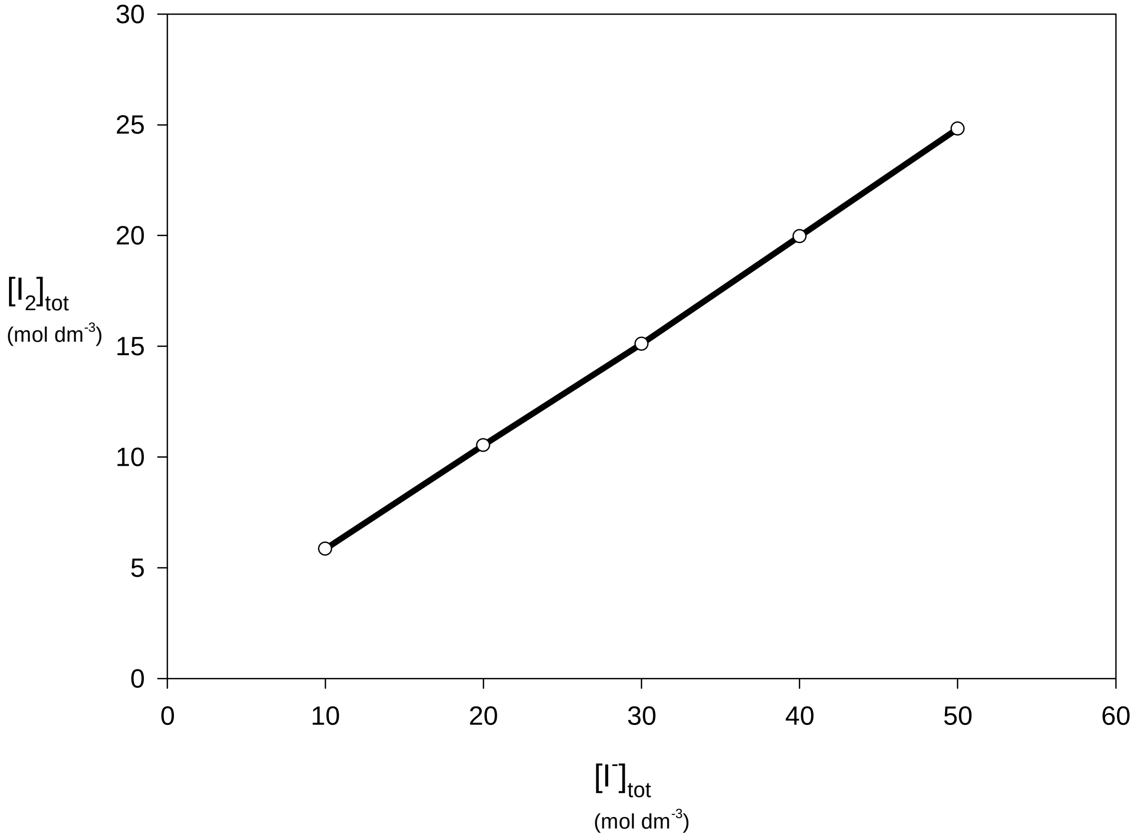
The following relations are valid for the concentrations of the aqueous solutions:

$$\left[I_2\right] = k_1$$

$$\frac{\left[I_3^-\right]}{\left[I^-\right]} = k_2$$

$$\frac{\left[I_3^-\right]}{\left[I_2\right]\left[I^-\right]} = k_3 = \frac{k_2}{k_1}$$

5.2 See diagram on the next page.



5.3 The relation between $[I_2]_{tot}$ and $[I^-]_{tot}$ is as follows:

$$[I_2]_{tot} = k_1 + \frac{k_2}{1+k_2}[I^-]_{tot}$$

5.4 $k_1 = 1.04 \times 10^{-3}$ mol dm^{-3} $k_2 = 0.90$ $k_3 = 8.6 \times 10^{2}$ mol^{-1} dm^{3}

(These values are calculated by the least square method.)

PROBLEM 6

A white solid organic acid, **A,** contains only carbon, hydrogen and oxygen. To obtain an approximate value for the molar mass, 10.0 g of the acid were dissolved in water. Crushed ice was added and vigorous shaking caused a decrease in temperature to – 2.5 °C. The ice was quickly removed. The mass of the solution was 76.1 g, and its pH value was determined to be 1.4. In a handbook the molar freezing point depression constant for water was found to be 1.86 K kg mol^{-1}. A more precise determination of the molar mass of the acid was then carried out. 0.120 g of the acid was titrated with a sodium hydroxide solution with a concentration of 0.100 mol dm^{-3}. Phenolphthalein was used as an indicator, and when 23.4 cm^3 of hydroxide solution was added the indicator turned red.

6.1 Give the molar mass and the structure of acid **A**.

Liquid **B** dissolves in water up to 10 %. The pH value of the solution is about 4. **B** is not easily oxidized, but following the iodoform reaction and subsequent acidification it is oxidized to acid **A**. 0.10 g of **B** consumes 1.5 g of iodine.

When **B** reacts with sodium, hydrogen is evolved and a metal organic compound is formed. The molar mass of **B** is approximately 100 g mol^{-1}.

6.2 Write the chemical equation for the iodoform reaction and for the reaction with sodium. For the organic molecules structural formulas should be used.

Compound **C** in aqueous solution has a conductivity which differs very little from that of pure water. Alkaline hydrolysis of **C** yields ammonia. 0.120 g of **C** was treated with hot, dilute sodium hydroxide solution and the gas formed was led into 50.0 cm^3 hydrochloric acid with a concentration of 0.100 mol dm^{-3}. The excess acid was titrated with 10.0 cm^3 sodium hydroxide solution with a concentration of 0.100 mol dm^{-3}.

Acid hydrolysis of **C** yields carbon dioxide. From the freezing point depression, the molar mass of **C** is estimated to be between 40 g mol^{-1} and 70 g mol^{-1}.

6.3 Give the structure of **C**. Write reaction equations for both the alkaline and the acid hydrolysis.

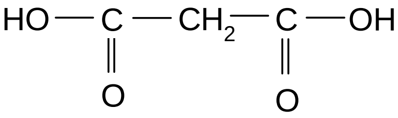
If **C** is allowed to react with the ethyl ester of acid **A** in the presence of a strong alkaline catalyst, ethanol and compound **D** are formed. The composition of **D** is 37.5 % C, 3.1 % H, 21.9 % N, and the reminder is oxygen. The compound is an acid.

6.4 Give the structure for **D**. Which is the "acid" hydrogen atom? Mark it with * in the structure.

SOLUTION

6.1 Molar mass of **A**: 103 g mol^{-1}

Structure of **A**:



$$HO-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OH$$

6.2 $CH_3\text{-}CO\text{-}CH_2\text{-}CO\text{-}CH_3 + 6\ I_2 + 8\ OH^- \rightarrow {}^-O\text{-}CO\text{-}CH_2\text{-}CO\text{-}O^- + 2\ CHI_3 + 6\ I^-$

${}^-O\text{-}CO\text{-}CH_2\text{-}CO\text{-}O^- + 2\ H^+ \rightarrow HO\text{-}CO\text{-}CH_2\text{-}CO\text{-}OH$

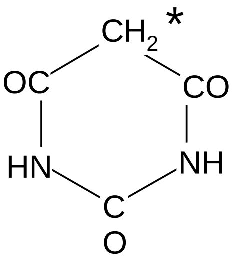
$2\ CH_3\text{-}CO\text{-}CH_2\text{-}CO\text{-}CH_3 + 2\ Na \rightarrow 2\ CH_3\text{-}CO\text{-}\underline{C}H\text{-}CO\text{-}CH_3 + H_2 + 2\ Na^+$

6.3 $H_2N\text{-}CO\text{-}NH_2$

$H_2N\text{-}CO\text{-}NH_2 + 2\ OH^- \rightarrow 2\ NH_3 + CO_3^{2-}$

$H_2N\text{-}CO\text{-}NH_2 + 2\ H^+ + H_2O \rightarrow 2\ NH_4^+ + CO_2\ CO_3^{2-}$

6.4



* - "acid" hydrogen

PROBLEM 7

Calcium oxalate, $CaC_2O_4.H_2O$, is a sparingly soluble salt of analytical and physiological importance. The solubility product is 2.1×10^{-9} at 25 °C. Oxalate ions can protolyse to form hydrogen oxalate ions and oxalic acid. The pK_a values at 25 °C are 1.23 ($H_2C_2O_4$) and 4.28 ($HC_2O_4^-$). At 25 °C the ionic product of water is 1.0×10^{-14}.

7.1 State those expressions for the equilibrium conditions which are of interest for the calculation of the solubility of calcium oxalate monohydrate.

7.2 State the concentration conditions which are necessary for the calculation of the solubility *s* (in mol dm^{-3}) of calcium oxalate in a strong acid of concentration *C*.

7.3 Calculate the solubility (in g dm^{-3}) of calcium oxalate monohydrate in a plant cell in which the buffer system regulates the pH to 6.5.

7.4 Calculate the solubility (in g dm^{-3}) of calcium oxalate monohydrate in hydrochloric acid with a concentration of 0.010 mol dm^{-3}. Give the concentration of hydrogen ions in the solution.

7.5 Calculate the equilibrium concentrations of all other species in solution d).

SOLUTION

7.1 $\left[Ca^{2+}\right]\left[C_2O_4^{2-}\right] = K_s$ (1) $\left[H^+\right]\left[OH^-\right] = K_w$ (2)

$$\frac{\left[H^+\right]\left[HC_2O_4^-\right]}{\left[H_2C_2O_4\right]} = K_{a1} \quad (3) \qquad \frac{\left[H^+\right]\left[C_2O_4^{2-}\right]}{\left[HC_2O_4^-\right]} = K_{a2} \quad (4)$$

7.2 $$s = \left[Ca^{2+}\right] = \left[C_2O_4^{2-}\right] + \left[HC_2O_4^-\right] + \left[H_2C_2O_4\right] \quad (5)$$

$$C = \left[H^+\right] + \left[HC_2O_4^-\right] + 2\left[H_2C_2O_4\right] - \left[OH^-\right] \quad (6)$$

Equations (5) or (6) may be replaced by

$$\left[H^+\right] + 2\left[Ca^{2+}\right] = \left[HC_2O_4^-\right] + 2\left[C_2O_4^{2-}\right] + \left[OH^-\right] + C \quad (7)$$

7.3 The solubility of calcium oxalate monohydrate is 6.7×10^{-3}. (Calculated according to equation (8)).

7.4 Elimination of the concentrations of oxalate species using equations (1), (3), and (4) yields the following expressions for (5) and (6). (The concentration of hydroxide ions can be neglected.)

$$s_2 = K_s + \frac{\left[\mathrm{H}^+\right] K_s}{K_{a2}} + \frac{\left[\mathrm{H}^+\right]^2 K_s}{K_{a1}\, K_{a2}} \qquad (8)$$

$$C = \left[\mathrm{H}^+\right] + \frac{\left[\mathrm{H}^+\right] K_s}{s\, K_{a2}} + \frac{2\left[\mathrm{H}^+\right]^2 K_s}{s\, K_{a1}\, K_{a2}} \qquad (9)$$

Elimination of s from (8) and (9) results in 4th order equation. For this reason, an iterative method is to be preferred. The first approximation is $\left[\mathrm{H}^+\right] = C$. This value of $\left[\mathrm{H}^+\right]$ can be used to calculate:

i) solubility s from (8),

ii) the last two terms in (9), which are corrections. Now a new value for $\left[\mathrm{H}^+\right]$ obtained from (9) may be used as a starting value for the next approximation. Two repeated operations give the following value for s:

$s = 6.6 \times 10^{-4}\ \mathrm{mol\ dm^{-3}} = 9.6 \times 10^{-2}\ \mathrm{g\ dm^{-3}}$

$\left[\mathrm{H}^+\right] = 9.3 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$

7.5 $\left[\mathrm{Ca}^{2+}\right] = 6.6\times10^{-4}\ \mathrm{mol\,dm^{-3}}$

$\left[\mathrm{Cl}^-\right] = 0.010\ \mathrm{mol\,dm^{-3}}$

$\left[\mathrm{OH}^-\right] = 1.1\times10^{-12}\ \mathrm{mol\,dm^{-3}}$

$\left[\mathrm{C_2O_4^{2-}}\right] = 3.2\times10^{-6}\ \mathrm{mol\,dm^{-3}}$

$\left[\mathrm{HC_2O_4^-}\right] = 5.7\times10^{-4}\ \mathrm{mol\,dm^{-3}}$

$\left[\mathrm{H_2C_2O_4}\right] = 9.0\times10^{-5}\ \mathrm{mol\,dm^{-3}}$

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

A pH buffer solution has a well defined acidity which changes only very slightly upon addition of moderate quantities of strong acid or base. The larger is the quantity of acid or base that must be added to a certain volume of a buffer solution in order to change its pH by a specific amount, the better is its action. A buffer solution is prepared by mixing a weak acid and its conjugate base in appropriate amounts in a solution. An example of a useful buffer system in aqueous solution is the phosphate system.

Your task is to prepare a phosphate buffer with properties specified by the following two conditions:

(1) pH = 7.20 in the buffer solution,

(2) pH = 6.80 in a mixture of 50.0 cm^3 of the butter solution and 5.0 cm^3 hydrochloric acid with a concentration of 0.100 mol dm^{-3}.

Chemicals and equipment

Aqueous solution of phosphoric acid, sodium hydroxide solution of known concentration, hydrochloric acid (0.100 mol dm^{-3}), solution of bromocresol green, distilled water.

Burettes, pipettes (25 and 5 cm^3), Erlenmeyer flasks (100 and 250 cm^3), volumetric flask (100 cm^3), beaker, and funnel.

Procedure

Determine the concentration of the phosphoric acid solution by titration with a sodium hydroxide solution using bromocresol green as an indicator (pH range 3.8 < pH < 5.4).

Make a buffer solution by mixing calculated volumes of phosphoric acid and sodium hydroxide solutions in the volumetric flask and filling the flask to the mark with distilled water.

Mix in an Erlenmeyer flask 50.0 cm^3 of the buffer solution with 5.0 cm^3 of the hydrochloric acid.

Hand in your answer sheet to the referee who will also measure the pH of your two solutions and note your results.

The pK_a values for phosphoric acid are:

pK_{a1} = 1.75, pK_{a2} = 6.73, pK_{a3} = 11.50

SOLUTION

The buffer solution must contain

$H_2PO_4^-$ (concentration **a** mol dm^{-3}) and

HPO_4^{2-} (concentration **b** mol dm^{-3}).

The concentrations should satisfy the condition

$$\frac{\mathbf{b}}{\mathbf{a}} = \frac{10^{-6.73}}{10^{-7.20}}$$

After addition of HCl the condition will be

$$\frac{50.0\,\text{b} - 0.50}{50.0\,\text{a} + 0.50} = \frac{10^{-6.73}}{10^{-6.80}}$$

From these equations,

a = 0.0122 **b** = 0.0361

Total concentration of the phosphate system = 0.0483 mol dm^{-3}

Total concentration of Na^+ = (**a** + 2 **b**) mol dm^{-3} = 0.0844 mol dm^{-3}

If the concentration of both phosphoric acid and sodium hydroxide solution are 0.500 mol dm^{-3}, then 100.0 cm^3 buffer solution will require:

$$\text{volume of } H_3PO_4 \text{ solution} = \frac{0.0483 \times 0.1000}{0.500\,\text{dm}^3} = 9.7\,\text{cm}^3$$

$$\text{volume of NaOH solution} = \frac{0.0844 \times 0.1000}{0.500\,\text{dm}^3} = 16.9\,\text{cm}^3$$

PROBLEM 2 (practical)

Each of 8 numbered test tubes contains a solution of one salt. In the solutions the following positive ions can be found (a maximum of one in each test tube):

Ag^+, Al^{3+}, Cu^{2+}, Na^+, NH_4^+, and Zn^{2+}

and the following negative ions (at most one in each test tube)

$Br^–$, $Cl^–$, $I^–$, NO_3^-, $OH^–$, and $S_3O_3^{2-}$.

A test plate, test tubes in a rack, dropping pipettes, indicator paper, and a gas burner are also provided.

Determine by means of mutual reactions which salt is dissolved in each test tube. Confirm your conclusions by carrying out as many reactions as possible. It may be necessary to use combinations of solutions and reagents.

Give a list of numbers and corresponding formulae of the substances, indicate the formation of a precipitate by a downward arrow, and gas evolution by an upward arrow in the square array provided for reporting the reactions.

Write chemical equations for all the reactions observed.

SOLUTION

Numbers of solutions mixed	Chemical equation for the observed reaction
1 + 2	$NH_4^+ + OH^– \rightarrow NH_3(g) + H_2O$
2 + 3	$2\ OH^– + 2\ Ag^+ \rightarrow Ag_2O(s) + H_2O$
2 + 3 + 1	$Ag_2O(s) + 4\ NH_4^+ + 2\ OH^– \rightarrow 2\ Ag(NH_3)_2^+ + 3\ H_2O$
2 + 4	$Zn^{2+} + 2\ OH^– \rightarrow Zn(OH)_2(s) \leftrightarrow Zn(OH)_2(s) + 2\ OH^– \rightarrow Zn(OH)_4^{2-}$
2 + 5	$Al^{3+} + 3\ OH^– \rightarrow Al(OH)_3(s) \leftrightarrow Al(OH)_3(s) + OH^– \rightarrow Al(OH)_4^-$

Reactions to distinguish Zn^{2+} from Al^{3+}:

Numbers of solutions mixed	Chemical equation for the observed reaction
2 + 4 + 1	$Zn(OH)_4^{2-} + 4\ NH_4^+ \rightarrow Zn(NH_3)_4^{2+} + 4\ H_2O$
2 + 5 + 1	$Al(OH)_4^- + 2\ NH_4^+ \rightarrow Al(OH)_3(s) + NH_3 + H_2O$
2 + 6	$Cu^{2+} + 2\ OH^– \rightarrow Cu(OH)_2(s)$

2 + 6 + 1	$Cu(OH)_2(s) + 4\ NH_4^+ + 2\ OH^- \rightarrow\ Cu(NH_3)_4^{2+} + 4\ H_2O$
3 + 4	$Ag^+ + Cl^- \rightarrow\ AgCl(s)$
3 + 6	$Ag^+ + Br^- \rightarrow\ AgBr(s)$
3 + 7	$Ag^+ + I^- \rightarrow\ AgI(s)$
3 + 8	$2\ Ag+ +\ S_2O_3^{2-} \rightarrow Ag_2S_2O_3(s)\ \leftrightarrow\ Ag_2S_2O_3(s) + 3\,S_2O_3^{2-} \rightarrow$ $\rightarrow 2\,Ag(S_2O_3)_2^{3-}$

Reactions to distinguish Cl^- from Br^- and from I^-

3 + 4 + 1 + 2	$AgCl(s) + 2\ NH_4^+ + 2\ OH^- \rightarrow\ Ag(NH_3)_2^+ + Cl^- + H_2O$
3 + 4 + 8	$AgCl(s) + 2\ S_2O_3^{2-} \rightarrow\ Ag(S_2O_3)_2^{3-} + Cl^-$
3 + 6 + 1 + 2	AgBr(s) does not dissolve
3 + 6 + 8	$AgBr(s) + 2\ S_2O_3^{2-} \rightarrow\ Ag(S_2O_3)_2^{3-} + Br^-$
3 + 7 + 8	AgI(s) does not dissolve
6 + 7	$2\ Cu^{2+} + 4\ I^- \rightarrow\ 2\ CuI(s) + I_2$
6 + 7 + 8	$I_2(s) + 2\ S_2O_3^{2-} \rightarrow\ 2\ I^- +\ S_4O_6^{2-}$

	1	2	3	4	5	6	7	8
1		↑						
2	↑		↓	↓	↓	↓		
3		↓		↓		↓	↓	↓
4		↓	↓					
5		↓						
6		↓	↓				↓	
7			↓			↓		
8			↓					

List of numbers and corresponding formulae for the substances:

1. NH_4NO_3
2. $NaOH$
3. $AgNO_3$
4. $ZnCl_2$
5. $Al(NO_3)_3$
6. $CuBr_2$
7. NaI
8. $Na_2S_2O_3$

PROBLEM 3 (practical)

Determination of the solubility product of lead(II) chloride

Shake solid lead(II) chloride:

a) with water,

b) with three solutions of sodium chloride of different concentrations,

until equilibrium is attained. Then determine the lead ion concentration by titration with EDTA. Calculate the solubility product of lead(II) chloride.

Equipment and chemicals

Volumetric flask (100 cm^3), pipettes (20 cm^3 and 10 cm^3), graduated cylinder (100 cm^3 and 25 cm^3), 4 Erlenmeyer flasks (200 – 250 cm^3) with stoppers, spatula, 4 filter funnels, filter papers, thermometer, 4 Erlenmeyer flasks (100 cm^3), titrating flasks (200 – 250 cm^3), beakers, stand with burette (50 cm^3), burette funnel, wash bottle with distilled water, glass rod.

Standard solutions of sodium chloride (0.1000 mol dm^{-3}) and EDTA (0.01000 mol dm^{-3}), solid lead(II) chloride, xylenol orange solution in a dropping bottle (0.5 % in water), solid hexamine (urotropine), nitric acid (2.5 mol dm^{-3}) in a dropping bottle.

Procedure

1. Prepare 100 cm^3 of sodium chloride solutions with concentrations of 0.0600 mol dm^{-3}, 0.0400 mol dm^{-3}, and 0.0200 mol dm^{-3}, respectively. Place the solutions in Erlenmeyer flasks with stoppers. Place 100 cm^3 of water in the fourth flask with a stopper. Add 5 spatulas of solid lead(II) chloride (about 2 g) to each, stopper the flasks and shake vigorously. Let the flasks stand for 30 minutes. Shake them occasionally. Prepare for filtration and titration in the meanwhile.
2. Measure the temperatures of the lead(II) chloride solutions and report them in the table of results. Filter the solutions through dry filters into small, dry Erlenmeyer flasks.
3. Using a pipette, transfer 10.00 cm^3 of the filtrate into a titration flask. Dilute with approximately 25 cm^3 of water, add 3 drops of xylenol orange (indicator) and 5 drops of nitric acid. Then add 5 spatulas (about 0.5 g) of solid hexamine (a weak base) and swirl gently until the solution is clear. Titrate with EDTA.

4. Calculate the concentration of lead ions and that of chloride ions in the solutions and give the solubility product K_s. Report the results in the table.
5. Answer the questions in the answer sheet.

Questions

3.1 Give the structure of EDTA. Mark those atoms which can coordinate to a metal ion with an asterisk (*).

3.2 Give the equation for the filtration reaction. EDTA may be written as H_2X^{2-}.

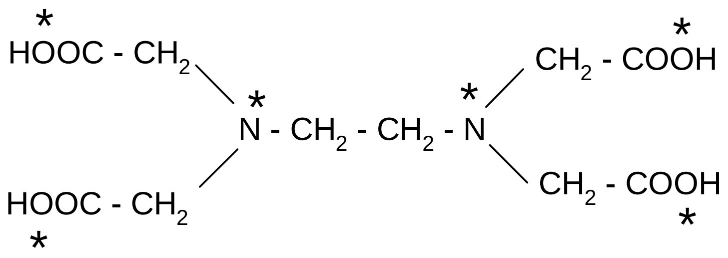
SOLUTION

A typical result:

c(NaCl) (mol dm^{-3})	Temperature (°C)	Volume EDTA solution (cm^3)	[Pb^{2+}] (mol dm^{-3})	[Cl^-] (mol dm^{-3})	K_s
0.0600	21	18.7	0.0187	0.0974	1.77×10^{-4}
0.0400	21	22.7	0.0227	0.0854	1.66×10^{-4}
0.0200	21	27.8	0.0278	0.0756	1.59×10^{-4}
-	21	34.2	0.0342	0.0684	1.60×10^{-4}

Answers to the questions:

3.1



3.2 $H_2Y^{2-} + Pb^{2+} \rightarrow PbY^{2-} + 2\ H^+$

15th

International Chemistry Olympiad

7 theoretical problems
3 practical problems

THE FIFTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
2–11 JULY 1983, TIMISOARA, ROMANIA

THEORETICAL PROBLEMS

PROBLEM 1

A) Describe the thermal decomposition of the following ammonium salts in terms of chemical equations:

a) $NH_4ClO_4 \xrightarrow{t\,°C}$

b) $(NH_4)_2SO_4 \xrightarrow{t\,°C}$

c) $(NH_4)_2S_2O_8 \xrightarrow{t\,°C}$

d) $NH_4NO_2 \xrightarrow{t\,°C}$

B) Indicate the right answer:

a) Can the molar mass be determined by measuring the density of a gaseous compound at a given temperature and pressure?

1. Yes, under any conditions.
2. Yes, if the gaseous compound does not dissociate and associate.
3. Yes, if the gaseous compound does not dissociate.
4. Yes, if the gaseous compound does not associate.

b) Is a liquid boiling at a constant temperature (at a given pressure) a pure substance?

1. Yes, if the liquid is not azeotropic.
2. Yes, if the liquid is azeotropic.

C) Complete and balance the following equation: (in H_2O)

$K_2Cr_2O_7 + SnCl_2 +$ .... $\rightarrow CrCl_3 +$ ....+ KCl + ...

D) The solubility of Hg_2Cl_2 in water is 3.0×10^{-5} g/100 ml solution.

a) What is the solubility product?

b) What is the solubility (in mol dm^{-3}) of this substance in a 0.01 M NaCl solution?

c) What is the volume of a 0.01 M NaCl solution which dissolves the same quantity of mercurous chloride as that dissolved in one litre of pure water?

A_r(Hg) = 200.61 A_r(Cl) = 35.45

E) Which of the following groups contains solid compounds at 10 °C?

a) H_2O, NH_3, CH_4

b) F_2, Cl_2, Br_2

c) SO_3, I_2, NaCl

d) Si, S_8, Hg

F) Which of the following salts forms an acidic aqueous solution?

a) CH_3COONa

b) NH_4Cl

c) Na_2HPO_4

d) Na_2CO_3

e) $NaHCO_3$

G) Write the electronic formulas for the following compounds so that the nature of the chemical bonds is evident:

a) $NaClO_3$, b) $HClO_3$, c) SiF_4, d) NH_3, e) CaF_2, f) H_2O

H) Solid perchloric acid is usually written as $HClO_4.H_2O$. Based on experimental data showing four equal bonds, suggest a structure accounting for the experimental result.

I) The compounds of the second row elements with hydrogen are as follows: LiH, BeH_2, B_2H_6, CH_4, NH_3, H_2O, HF.

a) Which compounds are solid at room temperature? Explain.

b) Which of them are ionic?

c) Which are polymeric?

d) Which ones do not react with water under normal conditions?

e) Give products of the following reactions.

$BeH_2 + H_2O \rightarrow$

$B_2H_6 + H_2O \rightarrow$

$B_2H_6 + LiH$

f) Supposing that NH_3, H_2O and HF are acids under some conditions, write their corresponding conjugated bases and arrange them in order of increasing basic strength.

J) The following E^0 values are given for the half-reactions:

$$MnO_4^- + 8\,H^+ + 5\,e^- = Mn^{2+} + 4\,H_2O \qquad E_1^0 = 1.52\ \text{V}$$

$$MnO_4^- + 4\,H^+ + 3\,e^- = MnO_2 + 2\,H_2O \qquad E_2^0 = 1.69\ \text{V}$$

Calculate E^0 for the following reaction:

$$MnO_2 + 4\,H^+ + 2\,e^- = Mn^{2+} + 2\,H_2O \qquad E_3^0 = ?$$

SOLUTION

A) a) $4\ NH_4ClO_4 \xrightarrow{t\ ^\circ C} 4\ HCl + 6\ H_2O + 2\ N_2 + 5\ O_2$

b) $3\ (NH_4)_2SO_4 \xrightarrow{t\ ^\circ C} SO_2 + N_2 + 4\ NH_3 + 6\ H_2O$

c) $2\ (NH_4)_2S_2O_8 \xrightarrow{t\ ^\circ C} 4\ SO_2 + 2\ N_2 + 8\ H_2O$

d) $NH_4NO_2 \xrightarrow{t\ ^\circ C} N_2 + 2\ H_2O$

B) a) 1, 2, 3, 4

b) 1, 2

C) $K_2Cr_2O_7 + 3\ SnCl_2 + 14\ HCl \rightarrow 2\ CrCl_3 + 3\ SnCl_4 + 2\ KCl + 7\ H_2O$

D) a) $s = 3.0 \times 10^{-5}$ g/100 cm^3 = 3.0×10^{-4} g dm^{-3} =

$$= \frac{3.0 \times 10^{-4}\ \text{g dm}^{-3}}{472\ \text{g mol}^{-1}} = 6.3 \times 10^{-7}\ \text{mol dm}^{-3}$$

$Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2\ Cl^-$

$K_s = 4\ s^3 = 4\ (6.3 \times 10^{-7})^3 = 1.0 \times 10^{-18}$

b) $c(Cl^-) = 0.01$ mol dm^{-3}

$$s = \frac{K_s}{[\mathrm{Cl}^-]^2} = \frac{1.0\times10^{-18}}{(0.01)^2} = 1.0\times10^{-14}$$

$$s = 1.0\times10^{-14}\ \mathrm{mol\,dm^{-3}}$$

c) The volume of 0.01 M NaCl solution in which dissolves the same quantity of Hg_2Cl_2 as in 1 dm^3 of water, is as follows:

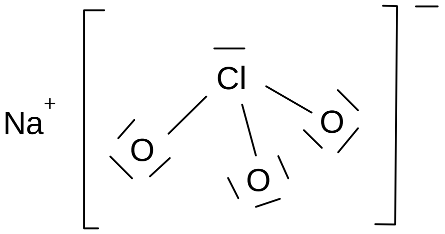
$$V = \frac{6.3\times10^{-7}}{1.0\times10^{-14}} = 6.3\times10^{7}\ \mathrm{dm^3}$$

E) c) SO_3, I_2, NaCl

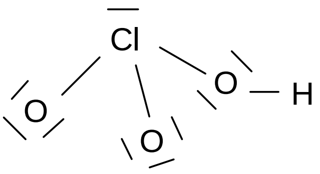
F) b)

G)

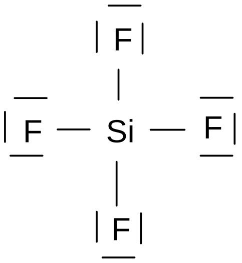
a)



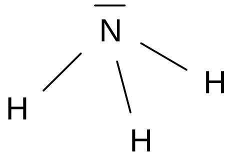
b)



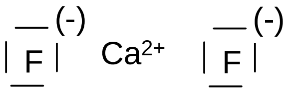
c)



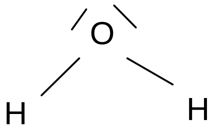
d)



e)

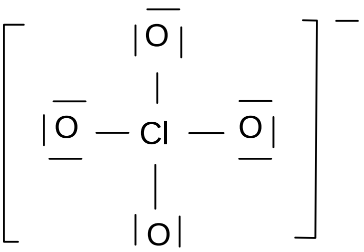


f)



H)

H_3O^+ + ClO_4^- or H_3O^+



I) a) LiH, $(BeH_2)_n$ polymer

b) LiH

c) $(BeH_2)_n$

d) CH_4

e) $BeH_2 + 2\ H_2O \rightarrow Be(OH)_2 + 2\ H_2$

$B_2H_6 + 6\ H_2O \rightarrow 2\ B(OH)_3 + 6\ H_2$

$B_2H_6 + 2\ LiH \rightarrow 2\ Li[BH_4]$

f) $NH_2^- > OH^- > F^-$

J) $MnO_4^- + 4\ H^+ + 3\ e^- = MnO_2 + 2\ H_2O$ $E_2^0 = 1.69\ V$

$MnO_2 + 4\ H^+ + 2\ e^- = Mn^{2+} + 2\ H_2O$ $E_3^0 = ?$

$MnO_4^- + 8\ H^+ + 5\ e^- = Mn^{2+} + 4\ H_2O$ $E_1^0 = 1.52\ V$

$5\,E_1^0 = 3\,E_2^0 + 2\,E_3^0$

$7.60 = 5.07 + 2\,x$

$x = 1.26\ V$

PROBLEM 2

In a gaseous mixture of CO and CO_2, a mass ratio of carbon : oxygen = 1 : 2 was determined.

2.1 Calculate the mass percent composition.

2.2 Calculate the volume percent composition.

2.3 Indicate values of the carbon: oxygen ratios for which both gases cannot be present simultaneously.

SOLUTION

Write x = number of moles of CO in 100 g

y = number of moles of CO_2 in 100 g

$28\,x + 44\,y = 100$

$$\frac{12\,(x+y)}{16\,(x+2y)} = \frac{1}{2}$$

x = 1.389 mol CO

y = 1,389 mol CO_2

2.1 $\frac{1.389\times 44}{100}\times 100 = 61.11\,\%\,CO_2$

$\frac{1.389\times 28}{100}\times 100 = 38.89\,\%\,CO$

2.2 X = y 50 % CO_2 + 50 % CO (by volume)

2.3 The two gases cannot be simultaneously present in the mixture if:

$$\frac{\text{carbon mass}}{\text{oxygen mass}} = \frac{12}{16} \text{ which correspeonds to pure CO}$$

$$\frac{12}{32} \text{ which correspeonds to pure } CO_2$$

PROBLEM 3

A sample containing a mixture of sodium chloride and potassium chloride weights 25 g. After its dissolution in water 840 ml of $AgNO_3$ solution (c = 0.5 mol dm^{-3}) is added. The precipitate is filtered off and a strip of copper weighing 100.00 g is dipped into the filtrate. After a given time interval the strip weights 101.52 g.

Calculate the mass percent composition of the mixture.

SOLUTION

$A_r(\text{Cu}) = 63.5$ $A_r(\text{Ag}) = 108$

$\text{Cu} + 2\,\text{AgNO}_3 \rightarrow \text{Cu(NO}_3)_2 + 2\,\text{Ag}$

y x

x = the quantity of deposited silver

y = the quantity of dissolved copper

$$\frac{63.5}{y} = \frac{2\times108}{x}$$

x – y = 101.52 – 100 x = 1.52 + y

$$\frac{63.5}{y} = \frac{2\times108}{1.52+x} \qquad y = 0.63 \qquad x = 2.15\text{ g Ag}^+$$

Mass of silver nitrate:

$$\frac{840}{1000}\times 0.5\times 170 = 71.4\text{ g AgNO}_3$$

$$\frac{170\text{ g AgNO}_3}{108\text{ g Ag}} = \frac{71.4}{\text{x}} \qquad \text{x} = 45.36\text{ g Ag}^+$$

Silver consumed for participation

45.36 – 2.15 = 43.21 g Ag^+

Total mass of chloride

$$\frac{108\ \text{g Ag}^+}{35.5\ \text{g Cl}^-} = \frac{43.2}{x} \qquad x = 14.2\ \text{g Cl}^-$$

M_r(NaCl) = 58.5 M_r(KCl) = 74.6

x = mass of NaCl in the mixture

y = mass of KCl in the mixture

mass of Cl^- in NaCl: $\frac{35.5\ x}{58.5}$

mass of Cl^- in KCl: $\frac{35.5\ y}{74.6}$

$$\frac{35.5\ x}{58.5} + \frac{35.5\ y}{74.6} = 14.2$$

$x + y = 25$

x = 17.6 g NaCl 70.4 % NaCl

y = 7.4 g KCl 29.6 % KCl

PROBLEM 4

The following data were gathered for the alkaline hydrolysis of certain chlorinated compounds:

a) A certain volume of a solution of the neutral potassium salt of chlorosuccinic acid is mixed with an equal volume of hydroxide solution. The initial concentration of each solution is 0.2 mol dm^{-3}. The potassium hydroxide concentration in the reaction mixture was determined at different time intervals at 25 °C. The following values were obtained:

t (minutes)	10	20	30	45	60	80	100
c(KOH) (mol dm^{-3})	0.085	0.074	0.065	0.056	0.049	0.042	0.036

The experiment was repeated with the same initial solutions at 35 °C. The hydroxide concentration is reduced to one half after 21 minutes.

b) In the hydrolysis of 3-chloro-3-methylhexane with potassium hydroxide, the concentration of potassium hydroxide was found to have been reduced to one half after 32 minutes at 25 °C or 11 minutes at 35 °C, r egardless of the initial reactant concentrations (identical).

c) In the alkaline hydrolysis of 3-chloro-2,4-dimethyl-3-isopropylpentane an identical reaction mechanism as for reaction b was found but the reaction rate was about 100 times faster under the same reaction conditions.

Considering the above data answer the following questions:

4.1 What is the reaction order in cases a, b, and c?

4.2 What is the rate constant at 25 °C for reaction a ? Indicate the units.

4.3 Calculate the activation energies for reactions a and b.

4.4 If in reaction a dipotassium salt of L-chlorosuccinic acid (which is levorotatory,) is used, what type of optical rotation will be exhibited by the corresponding salt of malic acid formed by hydrolysis?

4.5 If the levorotatory isomer is also used in reaction b, what optical rotation will be exhibited by 3-methyl-3-hexanol formed in the hydrolysis reaction?

4.6 Why is the rate of reaction c much faster than that of reaction b when both reactions are of the same type and occur under the same temperature and concentration conditions?

SOLUTION

4.1 For reaction a the reaction order is estimated as follows:

- assuming the first-order reaction:

$$k = \frac{1}{t}\ln\frac{\text{a}}{\text{a - x}}$$

t (℃)	10	20	30	45	60	80	100
k . 10^2	1.625	1.505	1.436	1.288	1.189	1.084	1.022

k is not constant, hence the reaction is not of the first-order.

- for the second-order reaction (with reactant concentrations equal at time zero):

$$k = \frac{1}{t}\left(\frac{\text{a}}{\text{a - x}} - \frac{1}{\text{a}}\right)$$

t (℃)	10	20	30	45	60	80	100
k	0.176	0.176	0.179	0.175	0.173	0.173	0.178

As *k* has almost a constant value the condition for a second-order reaction is fulfilled.

The half-life of reaction b is independent on the initial concentrations, i. e. it is a first-order reaction:

$$k = \frac{1}{t}\ln\frac{\text{a}}{\text{a - x}} = \frac{1}{t_{1/2}}\ln\frac{\text{a}}{\text{a - }\frac{\text{a}}{2}} = \frac{1}{t_{1/2}}\ln 2$$

Reaction c has the same mechanism as reaction b. Therefore, it will also be a first-order reaction.

4.2 The rate constant of reaction a is an average of the above calculated values.

k = 0.176 dm^3 mol^{-1} min^{-1}

4.3 In order to determine the activation energy, the rate constant, *k*', at 35 ℃ is to be calculated.

For the second-order reactions the relationship between the rate constants and half-lives is as follows:

$$k = \frac{1}{t}\left(\frac{a}{a-x} - \frac{1}{a}\right) = \frac{1}{t_{1/2}}\left(\frac{1}{a-\frac{a}{2}} - \frac{1}{a}\right) = \frac{1}{t_{1/2}}\,\frac{1}{a}$$

The half-life at 35 °C and the initial concentration, a = 0.1 mol dm^{-3}, are known. (By mixing equal volumes of the two solutions the concentration of each reacting species is reduced to a half.)

Calculation of the rate constant at 35 °C:

$$k' = \frac{1}{21}\cdot\frac{1}{0.1} = 0.476\ \text{dm}^3\ \text{mol}^{-1}\ \text{min}^{-1}$$

The activation energy of reaction <u>a</u> will be:

$$E_a = R\ln\frac{k'}{k}\cdot\frac{T'\cdot T}{T'-T} = 8314\ \ln\frac{0.476}{0.176}\cdot\frac{308\cdot 298}{308-298} = 7.592\times10^{7}\ \text{J mol}^{-1}$$

For reaction <u>b</u> that is a first-order reaction, the rate constants at the two temperatures are calculated from the half-lives:

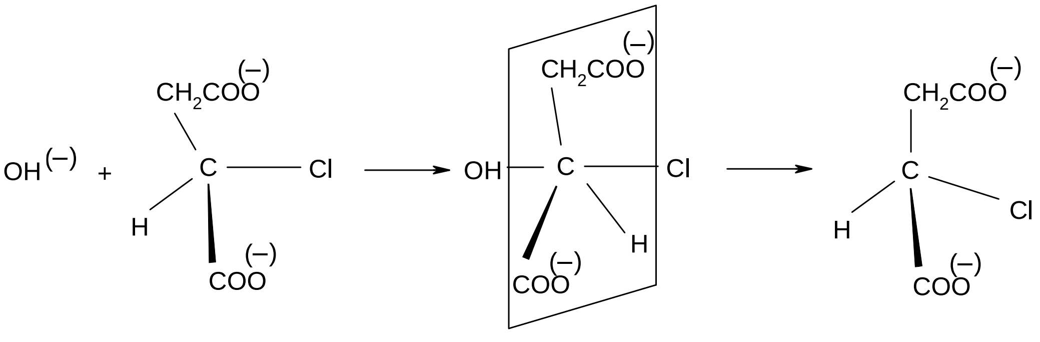
at 25 °C: $k = \frac{\ln 2}{32} = 2.166\times10^{-2}\ \text{min}^{-1}$

at 35 °C: $k' = \frac{\ln 2}{11} = 6.301\times10^{-2}\ \text{min}^{-1}$

Hence the activation energy is:

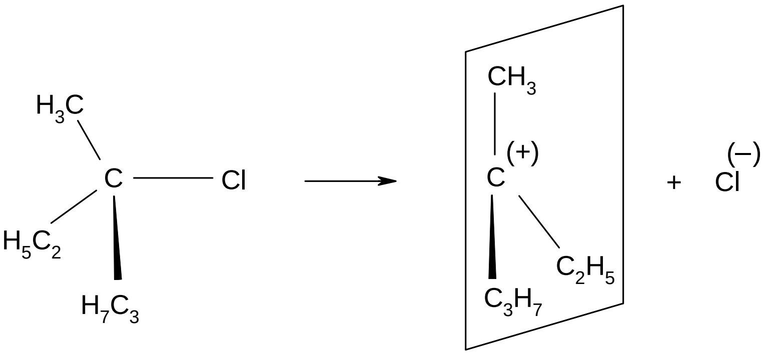
$$E_a = 8314\ \ln\frac{6.301\times10^{-2}}{2.166\times10^{-2}}\cdot\frac{308\cdot 298}{308-298} = 8.149\times10^{7}\ \text{J mol}^{-1}$$

4.4 The product of the hydrolysis reaction <u>a</u> will become dextrorotatory as a result of configuration inversion.



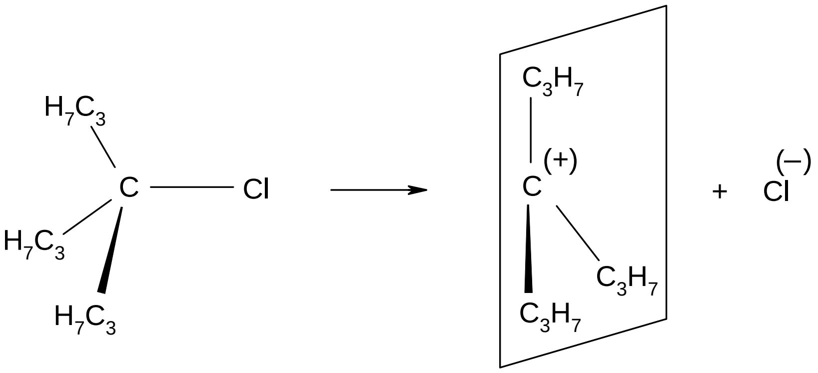
As an S_N2 type reaction, it involves a transition state in which the inversion of the configuration of the asymmetric carbon atom occurs. Thus, if the substrate is levorotatory, the product will become dextrorotatory.

4.5 The reaction b is a unimolecular S_N1 reaction and involves the transient formation of an almost stable carbonium ion in the rate-determining step.



The most probable structure of the carbonium ion is planar. The carbonium ion may be attached by the nucleophylic reagent (the OH^- ion) on both sides of the plane with the same probability. The product will result as a racemic mixture, with no optical activity, inactive by intermolecular compensation.

4.6 The same is true for the reaction c, the only difference being a more marked repulsion among bulkier substituents. The tendency towards carbonium ion formation with a planar structure and reduced repulsions is increased.



The rate of the carbonium ion formation, and therefore the overall reaction rate, is consequently increased.

PROBLEM 5

On passing ethanol over a catalyst at 400 K, a dehydration reaction occurs resulting in the formation of ethylene:

$C_2H_5OH(g) \rightarrow C_2H_4(g) + H_2O(g)$

At the above temperature and p_0 = 101.325 kPa, the conversion of ethyl alcohol is 90.6 mol %.

5.1 Calculate the equilibrium constant K_p of the reaction under given conditions.

5.2 Calculate the values of the equilibrium constants K_x and K_c at the above temperature.

5.3 Calculate the ethanol conversion at the following pressures:

5 p_0, 10 p_0, 50 p_0, 100 p_0, and 200 p_0.

5.4 Plot the graph for the variation of conversion *vs*. pressure.

SOLUTION

The reaction:	C_2H_5OH	$\rightarrow$ C_2H_4	+ H_2O	
Moles:				
initial:	1	0	0	
at equilibrium:	1 – x	x	x	total: 1 + x

	Molar fraction	Partial pressure
Ethanol	$\frac{1-x}{1+x}$	$\frac{1-x}{1+x}\,p$
Ethylene	$\frac{x}{1+x}$	$\frac{x}{1+x}\,p$
Water	$\frac{x}{1+x}$	$\frac{x}{1+x}\,p$

$p = \frac{p'}{p}$ $\qquad$ p' – total pressure, p_0 = 101.325 kPa

$$K_p = \frac{p_{C_2H_4} \cdot p_{H_2O}}{p_{C_2H_5OH}} = \frac{\left(\frac{x}{1+x}p\right)\left(\frac{x}{1+x}p\right)}{\frac{1-x}{1+x}p} = \frac{x^2}{1-x^2}p$$

5.1 $p' = 101.325$ kPa

$$K_p = \frac{x^2}{1-x^2} = \frac{0.906^2}{1-0.906^2} = 4.56$$

5.2 $K_x = K_p\, p^{-\Delta n}$; $p' = 101.325$ kPa; $\Delta n = 1$; $K_x = 4.56$

$$K_c = K_p \left(\frac{c_0 RT}{p_0}\right)^{\Delta n} \quad R = 8.314\ \text{J mol}^{-1}\,\text{K}^{-1};\ c^0 = 1\ \text{mol dm}^{-3};\ T = 400\,K$$

$K_c = 0.139$

5.3 $\dfrac{x^2}{1-x^2} = \dfrac{K_p}{p} = \dfrac{4.56}{p}$

a) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{5} = 0.912$ x = 0.69

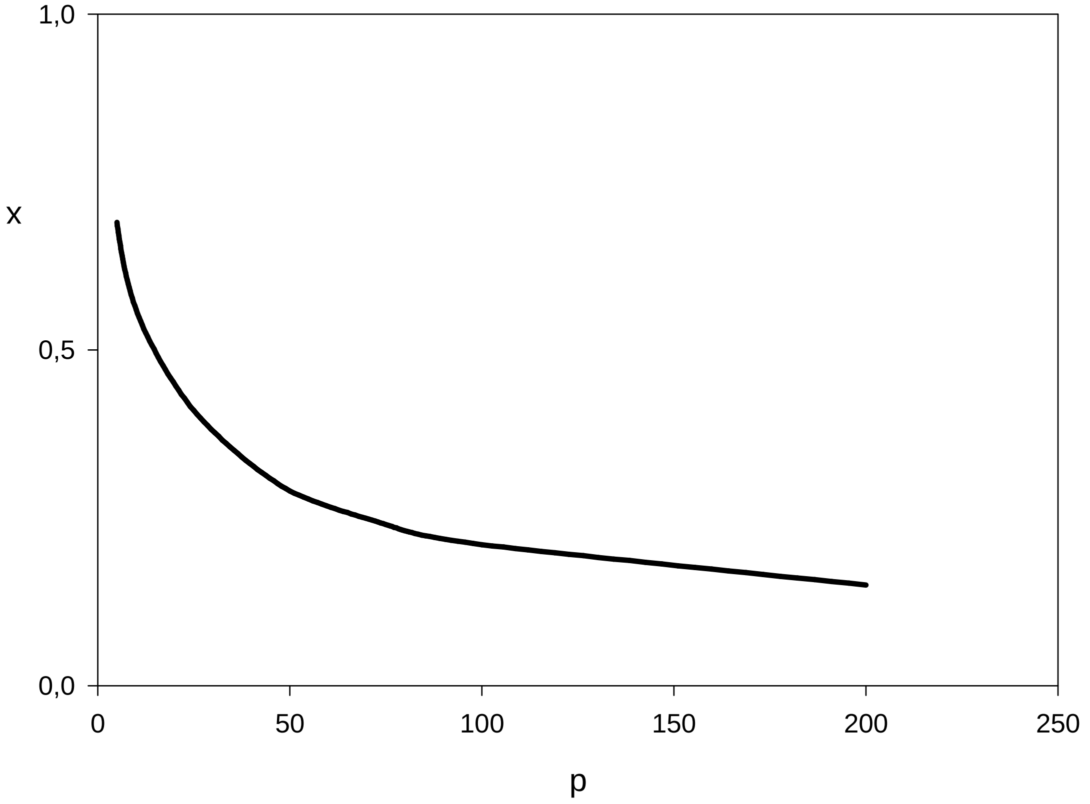
b) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{10} = 0.456$ x = 0.56

c) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{50} = 0.0912$ x = 0.29

d) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{100} = 0.0456$ x = 0.21

e) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{200} = 0.0228$ x = 0.15

5.4



PROBLEM 6

One mole of compound **A** reacts successively with 3 moles of compound **B** in aqueous solution in the presence of a basic catalyst (such as $Ca(OH)_2$):

$\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C}$

$\mathbf{C} + \mathbf{B} \rightarrow \mathbf{D}$

$\mathbf{D} + \mathbf{B} \rightarrow \mathbf{E}$

Hydrogenation of compound **E** yields compound **F**:

$\mathbf{E} + H_2 \rightarrow \mathbf{F}$

F has the composition: C = 44.18 %, H = 8.82 %, O = 47.00 %.

Its molar mass: $M = 136\ \text{g mol}^{-1}$

Knowing that 13.6 g of **F** reacts with 40.8 g acetic anhydride to form product **G** and acetic acid write down all chemical equations and assign the letters **A**, **B**, **C**, **D**, **E**, **F**, and **G** to particular formulas of compounds.

SOLUTION

The molecular formula of **F**:

$$C : H : O = \frac{44.18}{12} : \frac{8.82}{1} : \frac{47.00}{16} = 1.25 : 3 : 1 = 5 : 12 : 4$$

$(C_5H_{12}O_4)_n$

Since $M(\mathbf{F}) = 136$

and $(5 \times 12) + (12 \times 1) + (4 \times 16) = 136$

F = $C_5H_{12}O_4$

Since **F** reacts with acetic anhydride it could be a mono- or polyhydroxy alcohol. If it were a monohydroxy alcohol, 136 g of **F** (1 mol) could react with 102 g (1 mol) of acetic anhydride. In fact 13.6 g of **F** (i. e. 0.1 mol) reacts with 40.8 g of acetic anhydride (40.8 / 102 = 0.4 mol), i. e. **F** is a polyol (tetrahydroxy alcohol).

F is formed by the reduction of **E**, so that **E** has one carbonyl and three OH groups.

E is formed from 3 molecules of **B** and one molecule of **A**.

Since compound **E** has three OH groups and one CO group and the reaction conditions used are typical for aldol condensation, it is clear that **A** is acetaldehyde and **B** is formaldehyde. **C** and **D** are the products of successive aldol condensation of acetaldehyde with formaldehyde:

$$\underset{\mathbf{A}}{H_3C\text{-}CH=O} + \underset{\mathbf{B}}{H_2C=O} \rightarrow \underset{\mathbf{C}}{HO\text{-}CH_2\text{-}CH_2\text{-}CH=O}$$

$$\underset{\mathbf{C}}{HO\text{-}CH_2\text{-}CH_2\text{-}CH=O} + \underset{\mathbf{B}}{H_2C=O} \rightarrow \underset{\mathbf{D}}{(HO\text{-}CH_2)_2CH\text{-}CH=O}$$

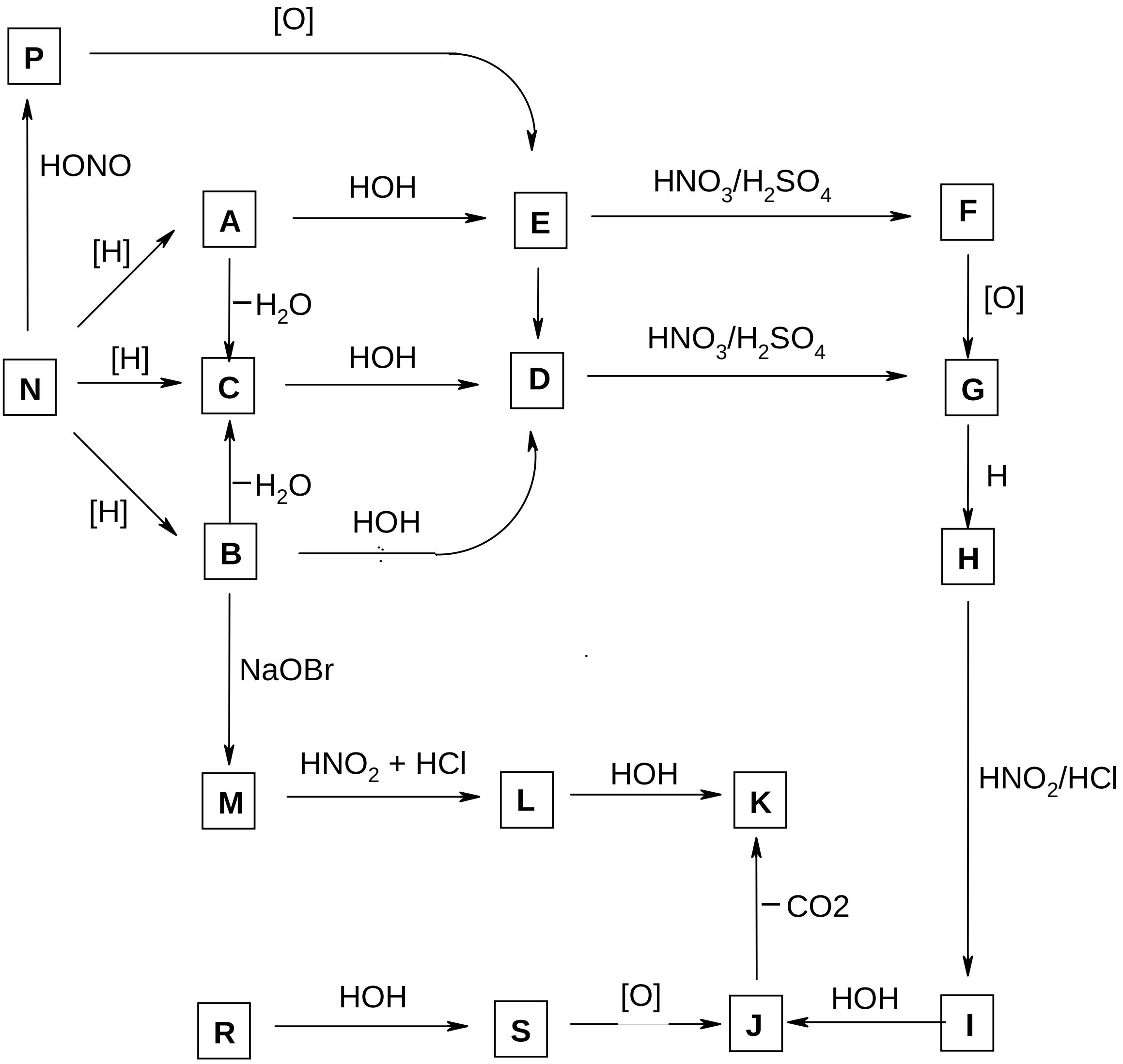
$$\underset{\mathbf{D}}{(HO\text{-}CH_2)_2CH\text{-}CH=O} + \underset{\mathbf{B}}{H_2C=O} \rightarrow \underset{\mathbf{E}}{(HO\text{-}CH_2)_3C\text{-}CH=O}$$

$$\underset{\mathbf{E}}{(HO\text{-}CH_2)_3C\text{-}CH=O} + H_2 \rightarrow \underset{\mathbf{F}}{(HO\text{-}CH_2)_4C}$$

$$(HO\text{-}CH_2)_4C + 4\ (CH_3CO)_2O \rightarrow \underset{\mathbf{G}}{(CH_3COO\text{-}CH_2)_4C} + 4\ CH_3COOH$$

PROBLEM 7

Knowing that compounds **A** and **B** are isomers with the molecular formula C_7H_7NO and the relative molecular mass of compound **M** is 93, determine the formulae of compounds **A** to **S** taking in account the reactions given in the following reaction scheme:



SOLUTION

A $C_6H_5\text{-CH=N-OH}$

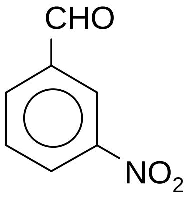
B $C_6H_5\text{-CO-NH}_2$

C $C_6H_5\text{-CN}$

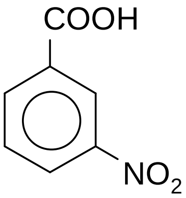
D $C_6H_5\text{-COOH}$

E $C_6H_5\text{-CHO}$

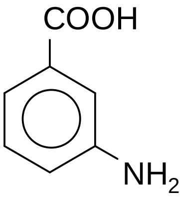
F



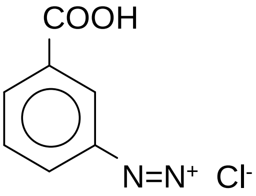
G



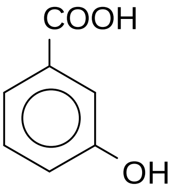
H



I



J



K $C_6H_5\text{-OH}$

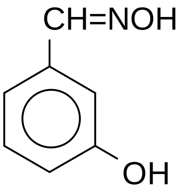
L $C_6H_5\text{-N=N}^+\ \text{Cl}^-$

M $C_6H_5\text{-NH}_2$

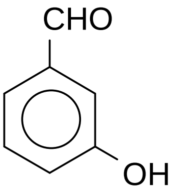
N $C_6H_5\text{-CH}_2\text{-NH}_2$

P $C_6H_5\text{-CH}_2\text{-OH}$

R



S



PRACTICAL PROBLEMS

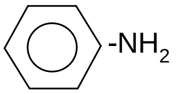
PROBLEM 1 (practical)

In test tubes **A**, **B**, **C**, and **D** there are four benzene derivatives containing one or two functional groups of three distinct types. Identify the functional groups of compounds **A**, **B**, **C**, and **D** using the available reagents.

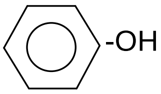
- Justify your choice by writing down the identification reactions.
- Using as reagents the four compounds **A**, **B**, **C**, and **D** synthesize four organic dyes and write the equations for the reactions performed.

SOLUTION

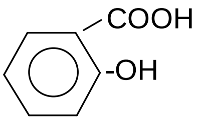
The four compounds are as follows:



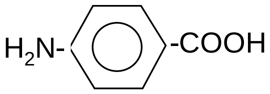
A



B



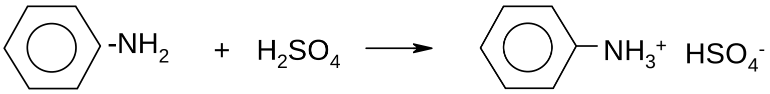
C

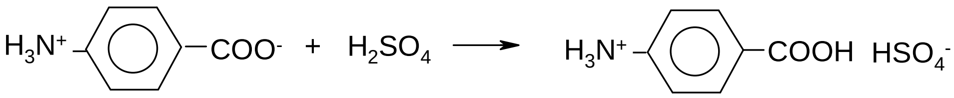


D

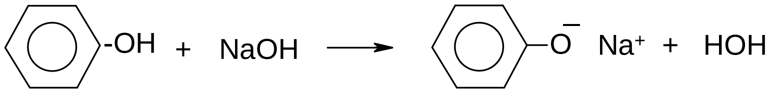
The identification reactions:

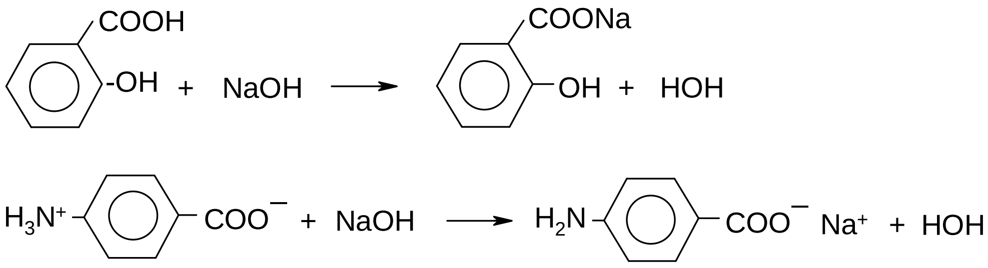
a) With H_2SO_4:



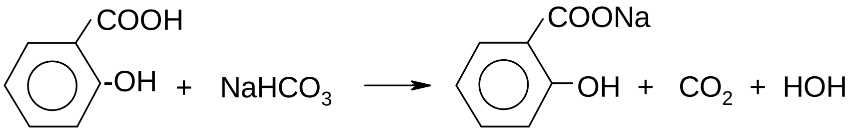


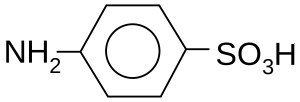
b) With NaOH:

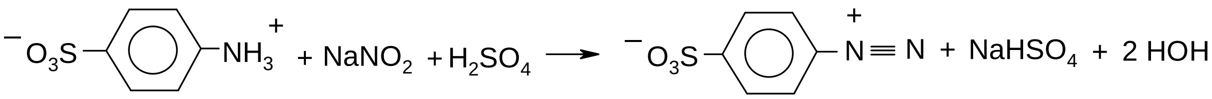


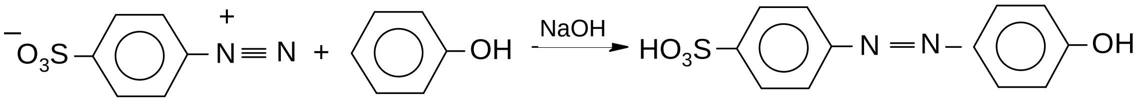


c) With $NaHCO_3$:

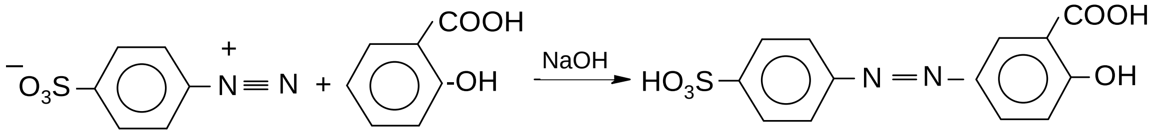


d) With 

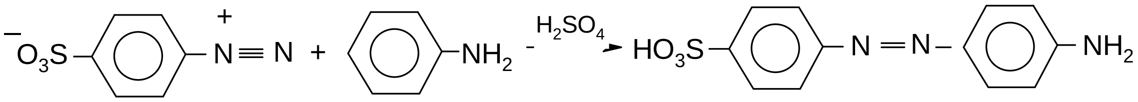




(orange)

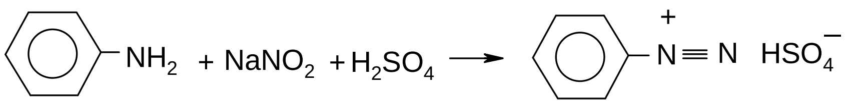


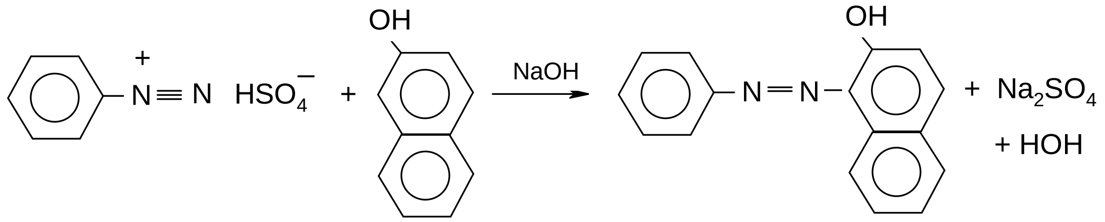
(orange)



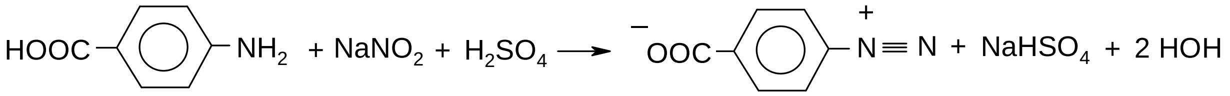
(orange)

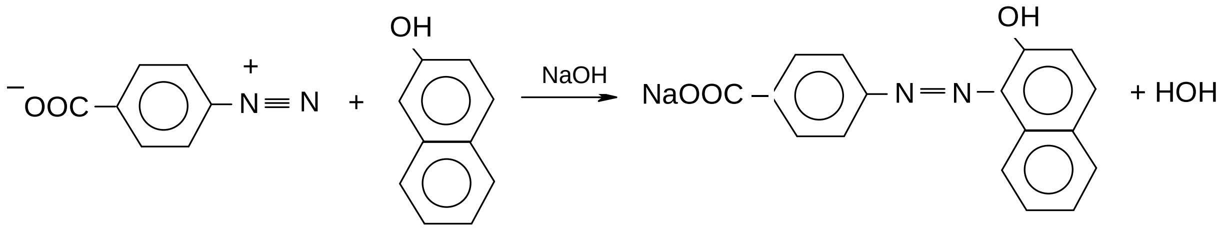
II. e) With β-naphthol:





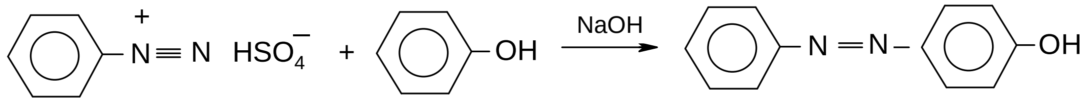
yellow - orange



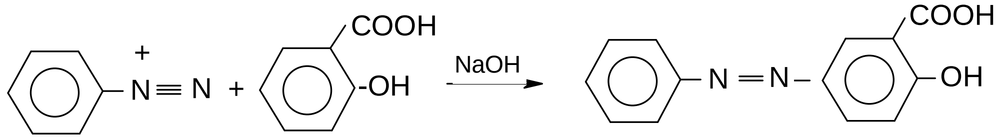


red

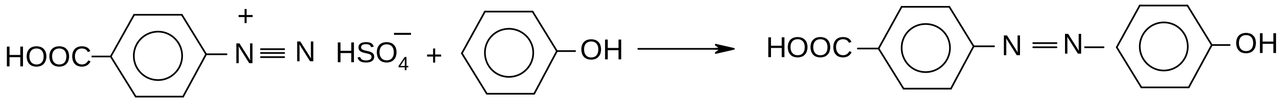
The following dyes can be obtained:



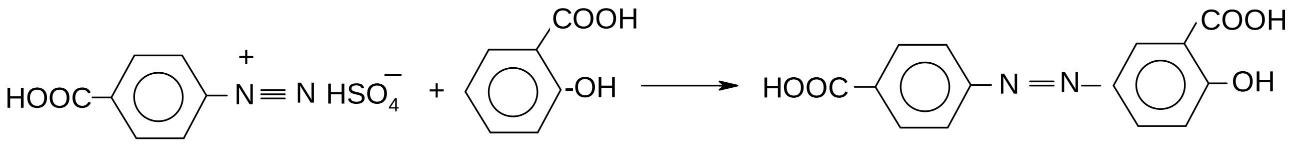
(red - orange)



(red - orange)



(red - orange)



(red - orange)

PROBLEM 2 (practical)

A solution in a graduated flask contains a mixture of oxalic acid and ammonium oxalate.

One of the bottles denoted X, Y, and Z contains a solution of a calibration substance with reducing character at a concentration of 0.1000 mol dm^{-3}.

You are required to solve the following tasks:

a) Determine the quantity of oxalic acid and of ammonium oxalate in the solution in the graduated flask. (The result will be given in grams.)

b) Write the formula for the substance with reducing character and the equations of the chemical reactions which led to its determination.

In order to carry out the analyses the following solutions are available:
HCl (c = 0.1000 mol dm^{-3}), NaOH (c = 2 mol dm^{-3}), $KMnO_4$ (c = 0.02 mol dm^{-3}), 25 % H_2SO_4, HNO_3 (c = 2 mol dm^{-3}), 5 % $BaCl_2$, 5 % $AgNO_3$, 5 % $Hg_2(NO_3)_2$, phenolphthalein 0.1 %, methyl red 1 %.

c) Describe the procedure used in the individual steps, indicators employed and partial results.

$M_r(H_2C_2O_4) = 90.04$

$M_r((NH_4)_2C_2O_4) = 124.11$

SOLUTION

ANSWER SHEET:

A_1 – Identification of the solution with the reducing substance X, Y, Z: $Fe(NH_4)_2(SO_4)_2$

A_2 – Identification reactions for the ions of the substance

- $Fe^{2+} + 2\ NaOH \rightarrow Fe(OH)_2 + 2\ Na^+$
- $NH_4^+ + NaOH \rightarrow NH_3\uparrow + H_2O + Na^+$
- $4\ NH_3 + 2\ Hg_2(NO_3)_2 + H_2O \rightarrow O(Hg)_2NH_2.NO_3 + 3\ NH_4OH$
- $SO_4^{2-} + BaCl_2 \rightarrow BaSO_4 + 2\ Cl^-$

B_1– Preparation of the 0.1 M NaOH solution

. . . . cm^3 in 200.0 cm^3

B_2 – Concentration of the NaOH in its solution: . . . . M

Indicator used: . . . .

C – Concentration of $KMnO_4$ in its solution . . . . M

D_1 – Mass of oxalic acid in the initial solution . . . . g

Indicator used . . . .

D_2 – Mass of ammonium oxalate in the initial solution . . . . g

Solution

A_1 – 1-2 cm^3 of solution X, Y and Z are put into three test tubes. 6 N H_2SO_4 and a drop of $KMnO_4$ solution are added. The solution which loses colour is the one with reducing character.

A_2 – Establishment of the formula:

. . . . + NaOH – greenish white precipitate ⇒ Fe^{2+}

. . . . + NaOH at the upper end of the test-tube, filter paper with a drop of $Hg_2(NO_3)_2$, black spot ⇒ NH_4^+

. . . . + $BaCl_2$ – white precipitate ⇒ SO_4^{2-}

. . . . + $AgNO_3$ + HNO_3 ⇒ Cl^- is absent

Accordingly the substance used is $Fe(NH_4)_2(SO_4)_2$.

The chemical reactions:

$Fe^{2+} + 2\ Na^+ + 2\ OH^- \rightarrow Fe(OH)_2 + 2\ Na^+$

$NH_4^+ + Na^+ + OH^- \rightarrow NH_3 + H_2O + Na^+$

$4\ NH_3 + 2\ Hg_2(NO_3)_2 \rightarrow O(Hg)_2NH_2 \,.\, NO_3 + 2\ Hg + 3\ NH_4NO_3$

$SO_4^{2-} + Ba^{2+} + 2\ Cl^- \rightarrow BaSO_4 + 2\ Cl^-$

B_1 – 5 cm^3 2 M solution ⇒ 100 cm^3 0.1 M solution

B_2 – *V* cm^3 0.1000 N HCl + 0.1 N NaOH in the presence of phenolphthalein.

C – *V* cm^3 solution X + 10.0 cm^3 H_2SO_4 + H_2O is titrated at elevated temperature with $KMnO_4$.

D_1 – The solution which is to be analyzed is filled to the mark; *V* cm^3 of this solution is titrated with NaOH in the presence of methyl red. The quantity of oxalic acid (moles and g) is calculated.

D_2 – *V* cm^3 solution to be analyzed + 10.0 cm^3 6 N H_2SO_4 + H_2O are heated and titrated with $KMnO_4$ solution.

The total amount of oxalate is calculated (in mol).

The difference gives the amount of ammonium oxalate (moles and g).

PROBLEM 3 (practical)

Six test-tubes contain aqueous solutions of $FeSO_4$, H_2SO_4, $Mn(NO_3)_2$, H_2O_2, $Pb(NO_3)_2$, NaOH.

a) Identify the content of each test-tube without using other reagents. Write the results in tabular form. Write the equations for the chemical reactions used for the identification.

b) After identification, perform four reactions each time using three of the identified compounds and write the equations.

SOLUTION

	$FeSO_4$	H_2SO_4	$Mn(NO_3)_2$	H_2O_2	$Pb(NO_3)_2$	NaOH
1) $FeSO_4$		–	–	$Fe(OH)SO_4$ yellowish	$PbSO_4\downarrow$ white	Fe(OH)2 $\downarrow$ white-greenish $\downarrow$ Fe(OH)3 $\downarrow$ brown-redish
2) H_2SO_4	–		–	–	$PbSO_4\downarrow$ white	–
3) $Mn(NO_3)_2$	–	–		–	–	$Mn(OH)_2\downarrow$ white $\downarrow$ $MnMnO_3\downarrow$ brown black
4) H2O2	$Fe(OH)SO_4$ yellowish	–	–		–	–
5) $Pb(NO_3)_2$	$PbSO_4\downarrow$ white	$PbSO_4\downarrow$ white	–	–		–
6) NaOH	$Fe(OH)_2\downarrow$ white-greenish $\downarrow$ $Fe(OH)_3\downarrow$ brown-redish	–	$Mn(OH)_2\downarrow$ white $\downarrow$ $MnMnO_3\downarrow$ brown black	–	$Pb(OH)_2\downarrow$ white $\downarrow$ $Pb(OH)_4^{2-}$	

	Reactions	Observation
(1) + (4)	$FeSO_4 + H_2O_2 \rightarrow 2\ Fe(OH)SO_4$	Colour change - yellowish (Fe^{3+})
(1) + (5)	$FeSO_4 + Pb(NO_3)_2 \rightarrow PbSO_4 \downarrow + Fe(NO_3)_2$	Appearance of a white precipitate.
(1) + (6)	$FeSO_4 + 2\ NaOH \rightarrow Fe(OH)_2 \downarrow + Na_2SO_4$ $Fe(OH)_2 + ½\ O_2 + H_2O \rightarrow Fe(OH)_3$	Appearance of a greenish white precipitate $Fe(OH)_2$ which after oxidation by air turns into a reddish brown precipitate $Fe(OH)_3$.
(2) + (5)	$H_2SO_4 + Pb(NO_3)_2 \rightarrow PbSO_4 \downarrow + 2\ HNO_3$	Appearance of a white precipitate $PbSO_4$.
(3) + (6)	$Mn(NO_3)_2 + 2\ NaOH \rightarrow Mn(OH)_2 + 2\ NaNO_3$ $2\ Mn(OH)_2 + ½\ O_2 \rightarrow MnMnO_3 + 2\ H_2O$ $Mn(OH)_2 + ½\ O_2 \rightarrow MnO_2 + H_2O$	Appearance of a white precipitate $Mn(OH)_2$ which after oxidation by air coverts into a brown-black precipitate $MnMnO_3$ which eventually changes into MnO_2 – a black-brown precipitate.
(5) + (6)	$Pb(NO_3)_2 + 2\ NaOH \rightarrow Pb(OH)_2 + 2\ NaNO_3$ $Pb(OH)_2 + 2\ NaOH \rightarrow Na_2Pb(OH)_4$	Appearance of a white precipitate $Pb(OH)_2$ which dissolves in excess reagent.
b)		
(1) + (2) + (4)	$2\ FeSO_4 + H_2O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2\ H_2O$	Colour change → yellowish (Fe^{3+})
(1) + (4) + (6)	$2\ FeSO_4 + H_2O_2 + 4\ NaOH \rightarrow Fe(OH)_3 +$ $+ 2\ Na_2SO_4$	Appearance of a brown-reddish precipitate $Fe(OH)_3$
(3) + (4) + (6)	$Mn(NO_3)_2 + H_2O_2 + 2\ NaOH \rightarrow MnO_2 + 2\ NaNO_3$ $+ 2\ H_2O$	Appearance of a brown precipitate MnO_2
(5) + (4) + (6)	$Pb(NO_3)_2 + H_2O_2 + 2\ NaOH \rightarrow PbO_2 + 2\ NaNO_3$ $+ 2\ H_2O$	Appearance of a brown precipitate PbO_2.

16th

International Chemistry Olympiad

8 theoretical problems
2 practical problems

THE SIXTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
1–10 JULY 1984, FRANKFURT AM MAIN, GERMAN FEDERAL REPUBLIC

THEORETICAL PROBLEMS

PROBLEM 1

A)

The element carbon consists of the stable isotopes ^{12}C (98.90 percent of atoms) and ^{13}C (1.10 percent of atoms). In addition, carbon contains a small fraction of the radioisotope ^{14}C ($t_{1/2}$= 5730 years), which is continuously formed in the atmosphere by cosmic rays as CO_2. ^{14}C mixes with the isotopes ^{12}C and ^{13}C via the natural CO_2 cycle.

The decay rate of ^{14}C is described by (N = number of ^{14}C atoms; t = time; λ = decay constant):

$$\text{decay rate} = -\frac{dN}{dt} = \lambda N \qquad (1)$$

Integration of (1) leads to the well-known rate law (2) for the radioactive decay:

$$N = N_0\, e^{-\lambda t} \qquad (2)$$

N_o = number of ^{14}C atoms at t = 0

1.1 What is the mathematical relationship between the parameters α and $t_{1/2}$ (= half l life)?

1.2 The decay rate of carbon, which is a part of the natural CO_2 cycle, is found to be 13.6 disintegrations per minute and gram of carbon. When a plant (e. g. a tree) dies, it no longer takes part in the CO_2 cycle. As a consequence, the decay rate of carbon decreases.

In 1983, a decay rate of 12.0 disintegrations per minute and gram of carbon was measured for a piece of wood which belongs to a ship of the Vikings. In which year was cut the tree from which this piece of wood originated?

1.3 Assume that the error of the decay rate of 12.0 disintegrations per minute and gram of carbon is 0.2 disintegrations per minute and gram of carbon. What is the corresponding error in the age of the wood in question b)?

1.4 What is the isotope $^{12}C/^{14}C$ ratio of carbon, which takes part in the natural CO_2 cycle (1 year = 365 days)?

B)

The elements strontium and rubidium have the following isotope composition:

Strontium: 0.56 % ^{84}Sr ; 9.86 % ^{86}Sr ; 7.00 % ^{87}Sr ; 82.58 % ^{88}Sr (these isotopes are all stable).

Rubidium: 72.17 % ^{85}Rb (stable) ; 27.83 % ^{87}Rb (radioactive; $t_{1/2} = 4.7 \times 10^{10}$ years).

The radioactive decay of ^{87}Rb leads to ^{87}Sr.

In Greenland one finds a gneiss (= silicate mineral) containing both strontium and rubidium.

1.5 What is the equation rate law describing the formation of ^{87}Sr from ^{87}Rb as a function of time?

1.6 Assume that the isotope ratio $^{87}Sr/^{86}Sr$ (as determined by mass spectrometry) and the isotope ratio $^{87}Rb : ^{86}Sr$ are known for the gneiss. What is the mathematical relationship with which one can calculate the age of the gneiss?

SOLUTION

A)

1.1 The relationship is:

$$\alpha = \frac{\ln 2}{t_{1/2}}$$

1.2

$$t = \frac{t_{1/2}}{\ln 2} \times \ln\left(\frac{N_0}{N}\right) = \frac{5730}{0.6930} \times \ln\left(\frac{13.6}{12.0}\right) = 1035 \text{ years}$$

1.3 For N_o/N = 13.6/12.0 t = 1035 years

For N_o/N = 13.6/12.2 t = 898 years

For N_o/N = 13.6/11.8 t = 1174 years

Thus, the tree was cut 1035 (+ 139/–137) years ago.

1.4

$$N = \frac{13.6 \times t_{1/2}}{\ln 2} = 5.91 \times 10^{10} \text{ atoms } ^{14}\text{C /g carbon}$$

1 g ≈ 0.989 g ^{12}C; 0.989 g ^{12}C ≈ (0.989/12) × 6.023 ×10^{23} atoms ^{12}C

$$^{12}\text{C} / ^{14}\text{C} = \frac{0.989 \times 6.023 \times 10^{23}}{12 \times 5.91 \times 10^{10}} = 8.40 \times 10^{11} : 1$$

B)

1.5 Equation (2) describes the decay of the ^{87}Rb:

$$^{87}\text{Rb} = ^{87}\text{Rb}_o \,.\, \exp(-\lambda\, t)$$

The symbol ^{87}Rb stands for the number of atoms of this nuclide.

Consequently, one obtains for the formation of ^{87}Sr from ^{87}Rb:

$$^{87}\text{Sr} = ^{87}\text{Rb}_o - ^{87}\text{Rb} = ^{87}\text{Rb} \,.\, \exp(\lambda t) - ^{87}\text{Rb} \qquad \text{(a)}$$

1.6 The formation of the radiogenic ^{87}Sr follows equation (a).

One has to take into account that at time t = 0, when the mineral was formed, there was some non-radiogenic strontium in it already:

$$^{87}\text{Sr} = (^{87}\text{Sr})_o + ^{87}\text{Rb} \,.\, [\exp(\lambda t) - 1]$$

The isotope ratio (^{87}Sr/ ^{86}Sr)$_o$ follows from the isotope composition of strontium. The time t in this equation corresponds to the age of the gneiss.

PROBLEM 2

Ludwig Mond discovered before the turn of this century that finely divided nickel reacts with carbon monoxide forming tetracarbonylnickel, $Ni(CO)_4$, a colourless, very volatile liquid. The composition of $Ni(CO)_4$ provides an example of the noble gas rule ("EAN rule").

Problems:

2.1 Use the eighteen-electron rule (noble gas rule) to predict the formula of the binary carbonyls of Fe(0) and Cr(0).

2.2 What composition would the eighteen-electron rule predict for the most simple binary chromium(0)-nitrosyl compound?

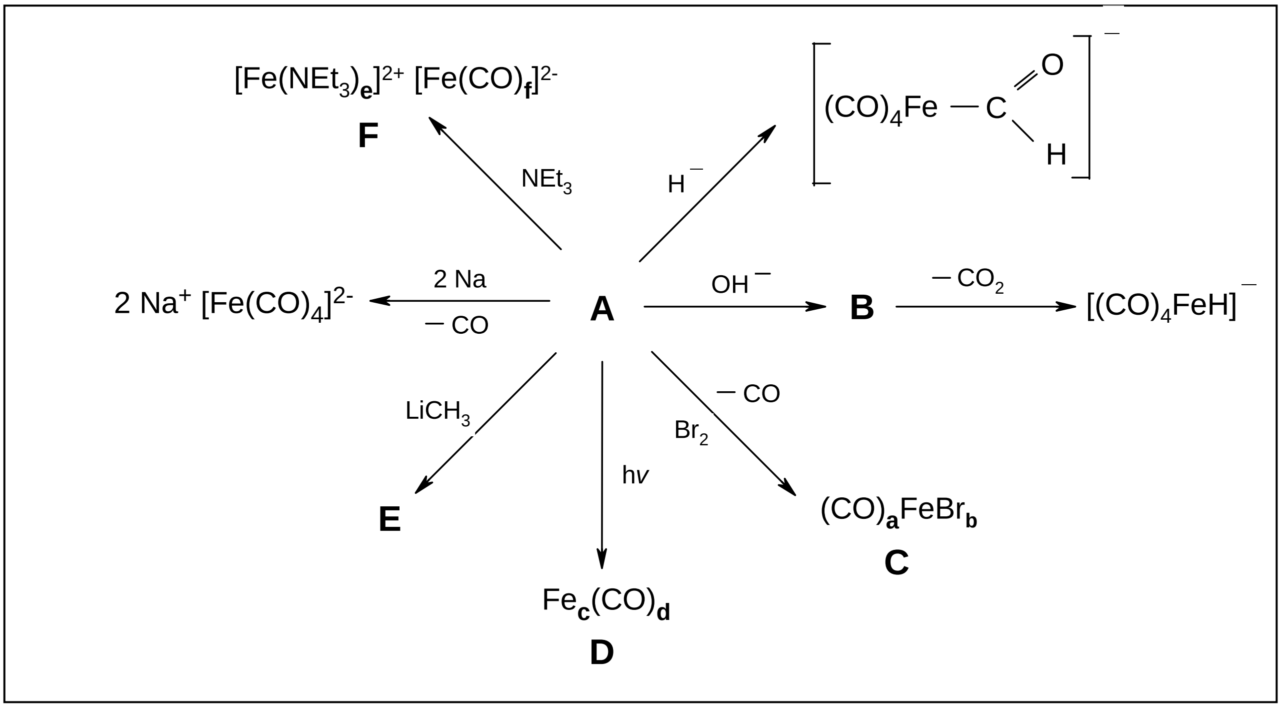
2.3 Explain why Mn(0) and Co(0) do not form so-called mononuclear carbonyl complexes of the type $M(CO)_x$ (M = metal), but rather compounds with metal-metal bonding.

2.4 Suggest structures of $Ni(CO)_4$, $Mn_2(CO)_{10}$ and $Co_2(CO)_8$.

2.5 State whether $V(CO)_6$ and the compounds mentioned in a) and d) are diamagnetic or paramagnetic.

2.6 Why are the carbon monoxide ligands bound to metals much more strongly than to boron in borane adducts (e.g. R_3B-CO; R = alkyl)?

2.7 Determine the composition of the compounds labeled **A** - **F** in the following reaction scheme:



Hints:

a) **C** has the following analysis: C, 14.75 % ; Br, 48.90 % .

b) **D** contains 30.70 % Fe; the molecular mass is 363.8 a.m.u.

c) Excess triethylamine is used for the synthesis of **F**. **F** contains 5.782 % C and 10.11 % N.

2.8 Why is the compound **F** formed in the disproportional reaction (given in g)), and not the compositional isomer $[Fe(CO)_f]^{2+}[Fe(NEt_3)_e]^{2-}$?

2.9 The eighteen-electron rule is also satisfied by a compound prepared from elementary chromium and benzene.

i) Draw the formula of this complex.

ii) Which complex with the analogous structure is prepared by the reaction of iron powder with cyclopentadiene? Write the chemical equation for its formation.

SOLUTION

2.1 $Fe(CO)_5$, $Cr(CO)_6$

2.2 $Cr(NO)_4$

2.3 Explanation: the odd number of electrons in the $Mn(CO)_5$ and $Co(CO)_4$ fragments.

2.4 $Ni(CO)_4$: tetrahedral geometry

$Mn_2(CO)_{10}$: - octahedral $Mn(CO)_5$-structure having a Mn-Mn bond,

- relative orientation (conformation) of the carbonyl groups.

$Co_2(CO)_{10:}$ CO-bridges and Co-Co bond

2.5 $Fe(CO)_5$, $Cr(CO)_6$, $Ni(CO)_4$, $Mn_2(CO)_{10}$, $Co_2(CO)_{10}$ are diamagnetic,

$V(CO)_6$ is paramagnetic.

2.6 Explanation using the so-called "back-bonding concept"

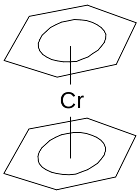
2.7 **A** = $[Fe(CO)_5]$ **B** = $[HOCOFe(CO)_4]$ **C** = $[FeBr_2(CO)_4]$

D = $[Fe_2(CO)_9]$ **E** = $[(CO)_4Fe=C(OLi)CH_3]$ **F** = $[Fe(NEt_3)_6]$ $[Fe(CO)_4]$

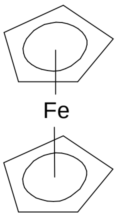
2.8 This observation is due to differing back bonding capability of NEt_3 and CO.

2.9

i) Structural formula of dibenzenechromium



ii) Structural formula of ferrocene.



PROBLEM 3

A weak acid of total concentration 2×10^{-2} M is dissolved in a buffer of pH = 8.8. The anion A^- of this acid is coloured and has a molar decadic absorption coefficient ε of 2.1×10^4 cm^2 mol^{-1}. A layer l of the solution with 1.0 cm thickness absorbs 60 percent of the incident luminous intensity I_o.

3.1 What is the equation relating the extinction to the thickness of the absorbing layer?

3.2 How large is the concentration of the acid anion in the buffer solution?

3.3 How large is the pK_a of the acid?

SOLUTION

3.1 The Lambert-Beer law e.g.:

$\log (I_o/I) = A = \varepsilon \,.\, c \,.\, l$

3.2 $\log [(100-60)/100] = - 2.1 \times 10^4 \times [A^-] \times 1$

$[A^-] = 1.895 \times 10^{-5}$ mol cm^{-3} = 1.895×10^{-2} mol dm^{-3}

3.3 According to the Henderson-Hasselbalch equation:

$$\text{pH} = pK_a + \log \frac{[A^-]_{eq}}{[HA]_{eq}}$$

and with the total concentration

$[HA]_{tot} = [HA]_{eq} + [A^-]_{eq} = 2 \times 10^{-2}$ mol dm^{-3}

$$8.8 = pK_a + \log \frac{1.895 \times 10^{-2}}{2 \times 10^{-2} - 1.895 \times 10^{-2}}$$

$pK_a = 7.5$

PROBLEM 4

15 cm^3 of a gaseous hydrocarbon C_xH_y are mixed with 120 cm^3 oxygen and ignited. After the reaction the burned gases are shaken with concentrated aqueous KOH solution. A part of the gases is completely absorbed while 67.5 cm^3 gases remain. It has the same temperature and pressure as the original unburned mixture.

4.1 What is the composition of the remaining gas? Explain.

4.2 How large is the change in the amount of substance per mole of a hydrocarbon C_xH_y when this is burned completely?

4.3 What is the chemical formula of the hydrocarbon used for the experiment?
Give the steps of the calculation.

SOLUTION

4.1 The remaining gas is oxygen since the burning products CO_2 and H_2O are completely absorbed in concentrated KOH solution.

4.2 The general stoichiometric equation for complete combustion of a hydrocarbon C_xH_y is as follows:

$C_xH_y + (x + y/4)\ O_2 \rightarrow x\ CO_2 + (y/2)\ H_2O$

The change in amount of substance per mole of hydrocarbon is

$[x + (y/2) - (1 + x + y/4)]$ mol = $[(y/4) - 1]$ mol

4.3 The equation of chemical conversion at the experimental condition is as follows:

$15\ C_xH_y + 120\ O_2 \rightarrow 15x\ CO_2 + (15/2)y\ H_2O + [(120 - 15x - (15/4)y]\ O_2$

For the residual oxygen:

(1) $120\ /b - 15x - (15/4)y = 67.5$

and for the total balance of amount of substance:

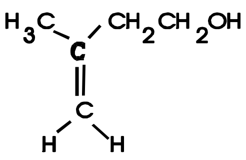
(2) $15x + (15/2)y + 67.5 = 15 + 120 + 15[(y/4) - 1]$

From equation (1) and (2) follows: $x = 2$ and $y = 6$.

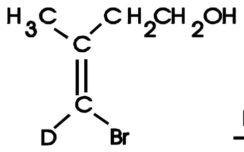
The hydrocarbon in question is ethane.

PROBLEM 5

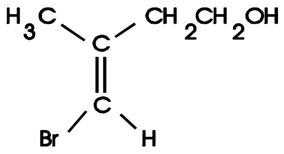
One of the diastereotopic methylene protons at the double bond of **A** was selectively substituted by deuterium. Bromination and subsequent dehydrobromation yields the deuteriated product **B** and the non-deuteriated product **C**.



A



B



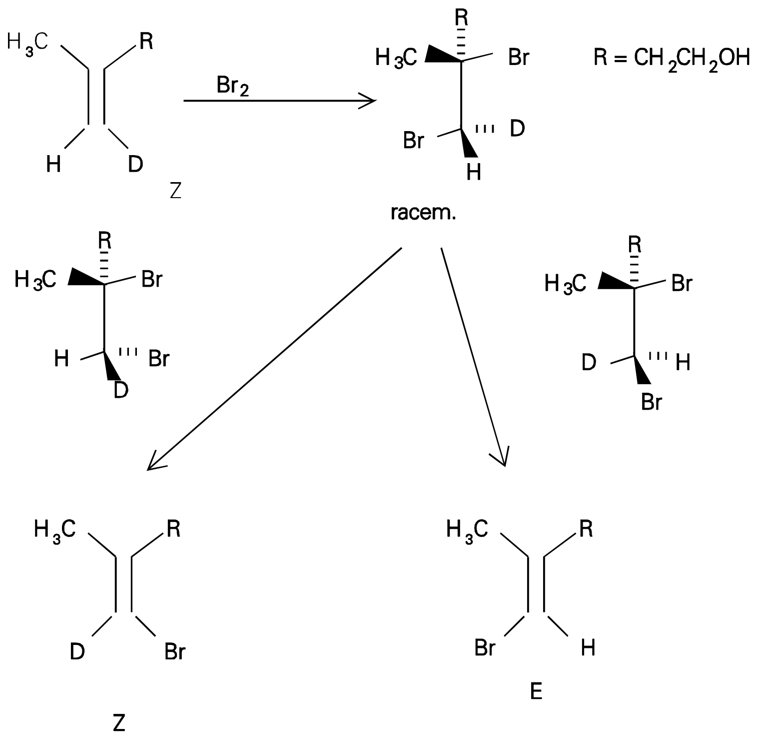
C

5.1 Which configuration follows for the monodeuteriated **A** from the given reaction products?

5.2 The solution of this question requires the formulation of the reaction and a short argumentation why only **B** and **C** are formed.

SOLUTION

5.1



5.2 The addition of bromine occurs trans (antarafacial). The elimination of HBr via an E2 mechanism also requires an anti-periplanar (= trans) arrangement of H and Br. The products given in this problem are only formed from a Z-configurated adduct.

The bromination of **A** and subsequent dehydrobromination yield both E,Z isomeric bromoolefins that have to be separated. Substitution of the bromine by deuterium in the Z-isomer proceeds by treatment with a metal (best: Na/t-BuOD) under retention to **A**.

PROBLEM 6

A technical interesting C_5 hydrocarbon **A** is separated via dimerization from the for-runnings of the benzene-pyrolysis fraction. This is achieved either by heating to 140 – 150 ^{o}C under pressure or by heating over several hours at 100^{o} C. Then it is distilled out at 200 ^{o}C. Treatment of **A** with peroxyacetic acid under neutral conditions (sodium acetate and sodium carbonate) in dichloromethane at 20^{o} C yields a product **B**. **B** yields two isomeric products **C** and **D** (summary formula $C_5H_8O_2$) by the reaction with aqueous sodium carbonate solution. The main product **C** contains three different bound carbon atoms whereas in the minor product **D** five different carbon atoms are present. **C** is chiral.

6.1 Write the formulas of **A**, **B**, **C**, and **D** considering the stereochemical representation.

6.2 What is the name of the chemical reaction which is used for the above mentioned separation procedure?

6.3 Which stereochemical rules hold for the dimerization reaction?

6.4 Give the structure of the dimerization product.

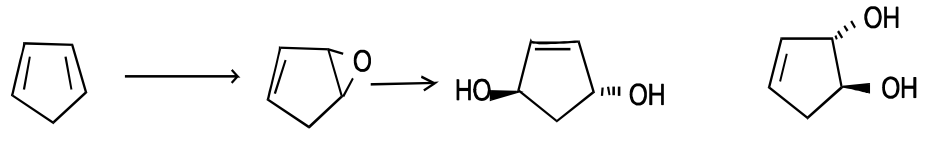
6.5 Give the mechanism of the formation of **C** and **D** from **B**.

6.6 Which kind of isomers are **C** and **D** ?

6.7 How many stereoisomers of **C** and **D** are principally (regardless of their synthetic availability) possible? Give their mutual stereochemical relations. Write their structural formulas.

SOLUTION

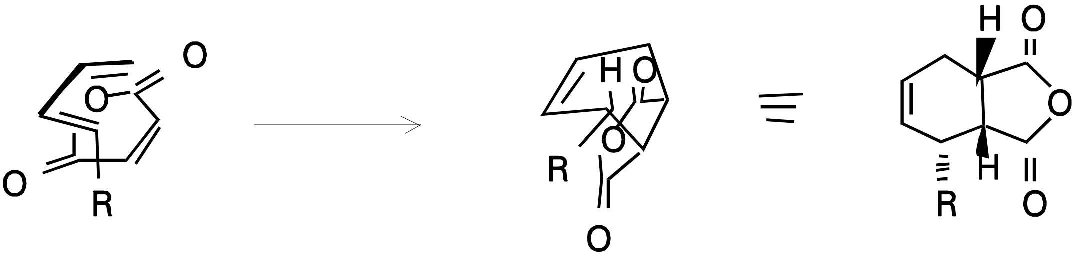
6.1



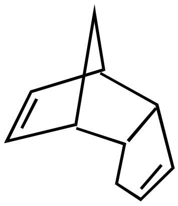
A B C rac. D rac.

6.2 Diels-Alder-reaction, 4+2-cycloaddition

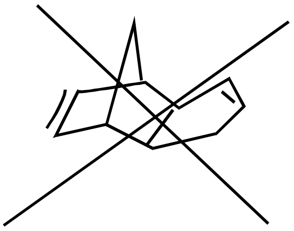
6.3 cis-addition = suprafacial addition with respect to diene and dienophile endo-rule: a substituent at the dienophile is oriented primarilly toward the diene . E.g.



d)



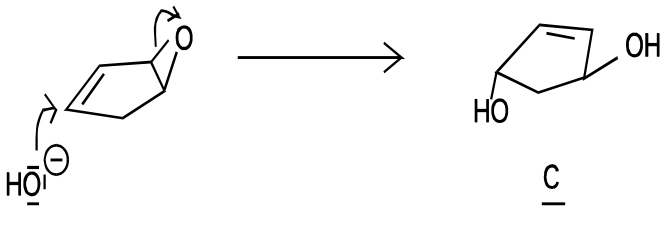
endo

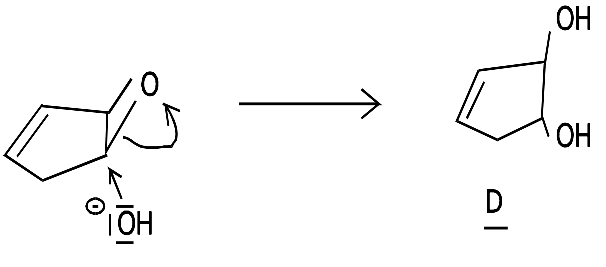


exo

6.4

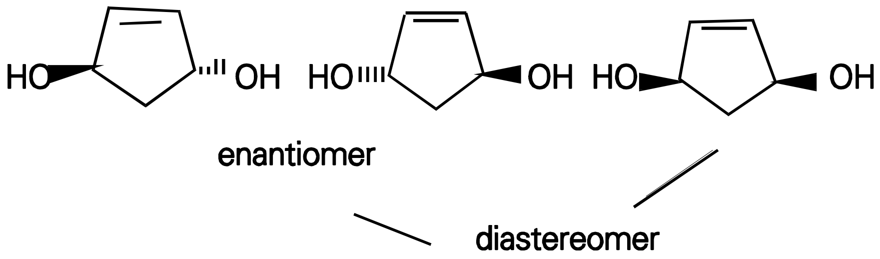
6.5 **C** is formed via a S_N2 reaction. This reaction can lead to a cis or a trans product. Because **C** is chiral, the trans product is formed. **D** is formed via S_N2 reaction.

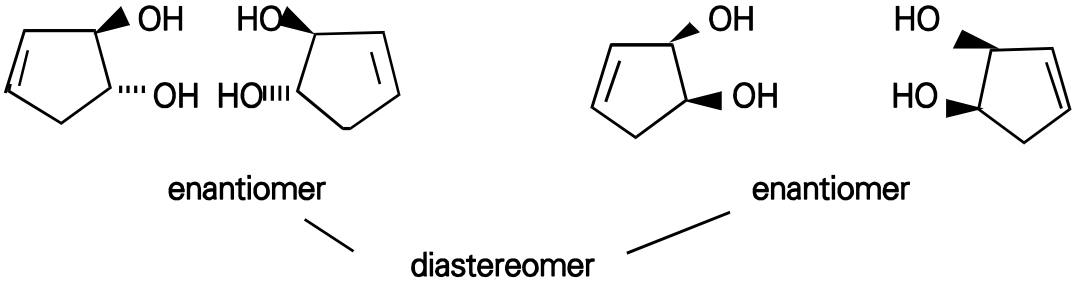




6.6 **C** and **D** are constitutional isomers.

6.7 There exist two diastereomers (cis and trans) of **C**.The trans form is chiral, i.e. there exists a pair of enantiomers. The cis form is achiral (reduction of the number of stereoisomers caused by constitutional symmetry, meso-form). **D** forms two diastereomers, each of them is chiral.





PROBLEM 7

Deoxyribonucleic acid (DNA) represents the genetic program of all living beings. The human genetic program is subdivided into 23 chromosomes.

7.1 Calculate the mass of a DNA thread in grams, which reaches form earth to the moon (340,000 km). A mass of 1 g represents 1,000 nucleotide pairs.
One nucleotide pair (base pair) has a length of 0.34 nm.

7.2 Give estimation on how many nucleotid pairs are stored in the chromosome set of a human being. Human cells can synthesize 50,000 different proteins, which are on the average 300 amino acids long. Only 2 % of the DNA code for proteins.

7.3 The DNA of the bacteriophage M13 shows the following base composition:
A: 23 %, T: 36 %, G: 21 %, C: 20 % (mole %)
What does the base composition tell about the structure of the DNA?

SOLUTION

7.1 1. Number of nucleotide pairs as calculated from the given length

$$\frac{3.4 \times 10^{8} \text{ m}}{3.4 \times 10^{-10} \text{ m}} = 10^{18} \text{ nucleotide pairs}$$

2. Calculation of the mass:

1,000 nucleotide pairs = 10^{-18} g

10^{18} nucleotide pairs = 1 mg

The mass of 340.000 km DNA is 1 mg.

7.2 Human DNA codes for 50,000 × 300 amino acids in form of proteins: Each amino acid is encoded by 3 nucleotides or due to the double stranded structure of DNA by 3 nucleotide pairs. This amounts to 4.5×10^{7} nucleotide pairs. Since only 2% of the DNA code for proteins one can calculate the number of nucleotide pairs in human DNA to 2.25×10^{9} nucleotide pairs.

7.3 The DNA has to be single stranded, since the ratio of adenine : thymine and guanine : cytosine is different from one.

PROBLEM 8

The sequence of the amino acids in a peptide can be determined by a combination of chemical and enzymatic methods. The peptide in question functions in the human body as a pain reliever.

a) Hydrolysis of the peptide in 6 M HCl at 110° C followed by an analysis of the liberated amino acids, resulted in a molar ratio of Gly, Leu, and aromatic amino acids Phe, Tyr 2 : 1 : 1 : 1.

b) Reacting the peptide with 2,4-dinitrofluorobenzene (DNFB), followed by hydrolysis and chromatographic analysis, yielded the tyrosine derivative.

c) Partial hydrolysis with chymotrypsin yielded Leu, Tyr and a smaller peptide. After hydrolysis of this peptide Gly and Phe were identified in a ratio 2 : 1. Chymotrypsin is a protease which cleaves a peptide bond following an aromatic amino acid.

Problems:

8.1 Determine the amino acid sequence from the given information.

8.2 Write the structural formula of the DNFB- and the dansyl derivative of tyrosine. What is the advantage of the dansylation in comparison to the DNFB-modification?
Dansyl means 5-N,N-dimethylaminonaphtalene-4-sulphonyl.

8.3 In a similar peptide which shows the same biological activity, leucine is replaced by methionine. Explain from the chemical structure of both amino acids why the replacement is possible without loss of biological activity.

SOLUTION

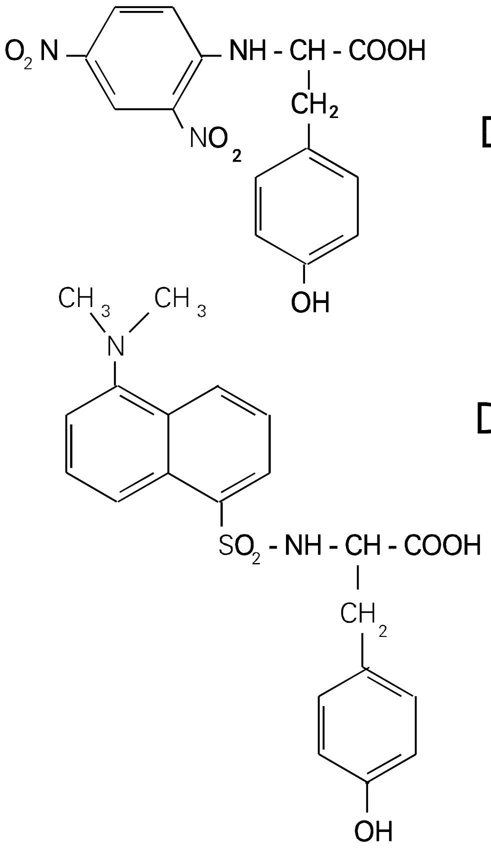
8.1 It can be derived from data in part 1 that the net composition of the peptide is 2 Gly, 1 Leu, 1 Phe and 1 Tyr.

From part 2 one can conclude that the N-terminal amino acid has to be Tyr since DNFB is specific for the N-terminus.

Part 3 shows that the internal peptide has to be Gly-Gly-Phe.

The sequence is Tyr-Gly-Gly-Phe-Leu.

8.2 The trivial name of the peptide is Leu-Enkephaline. It acts as a pain killer in the human body.



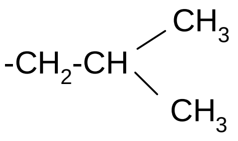
DNFB - Tyr

Dansyl - Tyr

Dansyl derivatives give increased sensitivity since they are highly fluorescent.

8.3 The compound is Met-Enkephaline. Leu and Met are both non-polar amino acids. Both side chains show comparable van der Waals radii.

$-CH_2-CH_2-S-CH_3$



$-CH_2-CH(CH_3)_2$

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Nitration of phenacetine (4-ethoxyacetanilide) with nitric acid in acetic acid as solvent

Caution:

Both acetic acid and 65 % nitric acid attack the skin. If it happens, the skin must be rinsed with water immediately and washed with a saturated aqueous solution of sodium carbonate. Vapours of nitric acid damage the respiratory tract; moreover, nitric gases evolved in the reaction flask are very toxic.

The glass joints of the various apparatus must be only slightly greased.

Apparatus:

250 ml four-necked flask with laboratory stirrer, thermometer, reflux condenser with gas vent, water bath, Bunsen burner.

Preparation:

40 ml of acetic acid are placed with a glass syringe pipette in the four-necked round bottom flask. 2.0 g of phenacetine are then dissolved in the acetic acid. Also, 2.5 ml 65 % nitric acid are added by using a glass syringe pipette under an effective hood. This mixture is heated for five minutes in a water bath at 90 ^oC.

Isolation and purification:

The hot water bath is replaced by ice water. After ca. 10 minutes the gas vent is removed and ca. 120 ml of distilled water are added through the reflux condenser into the flask in order to dilute the original solution. Stirring is continued until a temperature of ca. 5 ^oC is reached.

The precipitated solid is filtered off and then washed with a total of 100 ml of cold water and finally dried at 60^o C for 2.5 hours in a drying oven.

Evaluation of the experiment:

a) Melting points:

The melting point of phenacetine and its reaction product are to be determined and recorded in the note book. The melting point of phenacetine is higher than 120° C and that of the product is higher than 80° C.

b) Thin-layer chromatogram:

The relative position of the spots of the starting compound and its reaction product must be recorded. In order to reach it, little portions of the both samples must be dissolved in 1-2 ml of acetone. The solutions must be placed on the plate by using a capillary tube. To develop the chromatogram, a mixture of 90 ml toluene, 25 ml acetone, and 5 ml acetic acid is used.

After drying the spots are circled with a pen. The R_f -values must be recorded.

c) Developing reagent:

The developed TLC-plate must be sprayed under a hood with the available reagent solution consisting of iron(III) chloride and potassium hexacyanoferrate(III).

Interpretation of the results:

1.1 Which nitration product(s) has (have) been formed? The discussion should focused on the relative position of the spots in your chromatogram; describe your arguments in the note book.

1.2 Explain why such "mild conditions" have been used here for the nitration reaction. Explain why the nitration reaction has proceeded in spite of these "mild conditions".

1.3 Explain the observed colour reaction of phenacetine with the developing reagent.

1.4 Make a brief proposal, how the filtrate should be prepared to avoid environmental damage.

Chemicals:

Acetic acid (analysis grade)
Nitric acid (analysis grade); w = 65 % by mass
Phenacetine (analysis grade)
Toluene (analysis grade)

Acetone (analysis grade)
Developing reagent: 100 ml solution
200 ml solution
700 ml distilled water.

SOLUTION

a) Melting points:
4-ethoxy-N-acetylphenylamin (phenacetine) : 135 °C
4-ethoxy-2-nitroacetanilide : 103 °C (theoretic al value)

b), c) Documentation, Thin-layer chromatogram

Interpretation of the results:

1.1 The R_f -value of the nitration product is almost twice as great as that of the starting compound phenacetine. Although nitration has occurred, the molecules exhibit less dipolar character that indicates intramolecular hydrogen bridges. This is only possible if the acetylamino and nitro groups are located in 1.2-positions.

In accordance with the +M-effect of the acetyl amino group one should expect that the nitro group would be favoured in a (free) ortho-position because of the lowered activation energy. On the other hand, one would not expect multiple nitration because of the "mild reaction conditions" (see below) and also because of the electron withdrawing mesomeric effect (-M-effect) and the inductive electron withdrawal (-I-effect) of the nitro group that has entered the molecule.

Nitration product: 4-Ethoxy-2-nitroacetanilide
The melting point confirms this observation.

1.2 The nitration reaction is carried out relatively rapidly, at relatively low temperature in dilute solution and without using fuming nitric acid or "nitration acid".

Instead of sulphuric acid concentrated acetic acid is used. The molecules of the latter compound neither protonate the HNO_3 sufficiently nor do they do solvate the

NO_2^+ ions. As a result, the equilibrium reactions

$$HONO_2 + HONO_2 \rightleftharpoons H_2O^+\text{-}NO_2 + {}^-O\text{-}NO_2$$

and

$$H_2O^+\text{-}NO_2 \rightleftharpoons {}^+NO_2 + H_2O$$

are shifted far to the left. This effect is counterbalanced by the high reactivity (+M-effect) of phenacetine.

1.3 Phenacetine is oxidized by iron(III) ions and a molecule of p-quinone type and iron(II) ions are formed. The iron(II) ions react immediately with the hexacyanoferrate(III) ions to give Turnbull's Blue.

1.4 Neutralization with sodium or potassium hydroxide solution, use of calcium hydroxide solution and argumentation:

NO_3^--ions, CH_3COO^- ions and 4-ethoxy-2-nitroacetanilide are removed by biological metabolism.

PROBLEM 2 (practical)

Determination of the content of phosphoric acid in a cola drink

Apparatus:

500 ml round-bottom flask with stirrer, reflux condenser, heating mantle, magnetic stirrer, water bath.

Preparation of the sample:

The content of a cola drink bottle is stirred for two or three minutes in a round-bottom flask. Afterwards, 6.0 g powdered active charcoal are added. The entire suspension is carefully heated to reflux and is maintained there for ten minutes. The glass joint of the reflux condenser must not be greased!

The heating mantle is then exchanged with an ice water bath. After the sample has been cooled to 20 ^{o}C, it is filtered through a double fluted filter paper. The initial filtrate should be recycled several times.

Adjustment of the pH-meter:

The pH-meter is adjusted to the working electrode by using two buffer solutions.

Titration:

150 ml of the unknown solution are titrated using pH indication with a standardized sodium hydroxide solution (c(NaOH) = 0.0500 mol dm^{-3}).

The first equivalence point of the phosphoric acid is reached after about 6 ml of the NaOH solution have been consumed. The titration is to be continued until more than about 12 ml of sodium hydroxide solution have been added.

Results of the experiment:

a) Draw the titration curve and determine the first equivalence point.

b) Determine the pH value of the heated cola drink and the pH value at the first equivalence point.

c) Calculate the concentration of phosphoric acid in the cola drink. Write the calculation and the result in your report.

Interpretation of the experiment:

1. Describe and explain your observations during the titration.
2. Is it possible that the active charcoal could have influenced your titration result? Give reasons for your presumption.

Chemicals:

Powdered active charcoal

Sodium hydroxide solution; c(NaOH) = 0.0500 mol dm^{-3}

Buffer solutions

17th

IChO

International Chemistry Olympiad

8 theoretical problems
1 practical problem

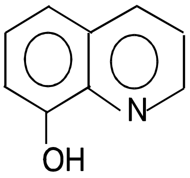
THE SEVENTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
1–8 JULY 1985, BRATISLAVA, CZECHOSLOVAKIA

THEORETICAL PROBLEMS

PROBLEM 1

A solution was formed from 0.5284 g of a sample of an alloy containing aluminium. The aluminium was then precipitated as aluminium 8-hydroxyquinolate. The precipitate was separated, dissolved in hydrochloric acid and the 8-hydroxyquinoline formed was titrated with a standard solution of potassium bromate containing potassium bromide. The concentration of the standard potassium bromate solution was 0.0200 M and 17.40 cm^3 of it were required. The resultant product is a dibromo derivative of 8-hydroxyquinoline.

The structural formula of 8-hydroxiquinoline is:



The relative atomic mass of aluminium is 26.98.

Problems:

1.1 Write the balanced equation for the reaction of the aluminium (III) ion with 8-hydroxyquinoline, showing clearly the structure of the products.

1.2 Give the name of the type of compound which is formed during the precipitation.

1.3 Write the balanced equation for the reaction in which bromine is produced.

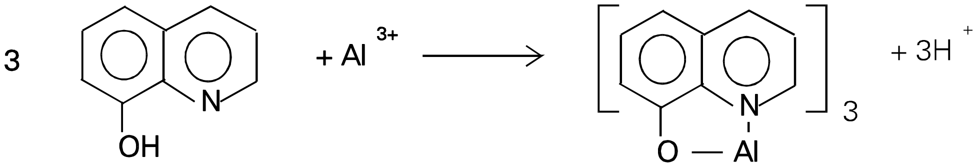
1.4 Write the balanced equation for the reaction of bromine with 8-hydroxyquinoline.

1.5 Calculate the molar ratio of aluminium ions to bromate ions.

1.6 Calculate the percentage by weight of aluminium in the alloy.

SOLUTION

1.1

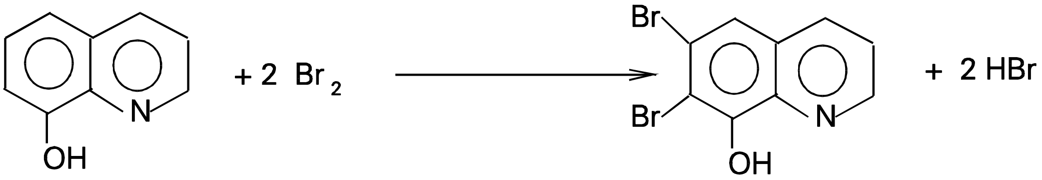


1.2 Chelate

1.3

$$BrO_3^- + 5\,Br^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O$$

1.4



1.5 As Al $\triangleq$ Al(oxine)$_3$ $\triangleq$ 3 oxine $\triangleq$ 12 Br $\triangleq$ 12 e,

the chemical equivalent of Al equals 26.98/12 = 2.248.

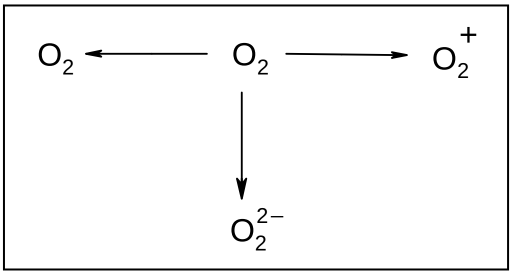
1.6 The percentage of the aluminium in the sample is

$$\%\,Al = \frac{17.40 \times 0.1000 \times 2.248 \times 100}{528.4} = 0.74$$

The alloy contains 0.74% of aluminium.

PROBLEM 2

It is possible to prepare compounds containing ions O_2^-, O_2^{2-} or even O_2^+. These ions are usually formed from molecules of oxygen during various reactions, as indicated in the scheme below:



2.1 Indicate clearly which of the above reactions correspond to the oxidation and which to the reduction of the oxygen molecule.

2.2 For each of the ions in the scheme give the formula of a compound containing that particular ion.

2.3 It has been found that one of the species in the scheme is diamagnetic. Which one is it?

2.4 Copy out the following table:

Species	Bond order	Interatomic distance	Bonding energy
O_2			
O_2^+			
O_2^-			
O_2^{2-}			

The interatomic distances, O-O, in the above species have the values 112, 121, 132 and about 149 pm. Write these values in the appropriate column in the table.

1 pm = 10^{-12} m.

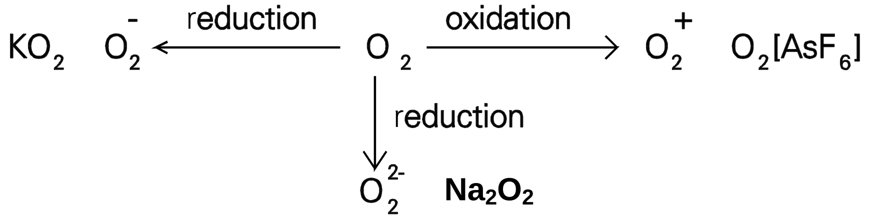
2.5 Three of the bond energies, $E_{o\text{-}o}$, have the values approximately 200, 490 and 625 kJ mol^{-1}. The value for one of the species is uncertain and, therefore, not given. Write the values in the appropriate spaces in the table.

2.6 Determine the bond order for the individual species and write the answers in the table.

2.7 Is it possible to prepare compounds containing the F_2^{2-} ion? Give reasons for your answer.

SOLUTION

2.1 and **2.2**



2.3 O_2^{2-}

2.4 - **2.6**

Species	Bond order	Interatomic distance (pm)	Bonding energy (kJ mol^{-1})
O_2	2	121	490
O_2^+	2.5	112	625
O_2^-	1.5	132	–
O_2^{2-}	1	149	200

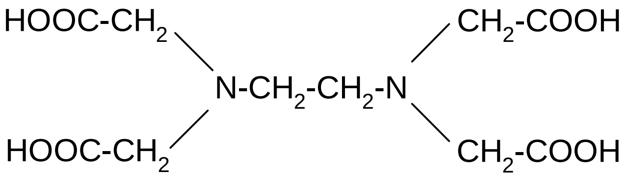
2.7 Ion F_2^{2-} does not exist. The number of electrons in the bonding and antibonding orbitals would be the same and thus, the bonding F–F cannot be formed. Therefore, there exists no compound containing ion F_2^{2-}.

PROBLEM 3

Calcium sulphate is a sparingly soluble compound. Its solubility product is given by:

$K_s(CaSO_4) = [Ca^{2+}][SO_4^{2-}] = 6.1 \times 10^{-5}$

Ethylenediaminetetraacetic acid (EDTA) has the formula $C_{10}H_{16}N_2O_8$ and the structure:



The anion of this acid, $C_{10}H_{12}N_2O_8^{4-}$, forms a stable complex $CaC_{10}H_{12}N_2O_8^{2-}$ with calcium ions. The stability constant of this complex ion is given by:

$$K = \frac{[\,CaC_{10}H_{12}N_2O_8^{2-}]}{[\,Ca^{2+}][C_{10}H_{12}N_2O_8^{4-}]} = 1.0 \times 10^{11}$$

EDTA is completely dissociated in strongly alkaline solution. The equation for this dissociation is:

$C_{10}H_{16}N_2O_8 \rightarrow 4\,H^+ + C_{10}H_{12}N_2O_8^{4-}$

Problems:

3.1 Calculate the concentration of calcium ions in a saturated solution of calcium sulphate.

3.2 Calculate the concentration of free Ca^{2+} cations in a solution of 0.1 M $Na_2(CaC_{10}H_{12}N_2O_8)$. You should ignore any protonation of the ligand.

3.3 How many moles of calcium sulphate will dissolve in 1 litre of a strongly alkaline solution of 0.1 M $Na_4C_{10}H_{12}N_2O_8$?

What would be the concentrations of the calcium and sulphate ions in the resulting solution?

3.4 Suggest a structure for the complex ion $[CaC_{10}H_{12}N_2O_8]^{2-}$ assuming that it is approximately octahedral.

3.5 Is the structure you have suggested in 4) optically active?

If your answer is "yes" then draw the structure of the other optical isomer enantiomer).

3.6 Explain why the complexes formed by the anion $C_{10}H_{12}N_2O_8^{4-}$ are exceptionally table.

SOLUTION

3.1 [Ca^{2+}] = 7.8×10^{-3} mol dm^{-3}

3.2 [Ca^{2+}] = 1.0×10^{-6} mol dm^{-3}

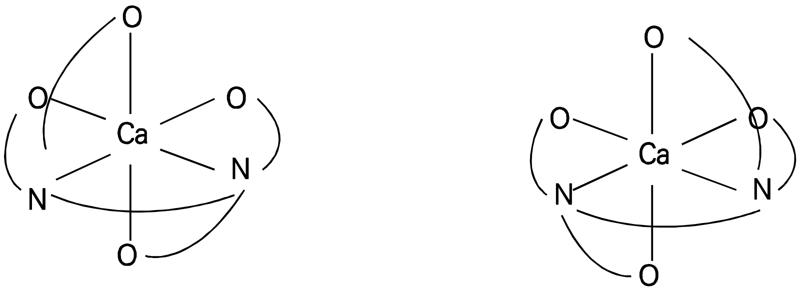
3.3 The $CaSO_4$ amount dissolved is 0.1 mol.

[SO_4^{2-}] = 0.10 mol dm^{-3}.

[Ca^{2+}] = 6.1×10^{-4} mol dm^{-3}

3.4 + **3.5**

The complex is optically active. The structures of both enantiomers are

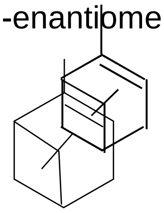


3.6 The high number of the chelate rings. Other factors also contribute to the complex ability, e.g. the character of the donor atoms, the magnitude and distribution of the charges in the anion, etc.

PROBLEM 4

At a temperature around 200 °C the racemisation of pinene can be followed in the gaseous phase by measuring the optical rotation.

If, for example, you take the (+)-enantiomer of α-pinene



an equilibrium is gradually established between the two enantiomers (optical isomers). The two opposing reactions are both of the first order.

In 1927 D. F. Smith obtained the following data in his study of racemisation of α-pinene:

T/K	α_1	α_2	t/min
490.9	32.75	18.01	579
490.9	29.51	15.59	587
503.9	30.64	8.74	371
505.4	12.95	8.05	120
510.1	23.22	6.15	216

α_1 and α_2 are the values for optical rotation in terms of the dimensions of the polarimeter scale; *t* is the time which has elapsed between the two measurements.

Problems:

4.1 What is the value for the equilibrium constant for the racemisation?

What is the corresponding value of $\Delta_r G^o$ (racemisation)?

What is the relationship between the forward and backward rate constants, k_1 and k_{-1}, in a state of dynamic equilibrium?

4.2 State the rate equation for the racemisation of pinene.

Derive a relationship which could be used to calculate the rate constant for the conversion of the (+)-enantiomer into the (-)-enantiomer using the data given in the table.

4.3 Calculate the rate constant for this reaction at the four temperatures given in the table.

4.4 Calculate the average value of the activation energy for this reaction. You should take the average of the values at a minimum of three temperatures or use a graphical method.

HINT:

If the loss of concentration of a substance obeys the rate equation:

$$-\frac{dc}{dt} = k(2c - constant)$$

Then the dependence of concentration on time is given by:

$$\ln\frac{2c_0 - constant}{2c - constant} = 2kt$$

where c_0 is the initial concentration at time $t = 0$.

SOLUTION

4.1 The racemisation equilibrium constant equals unity at all temperatures and $\Delta_r G^o = 0$.

4.2 If the concentration of one enantiomer is c and that of the other is c', then it holds for the rate of the loss of c that

$$-\frac{dc}{dt} = k_1 c - k_{-1} c' = k(c - c') \quad \text{for} \quad k_1 = k_{-1} = k$$

If the initial concentrations are c_0 and c_0', then

$c' = c_0 - c + c_0'$

can be substituted for c' in the rate equation, obtaining

$$-\frac{dc}{dt} = k\,(2c - c_0 - c_0')$$

It then holds for concentrations c_1 and c_2 measured at times t_1 and t_2, respectively, that

$$\ln\frac{2c_1 - c_0 - c_0'}{2c_2 - c_0 - c_0'} = 2k(t_2 - t_1)$$

and since $c_0 + c_0' = c_1 + c_1' = c_2 + c_2'$

$$\ln \frac{c_1 - c_1'}{c_2 - c_2'} = 2k\,(t_2 - t_1)$$

The measured optical rotation α is proportional to c - c'; hence $\ln \frac{\alpha_1}{\alpha_2} = 2\,k\,(t_2 - t_1)$

4.3

T/K	490.9	503.9	505.4	510.1
10^4 k min^{-1}	5.3	16.9	19.8	30.7

4.4 $\ln\frac{k_2}{k_1} = \frac{E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ $\qquad$ $E_A = \ln\frac{k_2}{k_1} \times \frac{R\,T_1\,T_2}{T_2 - T_1}$

If e.g. the value of k for 490.9 K (the average of two measurements) is combined with each of the remaining three values, three values of activation energy are obtained: 183400 J mol^{-1}, 177500 J mol^{-1}, 190500 J mol^{-1}. The average value equals 187100 J mol^{-1}.

PROBLEM 5

The equilibrium voltage of the cell,

Zn / $ZnSO_4$ (0.0125 M) ‖ Ag_2SO_4 (0.0125 M) / Ag

was measured at several temperatures and the results of the measurements are given in the following table:

t / °C	10	20	30
E / V	1.5784	1.5675	1.5566

Problems:

5.1 Give the equation for the reaction occurring in this galvanic cell.

5.2 Determine the value of the cell voltage at the temperature T = 298 K.

5.3 Determine $\Delta_r G_{298}$ of the cell reaction.

5.4 Determine $\Delta_r H_{298}$ of the cell reaction.

SOLUTION

5.1 $Zn + Ag_2SO_4 \rightarrow ZnSO_4 + 2\ Ag$

5.2 The temperature dependence is described by the equation,

$$E_T = E_{T_0} + \frac{dE}{dT}.(T - T_0)$$

It follows from the plot for the slope,

$$\frac{dE}{dT} = -1.09 \times 10^{-3}\ \mathrm{V\,K^{-1}}$$

Hence,

$E_{298} = 1.5675 - 1.09 \times 10^{-5} \times 5 = 1.562$ V

5.3 The relationship,

$\Delta_r G = -\, n\, F\, E$

holds for $\Delta_r G$. Then

$\Delta_r G_{298} = -\, 2 \times 96484.6 \times 1.563 = -\, 301417.9\ \mathrm{J\ mol^{-1}}$

5.4 The equation,

$$\Delta G = \Delta H - T\,\Delta S,$$

is employed to calculate $\Delta_r H_{298}$, substituting

$$\Delta S = -\frac{dG}{dT}$$

Rearrangement yields the relationship

$$\Delta H = \Delta G - T\,\frac{dG}{dT}$$

As it holds that

$$\frac{dG}{dT} = -n\,F\,\frac{dE}{dT}$$

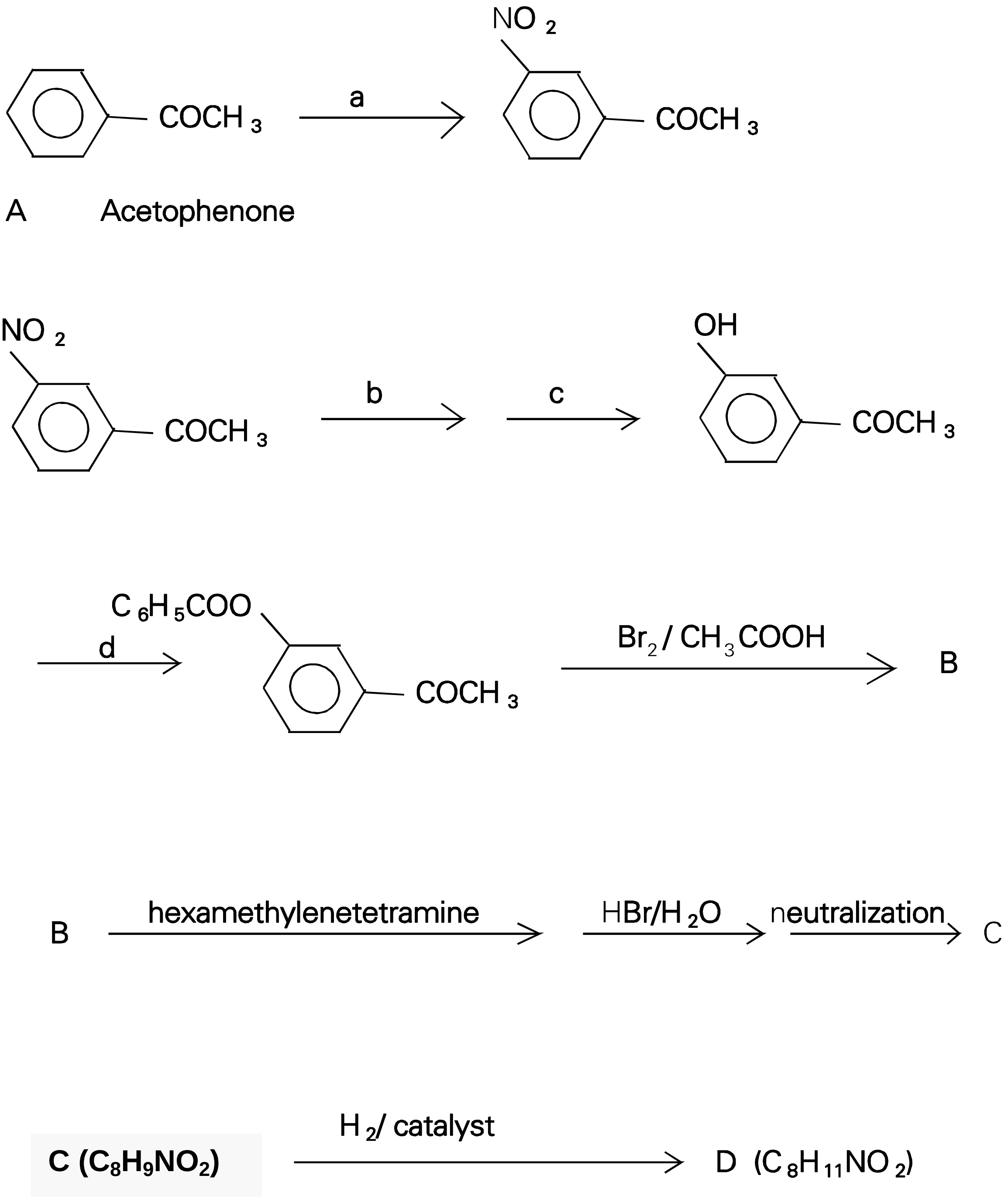
the final expression is:

$$\Delta_r H_{298} = \Delta G_{298} + n\,F\,T\,\frac{dE}{dT}$$

$$= -301417.9 + [2 \times 96\,484.6 \times 298 \times (-1.09 \times 10^{-3})] = 364098.1 \text{ J mol}^{-1}$$

PROBLEM 6

The following scheme describes the synthesis of a compound **D** (with sympathomimetic effects) whose skeleton consists of 2-phenylethylamine.



Problems:

6.1 What reagents were used in steps **a**, **b**, **c**, and **d**?

6.2 Give the structural formulae of compounds **B**, **C** and **D**.

6.3 Is it possible to prepare 3-hydroxyacetophenone from the reaction between phenol, acetylchloride and $AlCl_3$? Give reasons for your answer.

6.4 Give the formulae of the compounds that are formed by the reaction of compound **C** with a) 10% HCl and b) 10% NaOH.

6.5 By the asterisk denote the chirality centre in the formula of compound **D**.

6.6 Give the spatial formula of enantiomer (R) of compound **D**.

SOLUTION

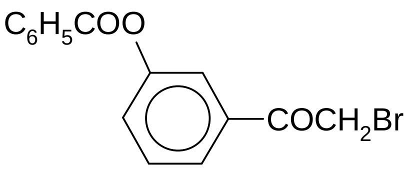
6.1 a) HNO_3/H_2SO_4

b) Fe/H^+

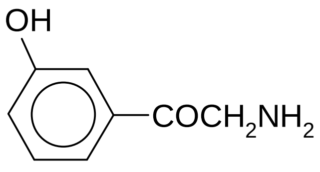
c) $NaNO_2/HCl$

d) benzoylchloride

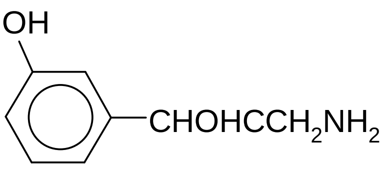
6.2



B



C

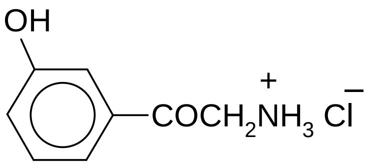


D

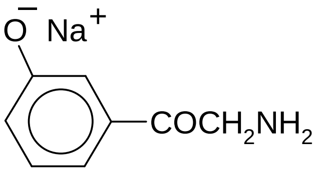
6.3 No

6.4

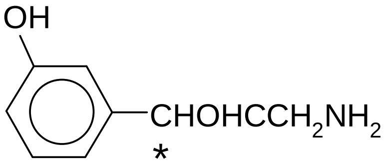
a)


OH
COCH2NH3 Cl

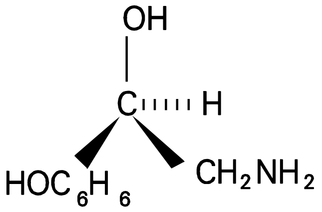
b)


O Na
COCH2NH2

6.5


OH
CHOHCCH2NH2
*

6.6


OH
C
H
HOC6H6
CH2NH2

PROBLEM 7

Propanal, **A**, reacts in an aqueous-ethanolic solution of sodium hydroxide to yield compound **B** that is readily dehydrated to give compound **C** ($C_6H_{10}O$).

Problems:

7.1 Give the structural formulae of substances **B** and **C**.

7.2 Give the formula of intermediate **M** that is formed from propanal **A** by the action of hydroxide ions.

7.3 Give the formulae of the two most important mesomeric structures of intermediate **M** and denote the nonbonding electron pairs and the charge distribution.

7.4 The reaction of propanal **A** with sodium hydroxide, producing substance **B**, can be described by the scheme:

$$\mathbf{A} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathbf{M} + H_2O \qquad \text{the first reaction step}$$

$$\mathbf{M} + \mathbf{A} \xrightarrow{k_1} \mathbf{B} \qquad \text{the second reaction step}$$

The rate of the formation of substance **B** is given by the equation:

$$v = k_2\,[\mathbf{M}]\,[\mathbf{A}] \qquad (1)$$

The above values of *k* are the rate constants for the individual reaction steps.

Assume that the concentration of intermediate **M** is small and constant during the reaction and express this fact by an aquation involving terms with constants k_1, k_{-1} and k_2.

$$\frac{d[\mathbf{M}]}{dt} = 0 \qquad (2)$$

Derive an expression for the concentration of **M** from equation 2 and then substitute for [**M**] in equation 1. This gives equation 3 which is the complete rate equation for the formation of substance **B**.

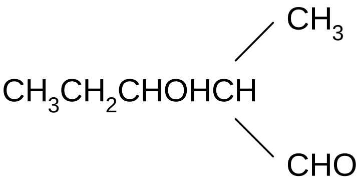
If it is assumed that the second reaction step is rate determining, then the rearrangement of equation 3 gives equation 4, the rate equation.

Give equations 2, 3, and 4.

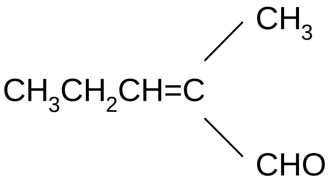
7.5 Determine the overall order of the reaction described by equation 4.

SOLUTION

7.1

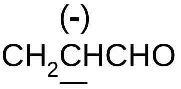


B



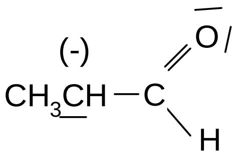
C

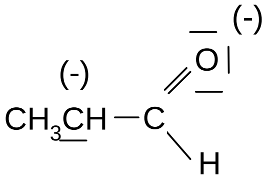
7.2



$CH_2\overset{(-)}{\underline{C}}HCHO$

7.3





7.4

$$\frac{d[\mathbf{M}]}{dt} = 0 = k_1\,[\mathbf{A}]\,[OH^-] - k_{-1}[\mathbf{M}] - k_2\,[\mathbf{A}][\mathbf{M}] \qquad (2)$$

$$[\mathbf{M}] = \frac{k_1\,[\mathbf{A}]\,[OH^-]}{k_{-1} + k_2[\mathbf{A}]} \qquad v = \frac{k_1 k_2\,[\mathbf{A}]^2\,[OH^-]}{k_{-1} + k_2[\mathbf{A}]} \qquad (3)$$

for $k_2[\mathbf{A}][\mathbf{M}] << k_{-1}[\mathbf{M}]$ it holds, that

$$v = \frac{k_1\,k_2\,[\mathbf{A}]^2\,[OH^-]}{k_{-1}} \qquad (4)$$

7.5 Rate equation (4) corresponds to the overall reaction order of (3).

PROBLEM 8

The following reaction scheme represents part of anaerobic degradation of saccharides, i.e. the glycolysis, involving equilibrium constants K_1 and K_2:

glucose-1-phosphate $\rightleftharpoons$ glucose-6-phosphate $K_1 = 19$

glucose-6-phosphate $\rightleftharpoons$ fructose-6-phosphate $K_2 = 0.50$

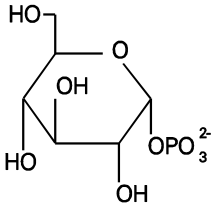
Problems:

8.1 Give the structural formulae for all the three reactants (compounds) that are mutually interconverted, i.e. α-D-glucose-1-phosphate, α-D-glucose-6-phosphate and α-D-fructose-6-phosphate.

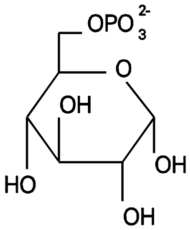
8.2 In the beginning of the reaction the reaction mixture contained 1 mmol of glucose-6-phosphate. Calculate the amounts of glucose-6-phosphate, glucose-1-phosphate and fructose-6-phosphate in the mixture at equilibrium. (As the reaction take place in a constant volume, the ratio of the amounts of substances equals that of their concentrations.)

SOLUTION

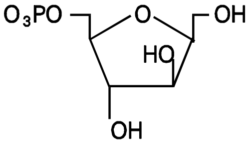
8.1 α-D-glucose-1-phosphate



α-D-glucose-6-phosphate



α-D-fructose-6-phosphate



8.2 It holds for the equilibrium constant of the successive reactions, that

$$\frac{\text{Fru-6-P}}{\text{Glc-1-P}} = 19 \times 0.5 = 9.5 \qquad \text{(i)}$$

If y mmoles of Glc-6-phosphate are converted into the same number of Glc-1-phosphate and another x mmoles of Glc-6-phosphate are converted into the same number of mmoles of Fru-6-phosphate, then (1 – x – y) mmoles of Glc-6-phosphate remain in the reaction mixture at equilibrium. It follows from relationship (i) that

Glc-1-phosphate = y $\qquad$ x/y = 9.5

Fru-6-phosphate = x $\qquad$ x = 9.5 y

After substituting,

Glc-6-phosphate = 1 – x – y = 1 – 10.5y,

it is possible to write for the reaction mixture at equilibrium that

$$\frac{\text{Glc-6-P}}{\text{Glc-1-P}} = \frac{1-10.5y}{y} = 19 \qquad 1-10.5y = 19\,y$$

$$y = 1/29.5 = 0.034 \text{ mmoles Glc-1-phoshate}$$

It is further calculated that

x = 9.5y = 9.5 × 0.034 or 9.5/29.5 = 0.322 mmoles of Fru-6-phosphate

1 – x – y = 1 – 0.322 – 0.034 = 0.644 mmoles of Glc-6-phosphate

At equilibrium the reaction mixture contains 0.034 mmoles Glc-1-phosphate, 0.644 mmoles Glc-6-phosphate and 0.322 mmoles Fru-6-phosphate.

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Determination of the relative molecular mass of a weak acid by acid-base titration in a non-aqueous solvent

Weak acid whose dissociation constants, K_a, are smaller than 1×10^{-7} can be satisfactorily titrated in ethanol or in a mixture of ethanol and benzene, using a standard ethanolic solution of potassium hydroxide or potassium alkoxide in the presence of phenolphthalein or thymolphthalein as an indicator.

Task:

Determine the molecular weight (chemical equivalent) of a weak monobasic acid by titration with potassium ethoxide in ethanolic solution using phenolphthalein as an indicator (the acid has the general formula $C_xH_yO_z$).

Chemicals and equipment:

Standard solution of potassium ethoxide in ethanol of concentration c = 0.1000 mol dm^{-3}

Indicator: 0.1% solution of phenolphthalein in ethanol

Solvent: A mixture of ethanol and benzene

1.000 g of sample, accurately weighed,

3 titration flasks of volume 200 or 500 cm^3, one 25 cm^3 burette, one 50 cm^3 pipette, one 250 cm^3 volumetric flask, one 100 cm^3 measuring cylinder, small funnels, beakers, filter paper.

Procedure:

You are provided with 1.000 g of the monobasic acid $C_xH_yO_z$. This sample is labelled with a number. This should be written clearly at the top of your answer paper.

Carefully transfer all the acid into the graduated (volumetric) flask and fill the solution in the flask with ethanol up to 250 ml. A portion of 50.00 ml of this solution should be titrated with the 0.1000 M alcoholic solution of potassium ethoxide using 5 drops of phenolphthalein as indicator. The first titration should be a rough titration for estimating the approximate volume necessary to determine the endpoint. Subsequent titrations should be carried out with precision, using the same quantity of indicator each time.

Record all titration values. An extra titration should be carried out to eliminate any error that might be due to the action of the potassium hydroxide on the solvent, indicator or ethanol. This type of titration is known as a blank titration, its value should be recorded and used to correct the results of previous titrations. Care should be taken to use the same quantity of indicator as in previous titrations.

The correct titration values should be used to calculate the relative molecular mass (molecular weight) of the sample.

Note: The waste material containing organic solvents must not be discharged in a sink. Use labelled containers for this purpose.

Questions:

1) Suggest the name and formula of a common, monobasic acid which corresponds to the value you determined experimentally for your sample.
2) Write a general equation for the neutralisation of a monocarboxylic acid with:
   i) potassium ethoxide,
   ii) potassium hydroxide.
3) During the titration of some weak carboxylic (fatty) acids, similar to the titration that you have carried out, turbidity or cloudiness is observed. Suggest an explanation for this turbidity.
4) How would you produce 1 dm^3 of a standard solution of 0.1 M potassium ethoxide? Which compound would you use, as a standard solution?
5) Why are the titrations of weak acids carried out in non-aqueous media?
6) Name another solvent which is suitable for use in the titration of weak acids.
7) How would you recover the organic solvent used in your experiment?
8) Sketch a schematic titration curve (pH as a function of volume) for the titration of 20 ml of a 0.1 M aqueous solution of a weak monobasic acid with a standard aqueous solution of 0.1 M potassium hydroxide.
9) Calculate the pH of 0.1 M aqueous solution of an acid which has a dissociation constant of 1×10^{-7}.

18th

7 theoretical problems
2 practical problems

THE EIGHTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
6–15 JULY 1986, LEIDEN, NETHERLANDS

THEORETICAL PROBLEMS

PROBLEM 1

Compounds containing divalent platinum with the general formula $PtX_2(amine)_2$ (X = Cl_2, SO_4^{2-}, malonate, etc.) have met a lot of scientific interest because of their biological activity, particularly in view of their properties in the treatment of tumours. The best known compound used clinically is $PtCl_2(NH_3)_2$. This compound, in which platinum is coordinated in a planar square, has two geometrical isomers of which only one shows the antitumour activity.

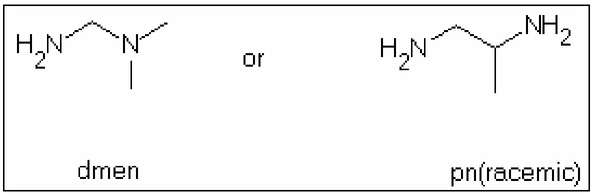
1.1 Sketch the spatial structures of the two possible isomers.

1.2 How many isomers has $PtBrCl(NH_3)_2$? Sketch all of them.

It is possible to replace the amine ligands by one ligand containing two donor atoms (N). Then one obtains a chelating ligand, such as 1,2-diaminoethane (en).

1.3 Show graphically that PtBrCl(en) has only one stable structure.

The ligand en can be substituted via methylation to form dmen or pn (racemic).



1.4 Give spatial structures of all isomers of the following compounds: $PtCl_2(dmen)$, $PtCl_2(pn)$, PtBrCl(dmen) and PtBrCl(pn).

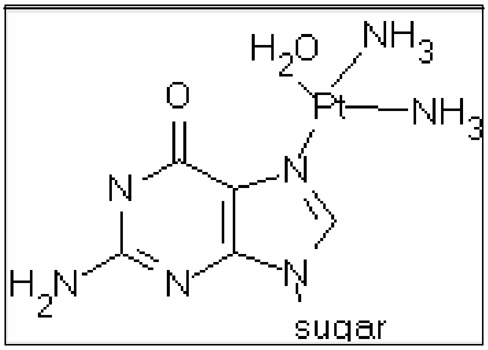
These compounds can isomerise in aqueous solution through dissociation of a ligand and transient replacement of the stronger ligands by the weak ligand water. Cl^- and Br^- are replaced relatively easily, but it is more difficult to replace the amine ligands, which usually requires heating.

1.5 Considering each of the isomers in the previous questions a-d, indicate which Isomers can be converted to another at room temperature. Give both the original molecule and the products.

1.6 $PtCl_2$(en) reacts with Br^- in a molar proportion of 1:2 at room temperature. Which compound would you expect to form in what proportion? You can assume that the Pt-Br and Pt-Cl bonds are equally strong and that there is no perturbing influence from hydrolysis.

1.7 Using the equation to express chemical equilibrium, show that hydrolysis hardly ever occurs in blood but that it does occur in the cells. Note: $PtCl_2(NH_3)_2$ hydrolyses to and 2 Cl^-. In cells the Cl^- concentration is low; in blood it is fairly high.

After hydrolysis in the tumour cell a reactive platinum ion is formed to which two NH_3 groups are still bound, as it was found in the urine of patients treated with this compound. The reactive platinum ion appears to be bound to cellular DNA, where the bonding occurs via guanine to one of the N-atoms.

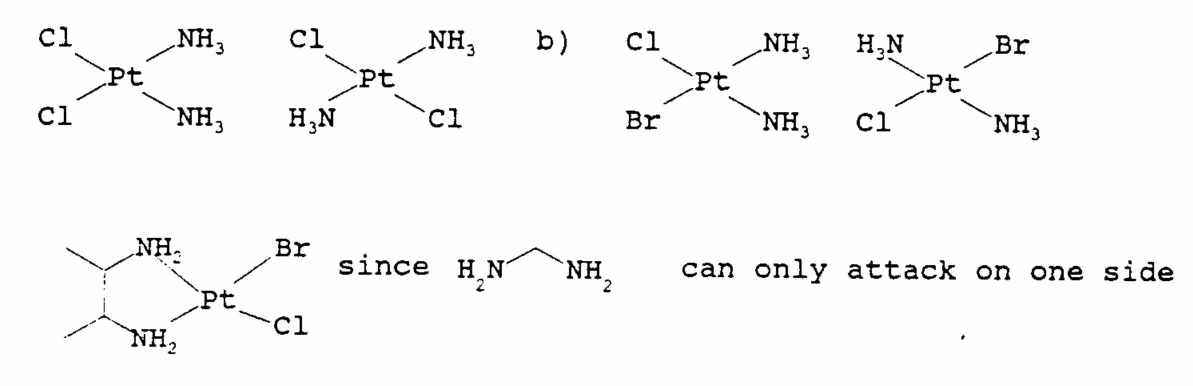


As a result of the two reactive sites of platinum and the two unreactive NH_3 ligands, it can form additionally a second bond to DNA. Research has shown that this happens in particular with a second guanine base from the same strand of DNA.

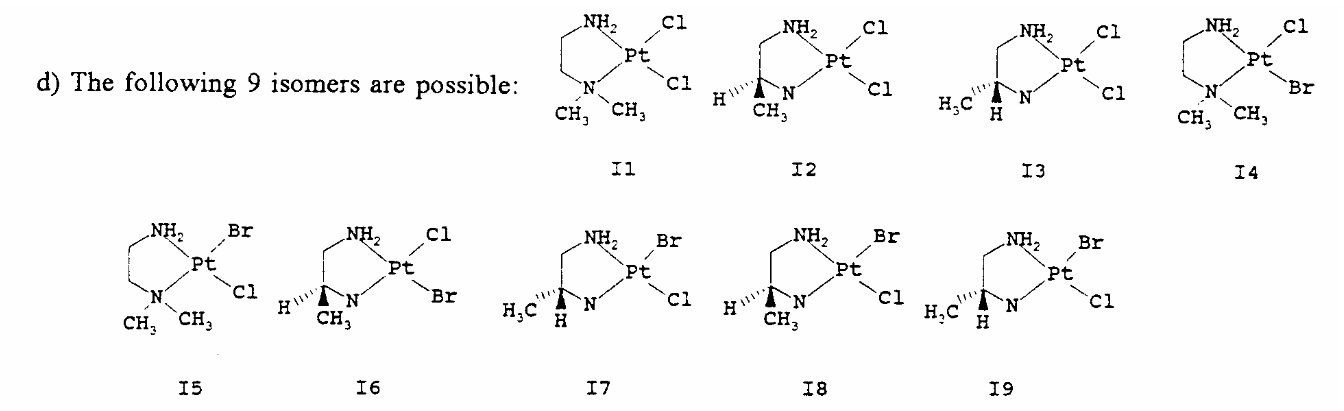
1.8 Show by calculations which of the two isomers in question a) can form this bond. (Note: Pt-N distance = 210 pm, DNA base distance = 320 pm).

SOLUTION

1.1 - 1.3 The isomers are:



1.4



1.5 In a-c) there is no change possible;

in d) I4 and I5, I6 and I7, I8 and I9 transform one into another. Via this isomerization also $PtCl_2$(dmen), $PtBr_2$(dmen), $PtCl_2$ (pn) and $PtBr_2$(pn) can be formed, even though they are not isomers.

1.6 $PtCl_2(en) : PtBr_2(en) : PtBrCl(en) = 1 : 1 : 2$

1.7 $PtCl_2(NH_3)_2 \rightleftharpoons (PtCl(H_2O)(NH_3)_2)^+ \rightleftharpoons Pt(H_2O)_2(NH_3)_2)^{2+}$

In blood the hydrolysis does not occur, because the concentration of Cl^- is rather high and the equilibrium is shifted to the left side.

1.8 The bond is formed by the cis-isomer, because in that case the distance between the bases (320 pm) has to change only to $210\sqrt{2} =$ 297 nm, whereas in the case of the trans-compound the distant would be $210 \times 2 = 420$ nm.

PROBLEM 2

The compound $Na_5P_3O_{10}$ is used as an additive for detergents to bind the Ca^{2+} and Mg^{2+} ions present in water in order to prevent the precipitation of their fatty acid salts on the laundry.

2.1 Draw the structure of the ions $(P_3O_{10})^{5-}$ and $(P_3O_9)^{3-}$ assuming that P-P bonds do not occur.

2.2 Assuming an octahedral coordination of the Mg^{2+} ion give a drawing of the $Mg(P_3O_{10})(H_2O)_n)^{3-}$ ion also indicating the value for n.

The complex ions of Mg^{2+} and Ca^{2+} and triphosphate are well soluble in water. They are, among other things, responsible for the wild growth of algae in surface waters. They could be removed by precipitation as an insoluble compound.

2.3 Give some possibilities (ions) to precipitate the triphosphates bound to Ca^{2+} or Mg^{2+}.

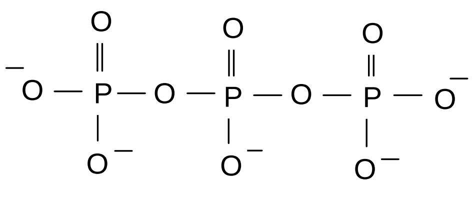
2.4 Calculate the mass of $Na_5P_3O_{10}$ (in grams) necessary in a washing machine to reduce the amount of Ca^{2+} in 20 litres of city water (0.225 g/l) to an acceptable maximum of 0.02 g/l. Effects of pH, the precipitation of $Ca(OH)_2$, and possible effects by other positive ions, can be neglected. The following data is given:

$$K_1 = \frac{[Ca^{2+}][P_3O_{10}^{5-}]}{[CaP_3O_{10}^{3-}]} = 1.0\times10^{-6}$$

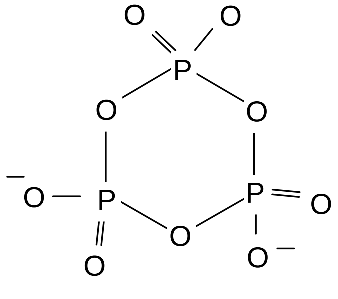
Molar mass of $Na_5P_3O_{10}$ is 366 g mol^{-1}, the molar mass of Ca is 40 g mol^{-1}.

SOLUTION

2.1 The structures are:

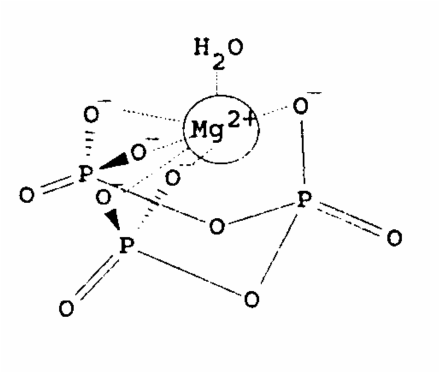


$P_3O_{10}^{5-}$



$P_3O_9^{3-}$

2.2 Since Mg^{2+} has the coordination number 6, one water molecule serves as the sixth ligand among the five O^- ligands already present in the $[P_3O_{10}]^{5-}$ - ligand:



2.3 Possible ions are Al^{3+} or Fe^{2+} because of their equal charge and similar size. The triphosphates are not soluble in water.

2.4 $[Ca^{2+}] + [CaP_3O_{10}]^{3-} = \frac{0.225}{40}\ \text{mol dm}^{-3}$;

$[Ca^{2+}] = \frac{0.020}{40}\ \text{mol dm}^{-3} \Rightarrow [CaP_3O_{10}^{3-}] = \frac{0.205}{40}\ \text{mol dm}^{-3}$

$[P_3O_{10}{}^{5-}] = \frac{K_1[CaP_3O_{10}^{3-}]}{[Ca^{2+}]} = 1.025 \times 10^{-5}\ \text{mol dm}^{-3}$

$[CaP_3O_{10}^{3-}] + [P_3O_{10}{}^{5-}] = 5.135 \times 10^{-3}\ \text{mol dm}^{-3} \equiv$ 37.6 g $Na_3P_3O_{10}$ in 20 dm^3 H_2O

PROBLEM 3

In order to explain why dyes are coloured, they can be considered as rod-like, one-dimensional molecules over which the electrons are distributed. The wave lengths of the electrons should fit to the available space which is the length l. When absorbing light, an electron makes a transition from a lower to a higher energy state. The energy difference is given by:

$$\Delta E = h \times coverlambda \;\; where \;\; \lambda = \frac{h}{p}$$

3.1 Give a general expression for possible wavelengths of the electron as a function of the length l.

In the 'particle in the box' model, only the variations in the kinetic energy of the electrons are considered.

3.2 Give an expression for the possible energies that electrons in the molecule can have (as a function of l).

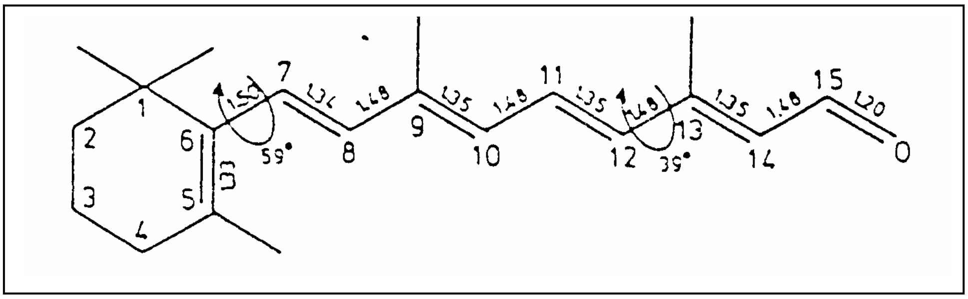
3.3 Show that for a chain of length l with k electrons, the longest wavelength absorption occurs at:

$$\lambda = \frac{8mcl^2}{h(k+1)} \quad \text{for even values of } k$$

3.4 Derive an expression for the wavelength of the first electronic transition as a function of the number of C-atoms for even values of n.

3.5 Calculate the minimum number of C-atoms (conjugated systems) to obtain a visible colour. C-C bond length is 142 pm.

The retina in the human eye contains rhodopsin, a light absorbent.



The molecule in the part of C-atoms 7 through 12 is planar. The angle between the bonds C5-C6, C7-C8, C11-C12 and C13-C14 is about 39°. According to the *'particle in the box'* theory fragment C7 through C12 should absorb at about 213 nm. In reality the absorption of retinal occurs at 308 nm.

3.6 Give a reason for the longer wavelength that is observed in practice using the above mentioned theories.

3.7 When retinal is bound to opsin to form rhodopsin, the absorption occurs around 600 nm. Which atoms must be forced into one plane by the protein? Show by calculation that it's true.

SOLUTION

3.1 $\lambda = c\nu$ = 2 l / n with n = 1, 2, 3, ...

3.2 $E = \frac{h\,c}{\lambda} = \frac{m\,v^2}{2} = \frac{p^2}{2\,m}\,;\; p = \frac{h}{\lambda} = \frac{h\,n}{2\,l} \;\Rightarrow\; \Delta E_n = \frac{h^2 n^2}{8\,m\,l^2} = \frac{h^2}{8\,m\,l^2} \times (n^2_{homo} n^2_{lumo})$

3.3 For k electrons and k ≡ 0 mod 2, k/2 orbitals are possible, so n_{homo}= k/2 and n_{lumo} = k/2 + 1

$$\Delta E_n = \frac{h^2}{8\,m\,l^2}[(1/2\,\mathrm{k} + 1)^2\;1/2\mathrm{k}^2] = \frac{h^2}{8\,m\,l^2} \times (\mathrm{k} + 1) \;\Rightarrow\; \lambda = \frac{h\,c}{\Delta E} = \frac{8\,m c\,l^2}{\mathrm{h}(\mathrm{k} + 1)}$$

3.4 If N is the number of C-atoms, N is equal to k+1 for even number of electrons k, so

$$\lambda = \frac{8\,m c\,l^2}{N\,h} = \frac{8\,m c\,l^2}{\mathrm{h}\,(\mathrm{k} + 1)}$$

for even N's, the length of the box would be a(N-1) with k = N electrons, so

$$\lambda = \frac{8\,m\,c\,(\mathrm{N1})^2\,\mathrm{a}^2}{\mathrm{h}\,(\mathrm{N}+1)}$$

3.5 For a conjugated system N has to be even. To obtain a visible colour, the wavelength should be greater than 400 nm. Therefore:

$$\frac{8 m c (\mathrm{N1})^2 \mathrm{a}^2}{h(\mathrm{N}+1)} \;\geq\; 4 \times 10^7 \;\text{ so accordingly}:\; \frac{(\mathrm{N1})^2}{\mathrm{N}+1} \;\geq\; 6.02$$

The equation $N^2 - 6.02\,N - 6.02 > 0$ derived from the equation above has the only positive solution N = 8.60. Since N must be even, the minimum number of C-Atoms is 10.

3.6 The angles between 5-6 and 7-8, as well as between 11-12 and 13-14 are smaller than 90° and therefore the effect of the double bonds between C5 and C6, C13, C14 and O cannot be neglected. They overlap to a small extent with the conjugated system C7 through C12 and enlarge the box significantly. A larger l leads to a larger λ, causing a shift towards a longer wavelength.

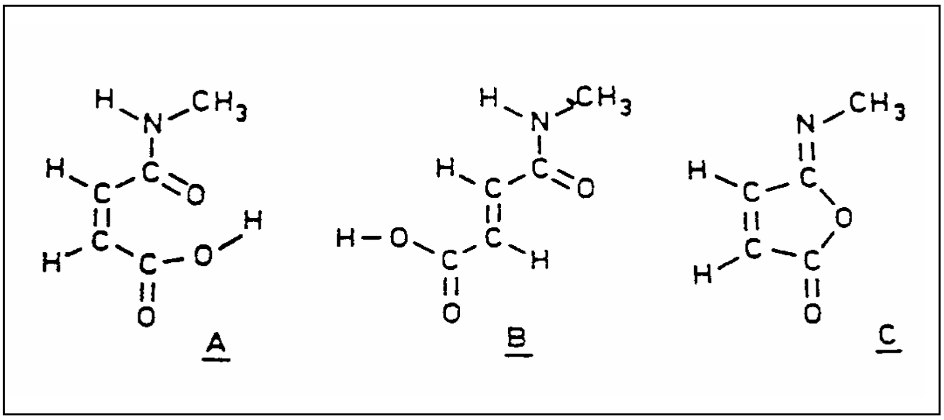
3.7 Obviously, the box must be much larger when bound to opsin. For λ = 600 nm the atoms C5 to O at the end of the chain must be forced into the plane:

$l = 0.133 + 0.150 + 4\,(0.134 + 0.148) + 0.120 = 1.54$ nm; $k = 12$;

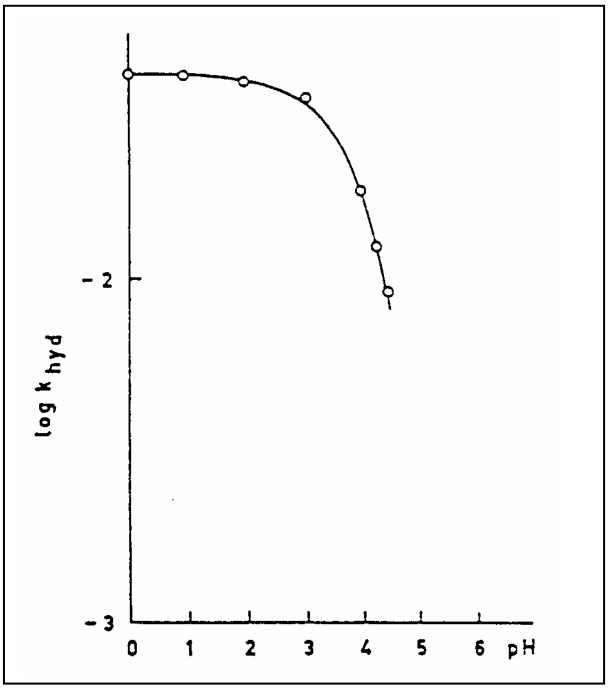
$\lambda = 3.30\times10^{12}\, l^2 / (k + 1) = \underline{602 \text{ nm}}$

PROBLEM 4

The high efficiency of catalysis by enzymes is mainly due to an enzyme-reactant complex in which the reacting group is placed in a favourable position for the reaction with respect to the catalyzing groups of the enzyme. Studies are carried out with model compounds in which a catalyzing group has been introduced in the proximity of the reaction centre of the molecule. As an example we consider the hydrolysis of the amide bond in compound **A**. This reaction proceeds in water at 39 °C and pH = 2 more than a million times faster than the hydrolysis of compound **B**.



The relation between the rate constant k_{hyd} and pH for the hydrolysis of **A** at 39 °C is shown in figure below.



Further observation:

Addition of water to the iso-imide **C** gives a rapid reaction, which initially yields **A**. Subsequently, hydrolysis of **A** occurs. The amid carbonyl group in **A** is labelled with ^{13}C and the hydrolysis is allowed to take place in $H_2{}^{18}O$ at pH = 2 and 39 °C. The diacid formed upon hydrolysis is isolated, converted into a disilver salt and completely decarboxylated with bromine in a anhydrous reaction medium. The carbon dioxide formed is a mixture of particles of masses 44, 45, 46 and 47 which are formed in equal amounts.

4.1 Why is the hydrolysis of **A** so much faster than that of **B**?

4.2 Explain why the rate of hydrolysis of **A** is independent on pH in the range between pH = 0 to pH = 2.

4.3 Why does k_{hyd} decrease so rapidly at pH values higher than 3.

4.4 Give a detailed reaction mechanism for the hydrolysis of **A**. Indicate which step in the reaction is rate determining.

4.5 Show that the observations further made are consistent with the reaction mechanism given under d.

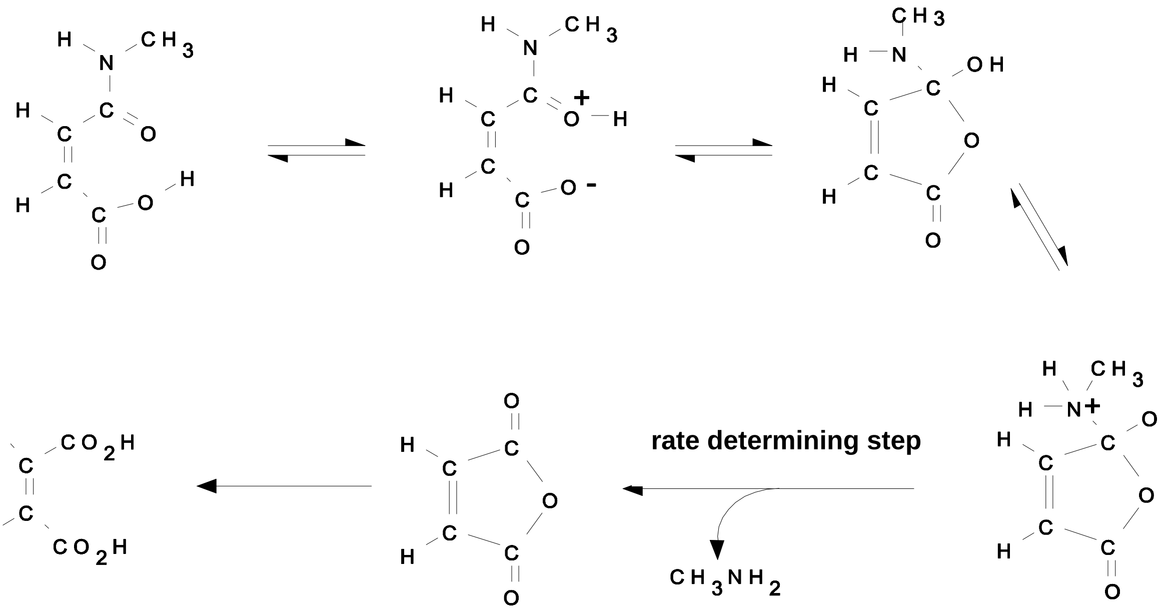
SOLUTION

4.1 The high rate of hydrolysis of **A** is caused by intramolecular catalysis of the COOH group in the cis-position. In **B** the COOH group is situated in the trans-position with respect to the amide group and therefore too far away for intramolecular catalysis.

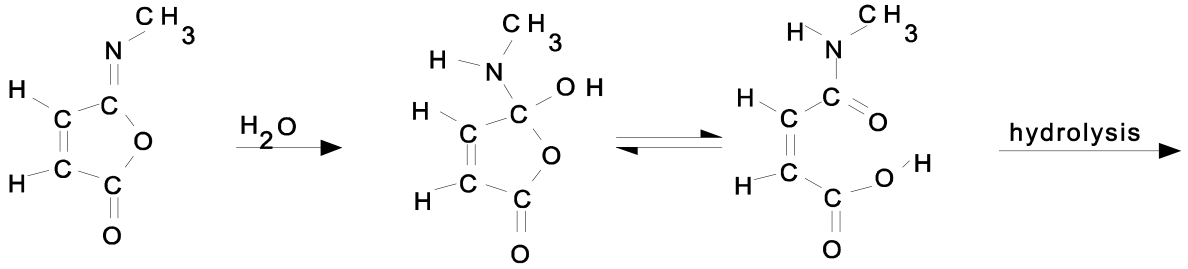
4.2 For 0 < pH < 2 the COOH group is not ionized and therefore, it can act as an intramolecular catalyser. If the hydrolysis in that pH-range is only the result of catalysis by the COOH-group and not competing with H_3O^+ the rate constant in that range is pH independent.

4.3 At pH > 3 the COOH group deprotonates giving COO^-. Intramolecular acid catalysis, in which proton transfer plays an important role, is then not possible anymore.

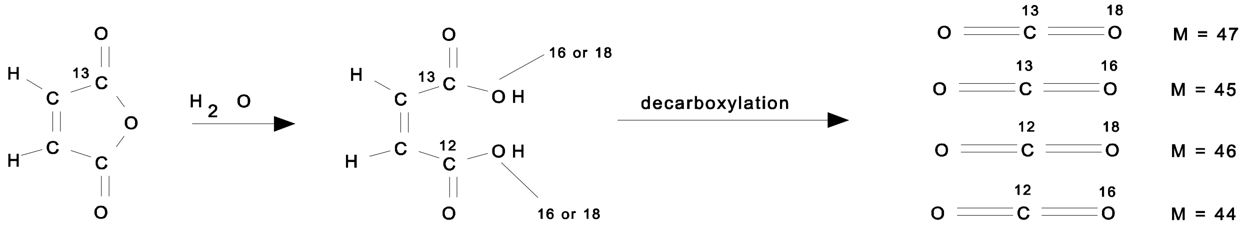
4.4 The mechanism of hydrolysis is indicated below:



4.5



With the observation given, the rate determining step can be identified.



PROBLEM 5

Bacterial conversion of saccharose leads to (S)-(+)-2-hydroxypropanoic acid (L-(+)-lactic acid), which forms a cyclic ester out of two molecules. This dilactide can be polymerized to a polylactide, which is used in surgery.

5.1 Give the spatial structures and Fischer projection of L-(+)-lactic acid and its dilactide.

5.2 Sketch the structure of the polylactide discussed above (at least three units). What is its tacticity (iso-, syndio- or atactic)?

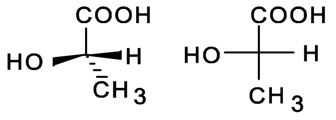
5.3 Draw the isomeric dilactides formed out of racemic lactic acid. Show the configuration of the chiral centres.

L-(+)-lactic acid is used for the preparation of the herbicide Barnon that is used against wild oats. In this case (+)-lactic acid is esterified with 2-propanol and then the hydroxyl group is treated with methanesulfonyl chloride. The product is then submitted to a S_N2-reaction with 3-fluoro-4-chloro-phenylamine, where the methanesulfonate group leaves as $CH_3SO_3^-$. Finally a benzoyl group is introduced with the help of benzoyl chloride.

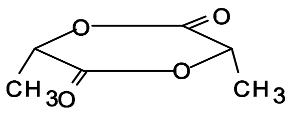
5.4 Draw the Fischer projection of the various consecutive reaction products.

SOLUTION

5.1

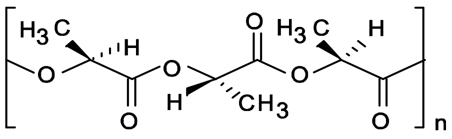


L-(+)-lactic acid and its Fischer projection



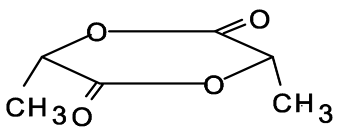
Dilactide of L-(+)-lactic acid - spatial formula

5.2

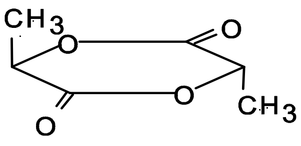


Polylactide of L-(+)-lactic acid

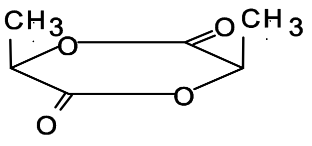
5.3 Dilactides of racemic lactic acid with the following configurations:



(*R*,*R*)

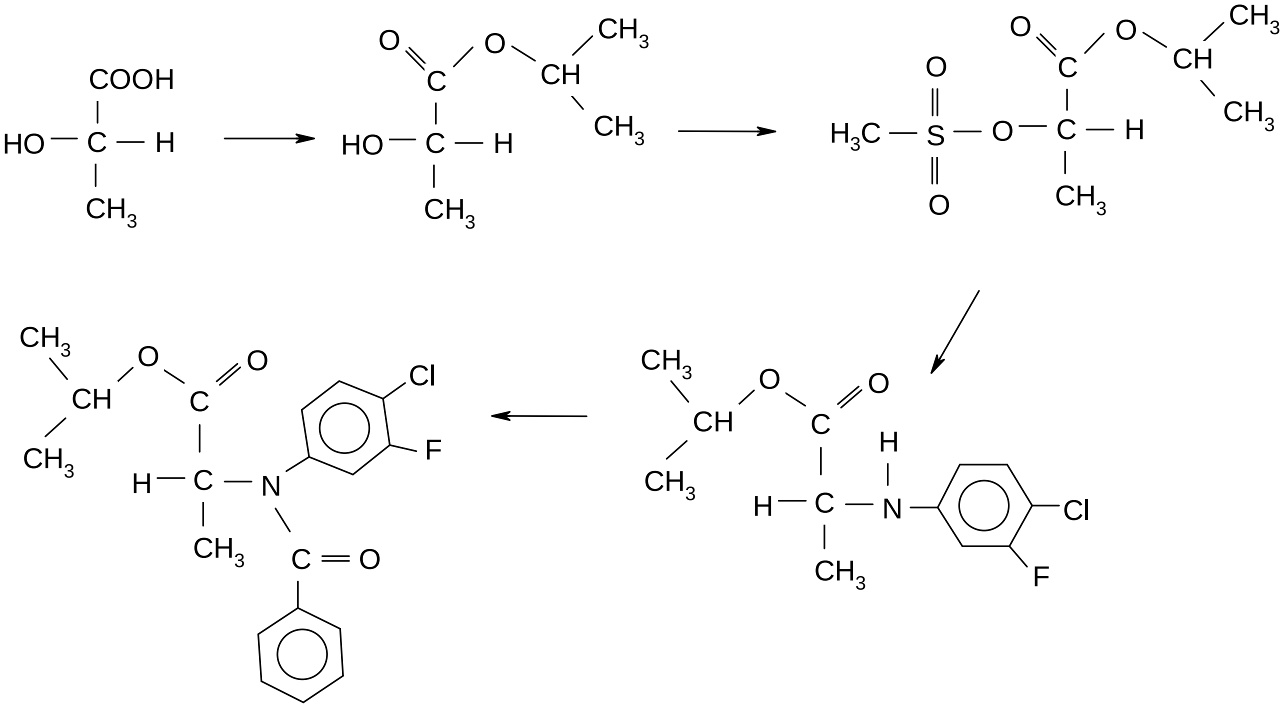


(*S*,*S*)



(*R*,*S*) meso compound

5.4



Barnon

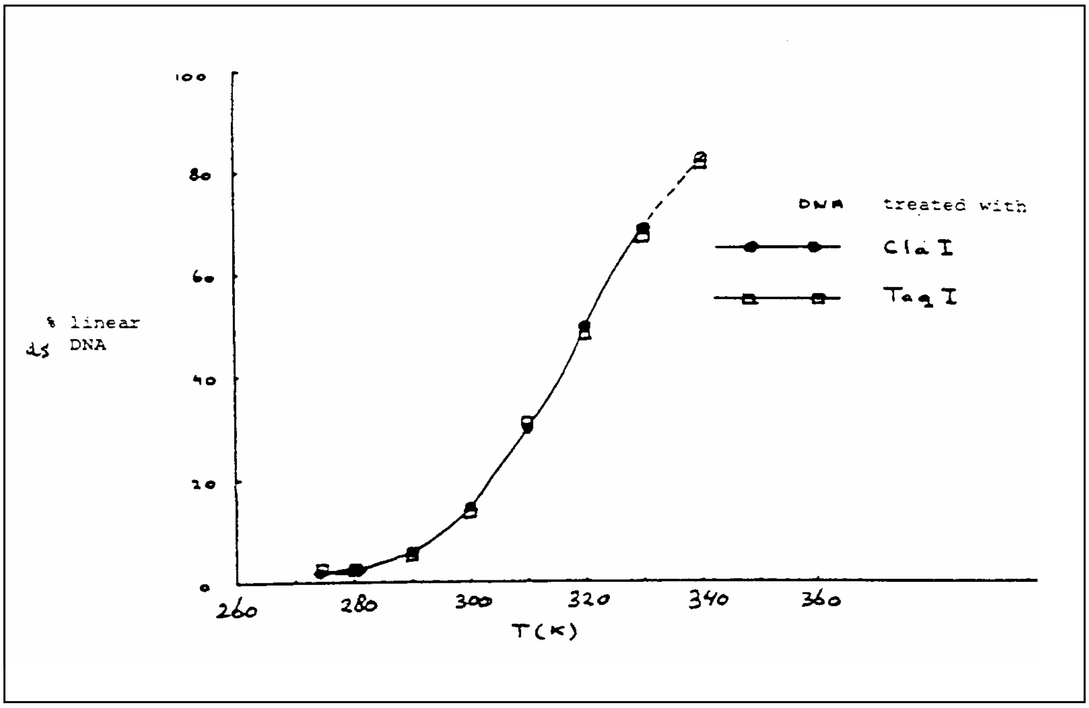
PROBLEM 6

In recombinant DNA technology specific endonucleases can recognize and hydrolyse the phosphoric ester bound in each of both strands. Cla I for example hydrolyses the bond between two nucleotides in the sequence:

5'-pApT│ pCpGpApT- 3'

6.1 Give the base sequence of the complementary strand in the 5' - 3' direction and indicate with arrows the location where the hydrolysis by Cla I would occur.

6.2 How often on average will this sequence occur in one strand of DNA molecule of 10^5 base pairs? You can assume that the four bases occur equally often and that they randomly distribute in the two chains.



Taq I hydrolyses a long double strand DNA molecule into fragments which are on average 256 base pairs long. The 3' end of these fragments treated by cleavage turns out to be a thymine(T)- and the 5' end a cytosine(C) -end.

6.3 How long is the sequence recognized by Taq I?

6.4 Give the two possible base sequences (in the direction 5' - 3') which form the recognition pattern for Taq I (must obviously have some symmetry).

The DNA of a phage which occurs as a close circle contains only 5'-pApTpCpGpApT-3' sequence in each of the two strands. After treatment with ClaI equilibrium is established: circular DNA $\rightleftharpoons$ linear DNA.

6.5 Give a schematic drawing of the circular and linear molecules. Indicate the bases adjacent to the cleaning site in both strands. Indicate also the 3' and 5' ends.

In Fig. 1 the percentage of linear DNA is given as a function of temperature, measured in a solution of 0.15 M NaCl buffered with citrate at pH = 6.5. With Taq I as cleavage enzyme, the same curve is obtained.

6.6 Is the reaction as written endothermic or exothermic? Explain your answer.

6.7 Show, considering the information given, which of the two base sequences of the answer to **6.4** is the correct one.

6.8 What would look the curve for Taq I like if the recognition pattern would have been the other possibility of d)?

A large DNA molecule is cut into fragments with the aid of Cla I. One fragment is isolated, purified and mixed in the ratio of 1:1 with phage DNA which was also cleaved with Cla I. Thereby recombinant molecules can be formed through the reaction:

phage-DNA + fragment DNA $\rightleftharpoons$ recombinant-DNA

6.9 Would the enthalpy of this reaction be positive, negative or about zero? Explain your answer.

6.10 Which combination of temperature, DNA concentration and ionic strength (high or low in each case) will give the maximum percentage of recombinant molecules?

SOLUTION

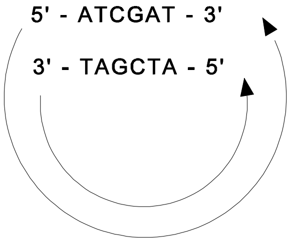
6.1 5' - pTpApGpCpT \pC

6.2 The probability of the sequence given is $(1/4)^6 = 1/4096$. Thus, this specific sequence may occur in the DNA $10^5/4096 = 24.4$ times on average

6.3 The sequence recognized by Taq I is 2 base pairs, that is 4 bases.

6.4 The sequence is 5' - pTpCpGpA - 3' or 5' - pGpApTpC - 3'

6.5



5' - CGAT________________________ AT - 3'
3' - TA____________________________TAGC - 5'

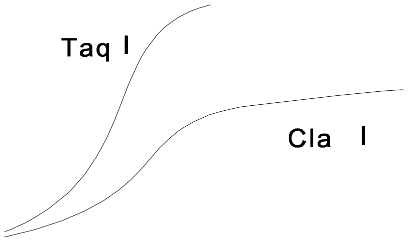
6.6 The reaction is endothermic. The reaction has a positive enthalpy, since the hydrogen bonds between the bases G and C in the complementary strands are broken.

6.7 The two relations show the same dependence on temperature. Therefore, the enthalpy of the two reactions is roughly the same. Then the interaction of the double helix must be identical and therefore we must choose TCGA for the first recognition sequence of question **6.4**. The cleavage in the two cases mentioned in d) occurs as follows:

Cla I:5' - pApT│$\underline{\text{pCpGp}}$ApT - 3'
3' - pTpApGpCp│TpA - 5'

Taq I: 5' - pT│$\underline{\text{pCpGp}}$A - 3'
3' - pApGpCp│T - 5'

6.8 The following curve would be obtained:

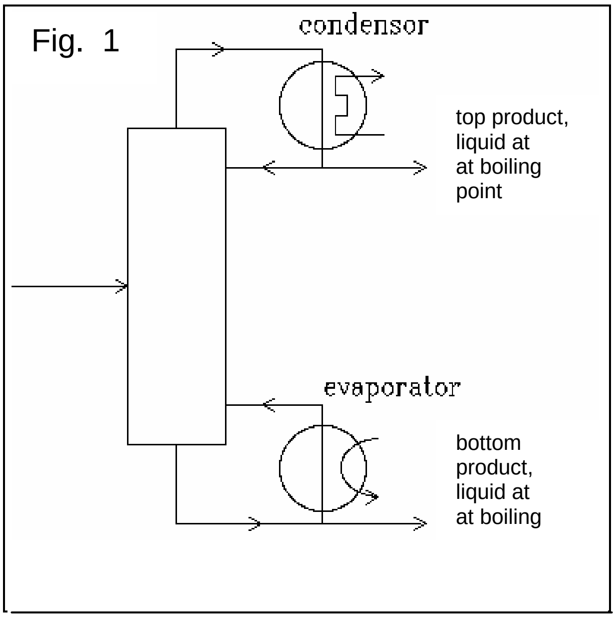


6.9 ΔH is negative.

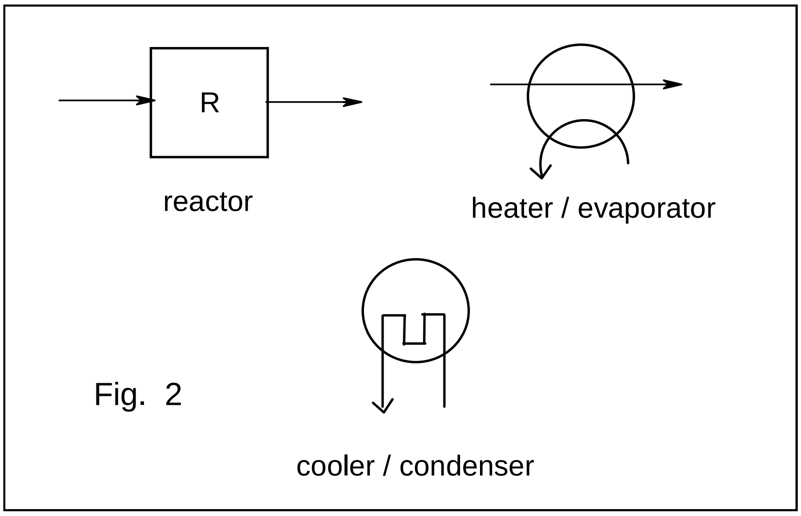
6.10 Low temperature, low DNA concentration and high ionic strength will give the maximum percentage of recombinant molecules.

PROBLEM 7

The equilibrium constant of the reaction $A_{(g)} + 2\ B_{(g)}$ _ $2\ C_{(g)}$ is $K_p = 10.0\ MPa^{-1}$. The starting materials are supplied at 25 ℃ and heated to 100 ℃ where complete equilibration takes place. Below 100 ℃ the reaction rate is negligibly small. The whole process is executed continuously in a stationary state. The boiling points at 0.1 MPa of **A**, **B**, and **C** are 40 ℃, 80 ℃, and 60 ℃, respectively. The three compounds have the same heat of evaporation: q J mol^{-1}. The heat capacities of **A**, **B**, and **C** may be neglected. A schematic diagram of a distillation is shown below (Fig. 1).



The total heat used at each of the two distillations is 3q J mol^{-1} (of the top product). Apart from distillation columns (each with its own evaporator and condenser) the pieces of apparatus shown of Fig. 2 are available.



7.1 Draw a flow diagram of the process in which all flows are given (flow sheet) and in which the starting materials are used as efficiently as possible using as few pieces of apparatus as possible.

7.2 Express the equilibrium constant in terms of the degree of conversion and of total pressure for the case that the feed to the reactor is stoichiometric. What is the value of the degree of conversion when total pressure is 0.100 MPa?

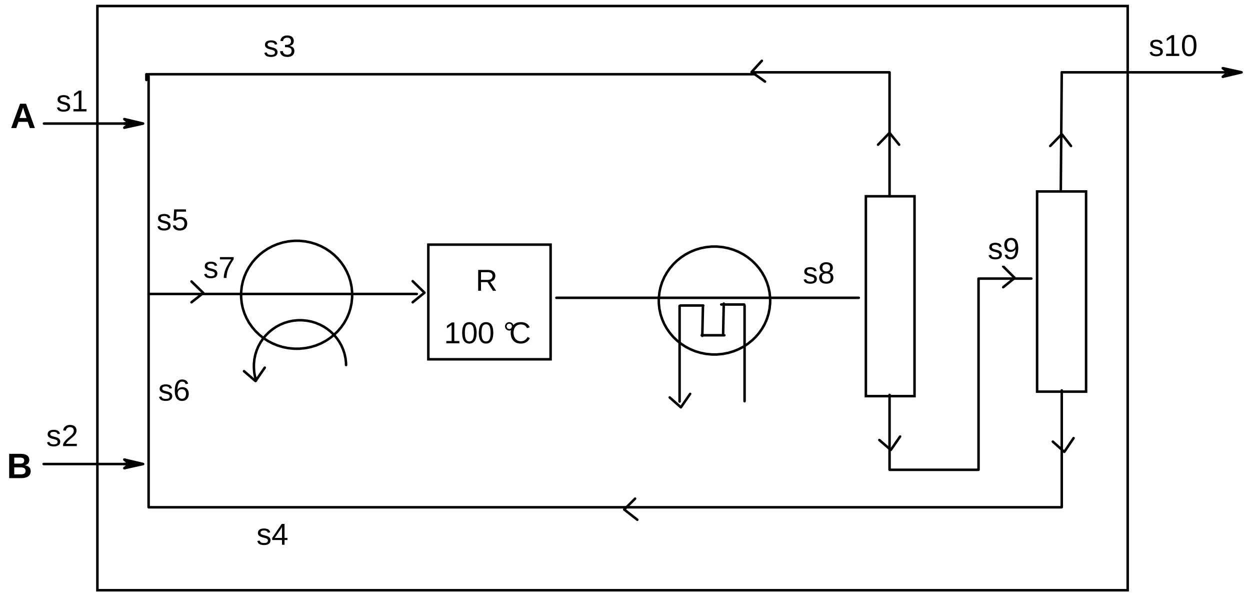
7.3 Number all flows. Calculate the composition of each flow in mol s^{-1} for a rate of production of 1 mole of **C** per second under the conditions of part b.

7.4 In what respect can the reaction conditions influence the composition of the mixture that leaves the reactor? (Refer to question b.)

7.5 The process requires energy. For the conditions of b explain where energy should be supplied in the flow diagram drawn in part a. Derive an expression for the total energy needed.

SOLUTION

7.1 In order to minimize the pieces of apparatus, the liquids A and B should evaporate together. For complete consumption of the starting materials, A and B are recirculated as feed for the reactor. The scheme of figure depicts the solution.



system boundary

7.2 **A** + 2 **B** → 2 **C**

1-x 2(1-x) 2x

In total 3-x mol gases are present after conversion. Supposing that the input of **A** is a mol (S5) and the input of B b mol (S6) we can write for the equilibrium:

$$K_p = \frac{p_C^2}{p_A \times p_B^2} = 10.0$$

If x mol of **A** are converted, S8 contains (a - x) mol of **A**, (b – 2x) mol of **B** and 2 x mol of **C**. Therefore S8 contains (a - x) + (9 b – 2x) + 2x = (a + b - x) moles and we can write for the partial pressures of A and B:

$$p_A = \frac{a - x}{a + b - x} P \qquad p_B = \frac{b - 2x}{a + b - x} P \qquad p_C = \frac{2x}{a + b - x}$$

Therefore the equilibrium can be written as

$$K_p = \frac{(2x)^2}{(a - x)\,(b - 2x)^2} \times \frac{a + b - x}{P} = 10$$

7.3 For P = 0.10 we obtain: $4x^2a + 4x^2b - 4x^3 = ab^2 - 4abx + 4ax^2 - xb^2 + 4x^2b - 4x^3$ and wherefrom:

$0 = ab^2 - 4abx - xb^2$ and since $b \neq 0$: $0 = ab - 4ax - bx$

With a total inflow of 0.5 mol s^{-1} **A** (S1) and 1 mol s^{-1} **B** (S2), the amount of **C** leaving the reactor (S10) is 1 mol s^{-1}. So 2x = 1 and x = 0.5. The relation between a and b can be written as: a = b / (2b - 4). Since the feed is stoichiometric a : b = 1 : 2. This leads to b = 3 and a = 1.5.

All flows (mol/s) can be calculated now:

s1 = 0.5 mol s^{-1} **A**

s2 = 1 mol s^{-1} **B**

s3 = 1.5 - 0.5 = 1 mol s^{-1} **A**

s4 = 3 - 1 = 2 mol s^{-1} **A**

s5 = a = 1.5 mol s^{-1} **A**

s6 = b = 3 mol s^{-1} **B**

s7 = 1.5 mol s^{-1} **A** + 3 mol s^{-1} **B**

s8 = 1 mol s^{-1} **A** + 2 mol s^{-1} **B** + 1 mol s^{-1} **C**

s10 = 1 mol **C**

s9$_1$ = 2 mol **B** + 1 mol **C**; s9$_2$ = 1 mol **A** + 1 mol **C**

7.4 By increasing the pressure, the equilibrium is pushed towards the side with the smallest number of molecules that means to the right side. Another possibility is changing the ratio of the feed. i. e. a : b. According to a = b / (2 b - 4), b will be larger if a decreases and vice versa. Because the net enthalpy change is 0, temperature has no effect.

7.5 Energy must be supplied for heating the evaporator and for the two distillation columns. The total energy consumed of the flow in scheme can be calculated as follows:

Q1 = q*S7 + 3q*S3 + 3q*S10 = 10.5 q

PRACTICAL PROBLEMS

Introduction:

The experimental assignment consists of the synthesis and subsequently, the analysis of amminenickel(II) chloride: $NiCl_x(NH_3)_y$.

The synthesis proceeds in three steps:

a) Preparation of a solution of nickel nitrate from nickel and concentrated nitric acid (green solution), time required about 20 min.

b) Preparation of amminenickel(II) nitrate (blue crystals)

c) Preparation of amminenickel(II) chloride (blue-violet crystals)

The analysis encompasses the determination of the percentages of the three components (ammonia, nickel and chlorine) of the salt, according to the instructions given in 2.

PROBLEM 1 (practical)

Synthesis of the nickel(II) salt:

All work on the synthesis must be carried out in the fume hood. Use of (safety) glasses is obligatory. If necessary use other safety equipment, such as rubber gloves and pipetting balloons.

a) Put a "dubbeltje" (Dutch coin of 10 c, containing 1.5 g of nickel), in a 100 ml conical flask (Erlenmeyer flask) and add 10 ml of concentrated nitric acid (65 %). Fit the flask with an "air cooled" condenser (no water) and heat the contents on a hot plate until a violent reaction occurs. Continue heating carefully until all metal is dissolved. Cool the green solution in an ice-water mixture.

Write in the report form the equation of the chemical reaction that has occurred.

b) Add, under continuous cooling, in small portions 25 ml of ammonia solution (25 %) to the ice cold solution. As soon as about 15 ml has been added, salt crystals start to precipitate. Having added all ammonia solution, filter the cold solution through a sintered glass filtering crucible by applying a vacuum with an aspirator. Wash the crystals three times with small portions of a cold ammonia solution (25 %). Remove as much liquid as possible from the crystalline mass by maintaining the vacuum.

c) Dissolve the moist crystalline mass in 10 ml of hydrochloric acid (18 %). Cool the blue solution in an ice-water mixture and then add slowly 30 ml of a solution of 30 g ammonium chloride in 100 ml of ammonia solution (25 %). This yields a blue-violet coloured crystalline mass. Cool the mixture and filter as in b). Wash with ammonia solution (25 %), then with ethanol and finally with diethyl ether. Leave the crystals on air until all ether has evaporated. Determine the mass of the dry product and record this on the report form.

PROBLEM 2 (practical)

Analysis of the Nickel Salt:

For the analysis of the salt, only one sample solution is prepared. The determination of the components is achieved by titrating each time 25 ml of the sample solution in duplicate.

For the determination of the ammonia and chlorine content a back titration is carried out. For that purpose a certain amount of reagent is added in excess. The total amount of reagent, available for the sample, is determined by following the same procedure for 25 ml of a blank solution. This titration should not be carried out in duplicate.

Prepare the following solutions:

A) Sample solution:

Pipette 25.0 ml of 1.6 M nitric acid into a volumetric flask of 250 ml. Add a sample of about 1.2 g of the amminenickel(II) chloride and dilute with water to a volume of 250 ml.

B) Blank solution:

Pipette 25.0 ml of the same 1.6 M nitric acid and dilute it with water to a volume of 250 ml.

Note:

1) For the chlorine determination use conical (Erlenmeyer) flasks with a ground glass stopper.
2) The nitric acid contains a small amount of hydrochloric acid. The total acid content is 1.6 M.

a) *Determination of the ammonia content*

Titrate the solutions with a standard solution of NaOH (about 0.1 M). Indicator: methylred, 0.1 % solution in ethanol.

Calculate the percentage of ammonia in the salt.

b) *Determination of the nickel content*

Add about 100 ml of water, 2 ml of ammonia solution (25 %) and 5 drops of murexide solution to the nickel solution, which now should have a yellow colour. Titrate the solution with a standard solution of EDTA (about 0.025 M) until a sharp colour change from yellow to violet is observed. Calculate the percentage of nickel in the salt.

c) *Determination of the chlorine content*

Execute the titration as quickly as possible after the addition of the reagent!

Add to each solution 25 ml of 0.1 M silver nitrate solution. Add about 5 ml of toluene, shake vigorously, add indicator and titrate with the standard solution of ammonium thiocyanate (-rhodanide, about 0.05 M) until a permanent colour change to red is observed. At the end of the titration, shake vigorously again. The red coloration should persist.

Indicator: 1 ml of a saturated solution of iron(III) sulphate.

Calculate the percentage of chlorine in the salt.

Data: Relative atomic masses: H = 1, Cl = 35.5, Ni = 58.7, N = 14.

Questions:

Calculate from the results obtained the molar ratio of the components to two decimal points and enter this on the report form in the format: Ni : Cl : NH_3 = 1.00 : x : y.

19th

International Chemistry Olympiad

5 theoretical problems
3 practical problems

THE NINETEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
6–15 JULY 1987, VESPZPRÉM – BUDAPEST, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

Treating waste water in a sewage plant, 45 % of its carbohydrate $(CH_2O)_n$ is completely oxidized, 10 % undergoes anaerobic decomposition by fermentation (two components) and the rest remains in the sludge. The total gas formation is 16 m^3 per day (25 °C, 100 kPa).

1.1 What is the amount of carbohydrate remaining in the sludge measured in kg per day?

1.2 Using the heat of combustion of methane (– 882 kJ mol^{-1}), calculate the amount of energy that can be produced by combustion of the methane formed per day.

1.3 Knowing that the concentration of the carbohydrate in the waste water is 250 mg dm^{-3}, calculate the daily amount of waste water processed in the plant in m^3 of water per day.

SOLUTION

1.1 $(CH_2O)_n + n\ O_2 \rightarrow n\ CO_2(g) + n\ H_2O(l)$ (1 mol gas/ mol carbohydrate)

$(CH_2O)_n \rightarrow 0.5\ n\ CO_2(g) + 0.5\ n\ CH_4(g)$ (1 mol gas/ mol carbohydrate)

For 16 m^3 of gases: $n(\text{gas}) = \dfrac{pV}{RT}$ = 646 mol (55 %) with the rest (45 %) therefore being in the sludge.

The amount in the sludge is $\dfrac{45}{55} \times 646$ = 528 mol, that is <u>15.85 kg/day</u>.

1.2 $n(CH_4) = \dfrac{5}{55} \times 646 = 58.71$ mol

$\Delta H = -\ 882 \times 58.71 = \underline{-\ 5.178 \times 10^4\ \text{kJ/day}}$

1.3 The sum of CH_2O is $\frac{646}{0.55}$ = 1174 mol. Since 250 mg dm^{-3} = 0.25 kg m^{-3}, the daily amount of water is: $V = \frac{1174 \times 30}{0.25 \times 10^3}$ = $\underline{140.9\ \text{m}^3/\text{day}}$

PROBLEM 2

500 mg of a hydrated sodium salt of phosphoric acid are dissolved in 50.0 cm^3 of 0.1 molar sulphuric acid. This solution is diluted with distilled water to 100.0 cm^3 and 20.0 cm^3 of it are titrated with 0.100 molar NaOH solution using thymolphthalein as indicator. The average of the burette reading is 26.53 cm^3. The pH at the end-point is 10.00.

Problems:

2.1 Calculate the percentage distribution by moles of all protonated $H_nPO_4^{n-3}$ species at the end-point.

2.2 What is the stoichiometric formula of the salt?

The cumulative protonation constants are given by

$$\beta_n = \frac{[H_nPO_4^{n-3}]}{[PO_4^{3-}][H^+]^n}$$

where $\log\beta_1 = 11.70$; $\log\beta_2 = 18.6$; $\log\beta_3 = 20.6$.

The relative atomic masses are: Na = 23.0; P = 31.0; H = 1.0; O = 16.0.

SOLUTION

2.1 $[H_3PO_4] + [HPO_4^{2-}] + [H_2PO_4^-] + [PO_4^{3-}] = T_{konst}$; $[H^+] = 10^{-10}$ mol dm^{-3}

$[H_3PO_4] = 1$ mol dm^{-3}

$[HPO_4^{2-}] = \beta_1[PO_4^{3-}][H^+] = 1.25 \times 10^{10}$ mol dm^{-3} = 97.97 %

$[H_2PO_4^-] = \beta_2[PO_4^{3-}][H^+]^2 = 1 \times 10^8$ mol dm^{-3} = 0.078 %

$[PO_4^{3-}] = (\beta_3 [H^+]^3)^{-1} = 2.5 \times 10^9$ mol dm^{-3} = 1.955 %

2.2 A general formula of the salt: $Na_{3-n}(H_nPO_4) \times m\ H_2O$ (n = 0,1,2)

The titrated solution contains 100 mg (y mol) of the salt and 1.00 mmol of sulphuric acid. The reacted protons (in mmol) can be calculated using the results of a):

$2 + (n - 0.9797 - 2 \times 0.00078)\ y = 2.653$

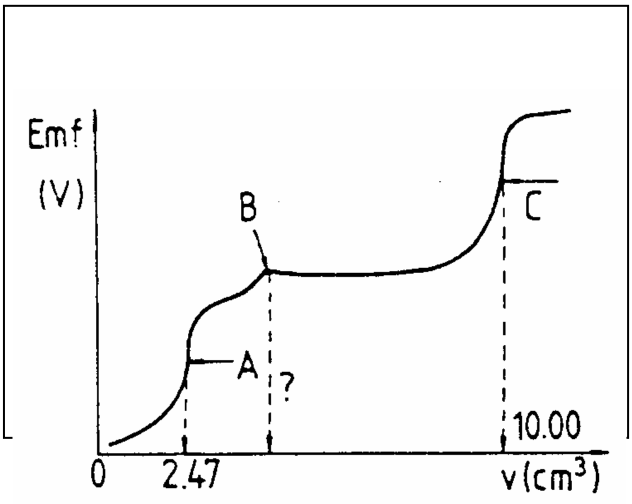
Since y = 100/M (in mmol) but $M \geq 120$ g mol^{-1}, the only real solution is n = 2.

Therefore M = 156 g mol^{-1}, m is (156-120)/18 = 2 ⇒ $\underline{NaH_2PO_4 \cdot 2\ H_2O}$

PROBLEM 3

25.00 cm^3 of a neutral solution containing potassium chloride and potassium cyanide are potentiometrically titrated with a standard 0.1000 molar silver nitrate solution at 25 ℃ using a silver electrode and a normal calomel half-cell with KNO_3 - salt bridge. The protonation of cyanide ions is negligible. The potentiometric curve obtained (emf (V)) vs. burette readings (in cm^3) is shown in Fig. 1.

Fig. 1



3.1 The end points of the reactions taking place during the titration, are marked with A, B and C. Write the balanced ionic equation for each reaction.

3.2 What volume of the titrant is required to reach point B?

3.3 Calculate the concentrations of KCl and KCN (in mol dm^{-3}) in the sample solution.

3.4 Calculate the emf readings at the points A and C in volts.

3.5 What is the molar ratio Cl^-/CN^- in the solution and in the precipitate at point C?

Data:

$E^o(Ag^+/Ag) = 0.800$ V

E^o(Calomel) = 0.285 V

$K_{sp}(AgCN) = 10^{-15.8}$

$K_{sp}(AgCl) = 10^{-9.75}$

$$\beta_2 = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = 10^{21.1}$$

SOLUTION

3.1 β_2 indicates that the complexation of Ag^+ with CN^- occurs easily. Thus A denotes the point where all Ag^+ is present in the complex form, having a higher potential than Ag^+, B shows the point where the precipitation of AgCN starts, thus leading to a constant Ag^+ concentration until all CN^- is precipitated. Now at point C the precipitation of the more soluble AgCl begins:

A: $Ag^+ + 2\ CN^- \rightarrow [Ag(CN)_2]^-$

B: $[Ag(CN)_2]^- + Ag^+ \rightarrow 2\ AgCN \downarrow$

C: $Ag^+ + Cl^- \rightarrow AgCl \downarrow$

3.2 $2 \times 2.47\ cm^3 = \underline{4.94\ cm^3}$

3.3 $[CN^-] = (4.94 \times 0.1 \times 40)/1000\ mol\ dm^{-3} = 1.98 \times 10^{-2}\ mol\ dm^{-3}$

$[Cl^-] = ((10 - 4.94) \times 0.1 \times 40)/1000\ mol\ dm^{-3} = 2.02 \times 10^{-2}\ mol\ dm^{-3}$

3.4 For the system Ag/Ag^+ at point A: $E = E_o + 0.059 \log[Ag^+]$.

The following equations are derived from the equilibrium conditions:

$$[Ag^+] = \frac{[Ag(CN^-)_2]}{[CN^-]^2\ \beta_2}$$

$$[Ag^+] + [Ag(CN^-)_2] = \frac{2.47 \times 0.1}{25 + 2.47}$$

$$[CN^-] = 2\ [Ag^+]$$

It yields an equation of third degree in $[Ag^+]$:

$$4\beta_2[Ag^+]^3 + [Ag(CN^-)_2] = 0$$

$[Ag(CN^-)_2]$ can be assumed to be $(2.47 \times 0.1) / 27.47\ mol\ dm^{-3}$, and therefore $[Ag^+]$ equals $1.213 \times 10^{-8}\ mol\ dm^{-3}$.

The emf will be: $E = 0.8 + 0.059 \log[Ag^+] - 0.285 = \underline{0.048\ V}$

At point C: $[Ag+] = \sqrt{K_{sp}(AgCl)} = 1.333 \times 10^{-5}$ and

$E = 0.8 + 0.059 \log[Ag^+] - 0.285 = \underline{0.227\ V}$

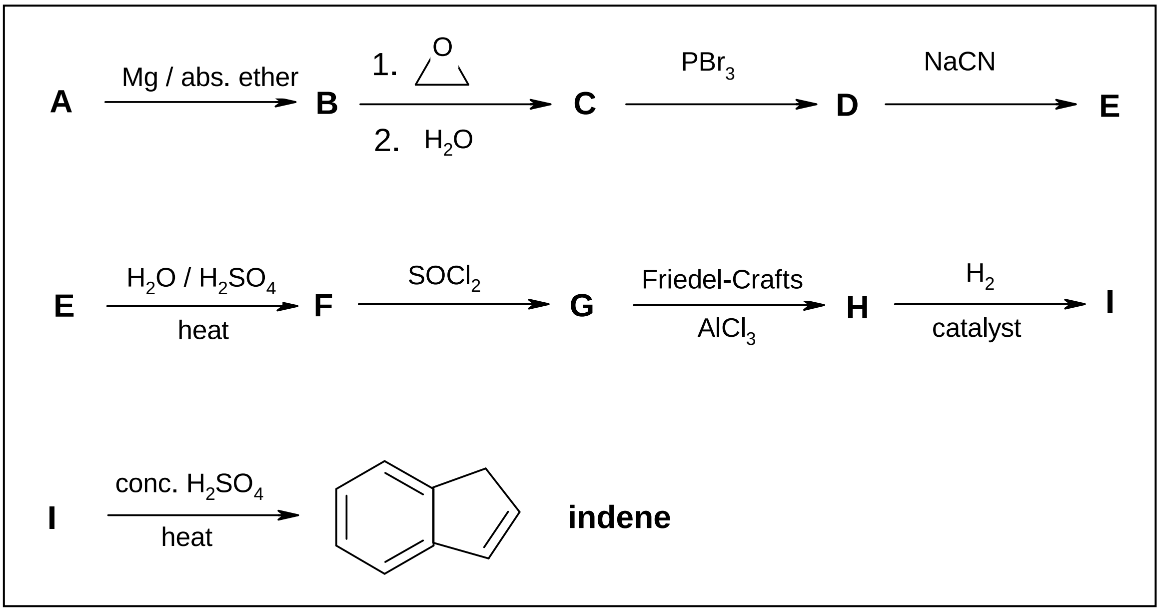
3.5 Since both AgCN and AgCl are present as the precipitate, the solution must be saturated:

In the solution: $[Cl^-]/[CN^-] = K_{sp}(AgCl)/K_{sp}(AgCN) = 10^{6.05} = \underline{1.222 \times 10^6}$

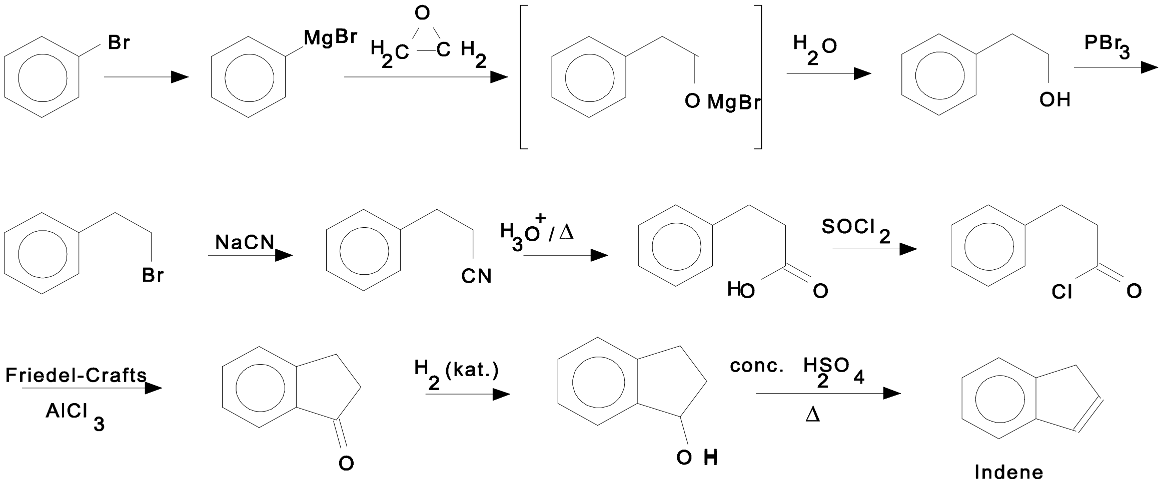
In the precipitate: $n(AgCl) / n(AgCN) = 2.02 / 1.98 = \underline{1.02}$

PROBLEM 4

Write the structural formulae of the compounds **A** to **I** in the following reaction sequence.



SOLUTION



PROBLEM 5

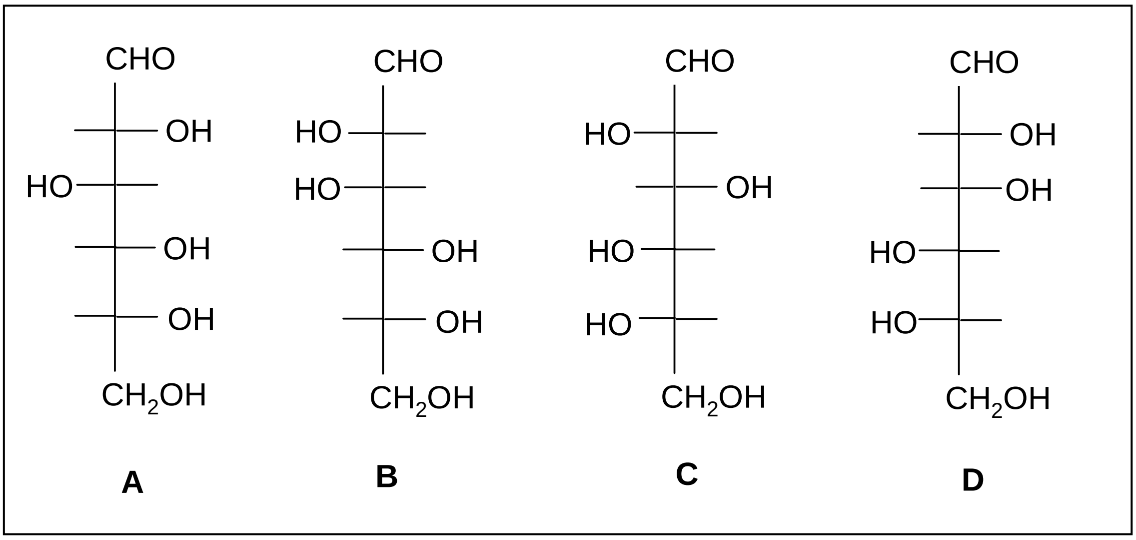
5.1 What ratio of primary / secondary / tertiary products can statistically be expected in the high temperature chlorination of methyl butane? Assume that the reaction rate of the substitution is equal for all C-H bonds.

5.2 Which of the following alcohols: pentan-1-ol, pentan-2-ol and 2-methyl-butan-2-ol react with the following reagents listed below?

1) cold, concentrated sulphuric acid; 2) CrO_3 / H_2SO_4; 3) $ZnCl_2$ / HCl; 4) I_2 / NaOH

5.3 Which of the following aldohexose structures are:

1) enantiomer pairs, 2) diastereomer pairs?



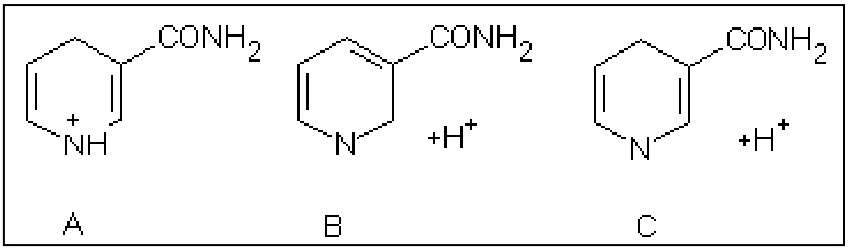
5.4 Two hydrocarbon compounds of the same molecular formula, C_4H_8, easily react with hydrogen in the presence of a platinum catalyst. During ozonolysis only ethanal (acetaldehyde) is formed in both cases. The ^{1}H-NMR spectra of the two compounds show two types of protons in a ratio of 3 to 1. Draw the structures of the described compounds.

5.5 Select the components of the group listed below that can be obtained during complete hydrolysis of lecithin (a phospholipid): serine, phosphoric acid, sphingosine, choline, glycerol, myo-inositol, phosphatidic acid and fatty acids).

5.6 Which of the following carboxylic acid can be formed in the tricarboxylic acid cycle (Krebs' citric acid cycle):

maleic acid (cis-butenedioic acid), mandelic acid (a-hydroxy-phenylethanoic acid), malic acid (2-hydroxy-butanedioic acid), tricarb-allylic acid (propane-1,2,3-tricarboxylic acid), oxalacetic acid (2-oxo-butanedioic acid), keto-glutaric acid (2-oxo-pentanedioic acid), fumaric acid (trans-butenedioic acid) and acetoacetic acid (3-oxo-butanoic acid).

5.7 To which structures is the nicotinamide moiety (part) of NAD^+ converted during the uptake of hydrogen to form NADH (A, B or C)?



SOLUTION

5.1 The ratio of primary, secondary and tertiary products will be 9 : 2 : 1.

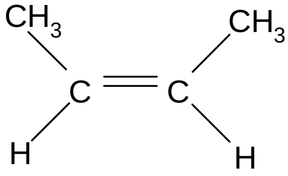
5.2 1-Pentanol reacts with 1) cold conc. sulphuric acid (elimination) and with 2) CrO_3/H_2SO_4 (oxidation).

2-Pentanol reacts with 1) under elimination, with 2) under oxidation, with 3) under reduction and with 4) (haloform oxidation).

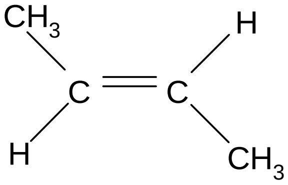
2-Methyl-2-butanol reacts with 1) under elimination and with 3) under reduction.

5.3 a/c and b/d are enantiomers, a/b, a/d, b/c and c/d are diastereomers.

5.4



cis-2-butén



trans-2-butén

5.5 Glycerol, choline, phosphoric acid and fatty acids can be found during complete hydrolysis of lecithin.

5.6 maleic acid, oxalacetic acid, ketoglutaric acid, fumaric acid

5.7 c) is correct since the NAD^+ is converted into $NADH/H^+$

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

You are required to investigate seven inorganic compounds.

Your test-tube rack is numbered 1 to 9. Two of the positions are empty. Each of the seven test-tubes provided contains only one compound in aqueous solution. Using only these solutions, pH indicator paper, and test-tubes, you are to identify as many of the ions present as you are able.

For your information, record in the table the observations you make on mixing the solutions. Use the following symbols:

elimination reactions: ↓ precipitate; ↑ gaseous product;

$\downarrow_s$ precipitate soluble in the excess of a precipitating agent.

colours: w - white or colourless, b - blue, g - green, y - yellow, p - pink, r - red, br - brown.

pH: a - acidic, b - alkaline, n - neutral.

Equipment:

A home-made rack contained 9 test-tubes with the unknown solutions, 30 empty Wassermann-tubes and one small beaker containing the pH indicator paper. Into each solution a dropper was inserted, and thus, the test-tubes need not to be removed from the rack while handling them. According to the original plan the following nine unknown solutions were expected to be given to the participants: $CoCl_2$, $Fe(SCN)_3$, NH_4OH, KI, $AgNO_3$, Na_2HAsO_4, $HgCl_2$, $NiCl_2$, $CuCl_2$.

During the discussion of the International Jury it became known that in some countries the corresponding laws forbid the pupils in secondary schools to handle mercury and arsenic compounds. For this reason these two compounds were removed from the rack and consequently the number of ions to be detected - and the marks available - were reduced to 12 (from the original 15). (Under these conditions the alkali and nitrate ions cannot be detected.)

The order of the test-tubes varied individually, but the first two contained invariably red solutions ($CoCl_2$ and $Fe(SCN)_3$), while the last two were the green $NiCl_2$ and $CuCl_2$ symbolizing the Hungarian national colours, red-white-green.

SOLUTION

The ions of the remaining seven solutions can easily be identified by mutual reactions. Out of the 21 possible reactions, 12 are common positive reactions. Additional information is available from the colour of 4, and the smell of one solution.

$AgNO_3$: reacts with all the six compounds;

NH_3: with the exception of iodide it gives a characteristic reaction with all the others salts;

$Fe(SCN)_3$: its colour and reaction with NH_3, I^-, Ag^+ are characteristic;

$CoCl_2$: can be detected from its colour and by adding NH_3 or Ag^+;

KI: can be identified by its reaction with Ag^+ and from the evolution of I_2 due to an addition of Fe^{3+} or Cu^{2+};

$CuCl_2$: can be detected from its colour and reaction with NH_3, I^- and Ag^+;

$NiCl_2$: has a characteristic colour and reacts with NH_3 and Ag^+.

PROBLEM 2 (practical)

You are required to estimate the heat (enthalpy) change on mixing a series of 5 liquids to produce equimolar mixtures and to explain the temperature changes.

Procedure:

1. A mixture of trichloromethane (chloroform) and propanone (acetone)

Measure 0.5 mol of trichloromethane in the measuring cylinder labelled A_1 and measure its temperature. Dry the thermometer with a piece of tissue paper. Measure 0.5 mol of propanone using measuring cylinder B_1, pour it into a beaker and measure its temperature. Record the average of the two temperatures as temperature t_1 (to 0.1 ^{o}C). Leave the thermometer in the beaker. Add the trichloromethane to the propanon, stir the mixture carefully and follow the temperature changes until a maximum or minimum is reached. Record this extreme temperature as temperature t_2. Dispose the mixture into a special bottle labelled "waste solution", dry the reaction beaker and the thermometer and proceed to the next part of the experiment.

2. A mixture of methanol and propanone (acetone)

Measure 0.5 mol of propanone in measuring cylinder B_1 and 0.5 mol of methanol in measuring cylinder A_2, and continue as in part 1.

3. A mixture of methanol and n-hexane

Measure 0.5 mol of methanol into measuring cylinder A_2 and 0.5 mol of hexane into measuring cylinder B_2, and continue as in part 1.

4. A mixture of methanol and water

Measure 0.5 mol of methanol into measuring cylinder A_2, measure its temperature and pour it into the beaker. Rinse the cylinder thoroughly with distilled water and then measure 0.5 mole of water using this measuring cylinder. Continue as instructed in the above part 1.

Tasks:

Calculate the enthalpy (heat) changes involved in the mixings on the basis of the temperature changes observed. In your calculations you should neglect heat exchanges with the surroundings as well as the heat capacity of the beaker and thermometer. Briefly explain your results in terms of the molecular interactions in the pure liquids and in the mixture, preferably using sketches.

Data:

Substance	Relative molecular mass	Density (g cm^{-3})	Molar heat capacity (J K^{-1} mol^{-1})
methanol	32.04	0.79	80.61
chloroform	119.38	1.49	114.94
acetone	58.08	0.79	124.96
n-hexane	86.18	0.66	190.10
water	18.02	1.00	75.35

PROBLEM 3 (practical)

You are required to determine the concentrations of hydrochloric acid and potassium iodate in the diluted solution containing both.

Procedure:

A solution containing potassium iodate and hydrochloric acid has already been measured into the volumetric flask provided. Fill the flask to the mark with distilled water using the wash bottle, close it with a stopper and shake it thoroughly. Fill the burette with the standard sodium thiosulphate solution using one of the beakers provided. (The exact concentration of the thiosulphate is given on the label of the bottle.)

a) First titration

Pipette a 10.00 cm^3 aliquot (portion) of the solution from the volumetric flask into a glass stoppered conical flask. Dilute it with 10 cm^3 of distilled water, add 1 g (a small spatula end-full) of potassium iodide and acidify with 10 cm^3 of 10 % sulphuric acid using a measuring cylinder. Titrate immediately the iodine formed with the standard sodium thiosulphate solution until the solution in the flask is pale yellow. Add with a pipette 1 cm^3 of starch indicator solution and continue the titration to completion. Repeat the titration twice more and record your readings on the result sheet.

b) Second titration

Pipette a 10.00 cm^3 aliquot of the solution into another glass stoppered conical flask, dilute with 10 cm^3 of distilled water, add 1 g of solid potassium iodide, and leave to stand for 10 minutes. Then titrate the iodine formed using the standard sodium thiosulphate solution, adding 1 cm^3 of starch indicator solution when the mixture is pale yellow. Repeat the titration twice more, recording your readings on the result sheet.

Task:

Calculate the concentration of the HCl and the KIO_3 in the solution that you prepared by dilution (in mol dm^{-3}).

SOLUTION

The reaction:

$$IO_3^- + 5\ I^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$$

occurs to be quantitative both with respect to IO_3^- and H^+. Consequently the first titration (in the presence of sulphuric acid) is suitable for the determination of iodate, while the second one for the determination of the hydrochloric acid content.

20th

6 theoretical problems
2 practical problems

THE TWENTIETH
INTERNATIONAL CHEMISTRY OLYMPIAD
2–9 JULY 1988, ESPOO, FINLAND

THEORETICAL PROBLEMS

PROBLEM 1

The periodic system of the elements in our three-dimensional world is based on the four electron quantum numbers n = 1, 2, 3,....; l = 0, 1,....,n – 1, m = 0, ± 1, ± 2,...., ± 1; and s = ± 1/2. In Flatlandia, a two-dimensional world, the periodic system is thus based on three electron quantum numbers: n = 1,2,3,...; m_l = 0, ±1, ±2, ..., ± (n-1); and s = ±1/2 where m_l plays the combined role of l and m_l of the three dimensional world. The following tasks relate to this two-dimensional world, where the chemical and physical experience obtained from our world is supposed to be still applicable.

1.1 Draw the first four periods of the Flatlandian periodic table of the elements. Number them according to their nuclear charge. Use the atomic numbers (Z) as symbols of the specific element. Write the electron configuration for each element.

1.2 Draw the hybrid orbitals of the elements with n = 2. Which element is the basis for the organic chemistry in Flatlandia? Find the Flatlandian analogous for ethane, ethene and cyclohexane. What kind of aromatic ring compounds are possible?

1.3 Which rules in Flatlandia correspond to the octet and the 18-electron rules in the three dimensional world?

1.4 Predict graphically the trends in the first ionization energies of the Flatlandian elements with n = 2. Show graphically how the electronegativities of the elements increase in the Flatlandian periodic table.

1.5 Draw the molecular orbital energy diagrams of the neutral homonuclear diatomic molecules of the elements with n = 2. Which of these molecules are stable in Flatlandia?

1.6 Consider simple binary compounds of the elements (n = 2) with Z = 1. Draw their Lewis structure, predict their geometries and propose analogues for them in the three dimensional world.

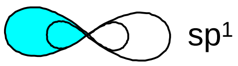
1.7 Consider elements with n ≤ 3. Propose an analogue and write the chemical symbol from our world for each of these Flatlandian elements. On the basis of this chemical and physical analogue predict which two-dimensional elements are solid, liquid or gaseous at normal pressure and temperature.

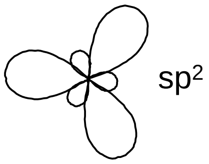
SOLUTION

1.1 In the two dimensional world and the electron quantum numbers given, we obtain the following Flatlandian periodic table:

1 $1s^1$									**2** $1s^2$
3 $[\ ]2s^1$	**4** $[\ ]2s^2$					**5** $[\ ]2s^2\,2p^1$	**6** $[\ ]2s^2\,2p^2$	**7** $[\ ]2s^2\,2p^3$	**8** $[\ ]2s^2\,2p^4$
9 $[\ ]3s^1$	**10** $[\ ]3s^2$					**11** $[\ ]3s^2\,3p^1$	**12** $[\ ]3s^2\,3p^2$	**13** $[\ ]3s^2\,3p^3$	**14** $[\ ]3s^2\,3p^4$
15 $[\ ]4s^1$	**16** $[\ ]4s^2$	**17** $[\ ]4s^2\,3d^1$	**18** $[\ ]4s^2\,3d^2$	**19** $[\ ]4s^2 3d^3$	**20** $[\ ]4s^2\,3d^4$	**21** $[\ ]4s^2\,3d^4$ $4p^1$	**22** $[\ ]4s^2\,3d^4$ $4p^2$	**23** $[\ ]4s^2\,3d^4$ $4p^3$	**24** $[\ ]4s^2\,3d^4$ $4p^4$

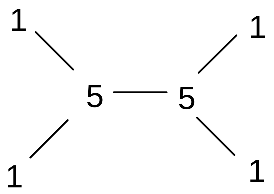
1.2 sp^1 and sp^2 hybrid orbitals are possible:





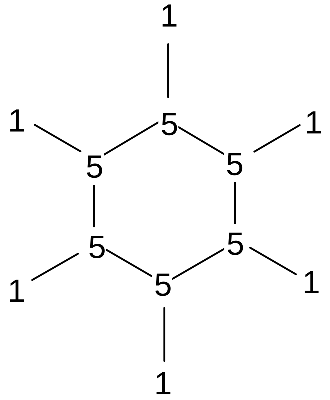
The element of life is the element with Z = 5. The corresponding compounds of ethane, ethene and cyclohexane are:

$C_2H_6 \leftrightarrow$



$C_2H_4 \leftrightarrow$ 1 — 5 — 5 — 1

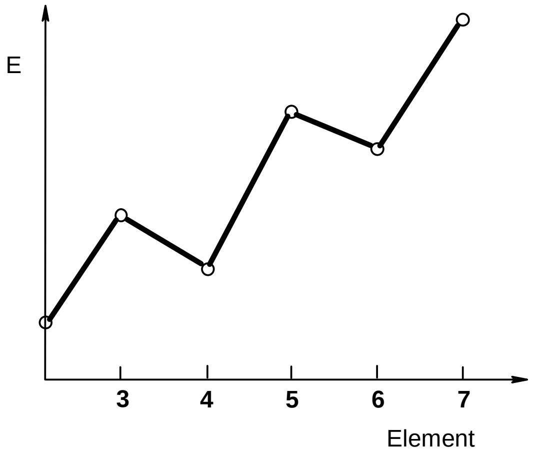
$C_6H_{12} \leftrightarrow$

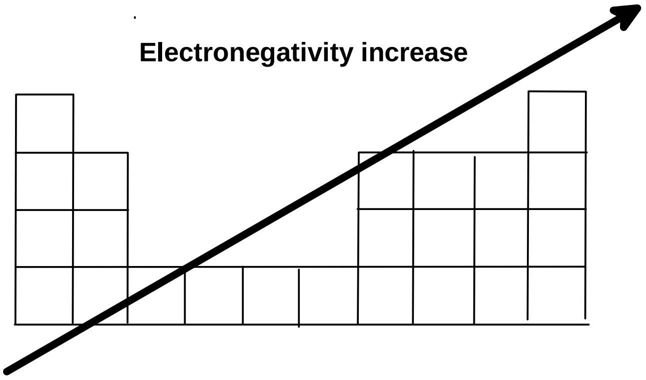


Aromatic ring compounds are not possible since there are no electron orbitals left that may overlap in the case of sp^2.

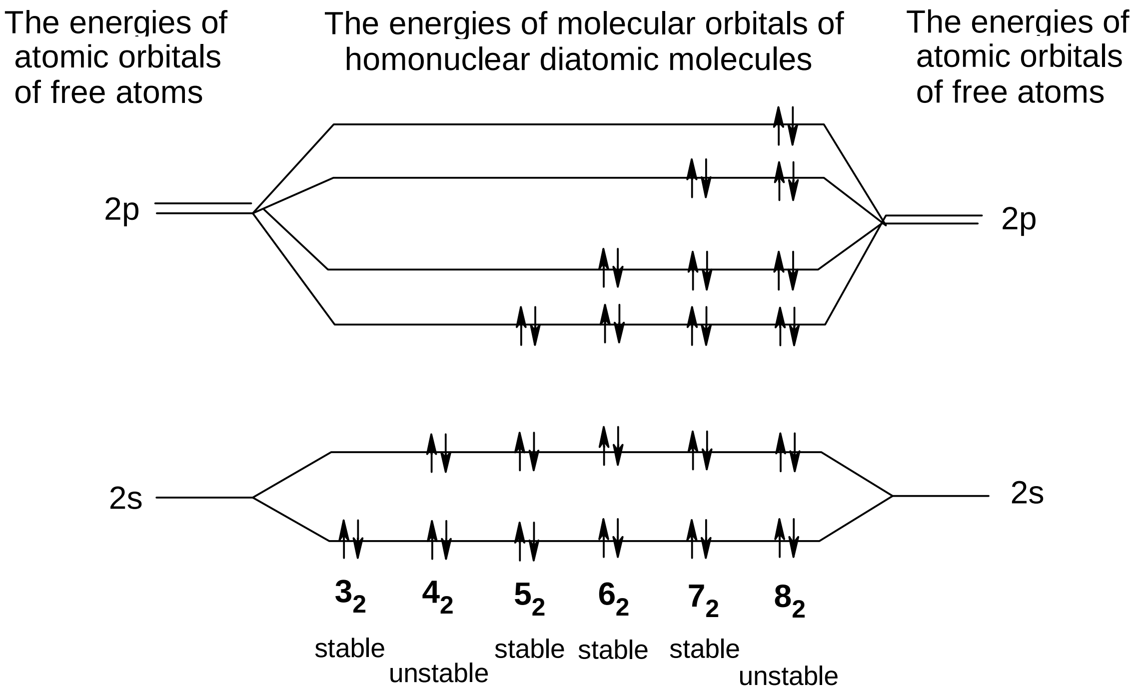
1.3 The Octet rule is changed to a Sextet rule, the 18-electron rule corresponds to a 10-electron rule.

1.4 The ionization energies and the trends in electronegativity

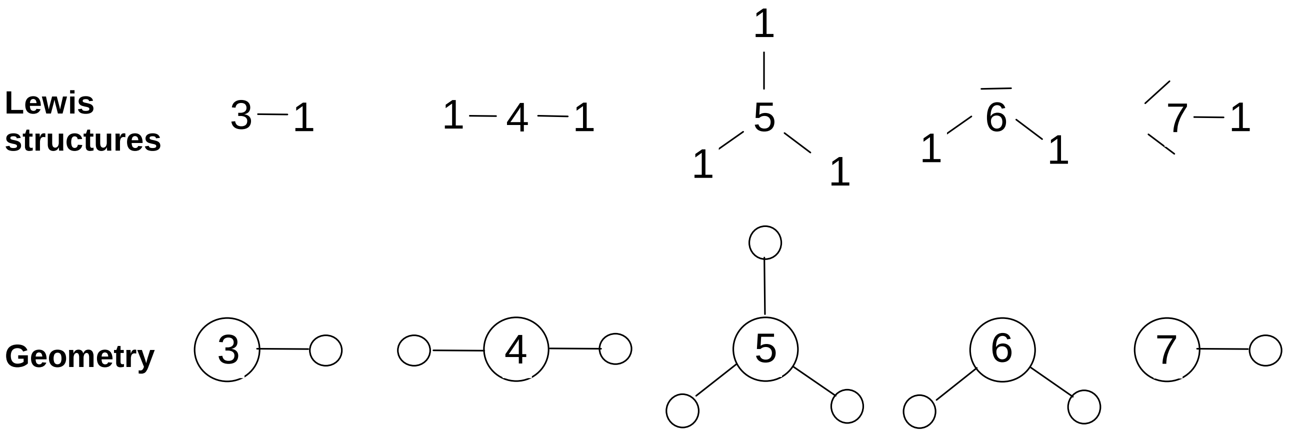




1.5 The molecular orbital diagram of the homonuclear X_2 molecules:



1.6 The Lewis structures and geometries:



1.7 The three-dimensional analogues of Flatlandian elements are:

1: H, gas
2: He, gas
3: Li, solid
4: Be, solid
5: B or C, solid
6: N or O, gas
7: F, gas
8: Ne, gas
9: Na, solid
10: Mg, solid
11: Al or Si, solid
12: P or S, solid
13: Cl, gas
14: Ar, gas

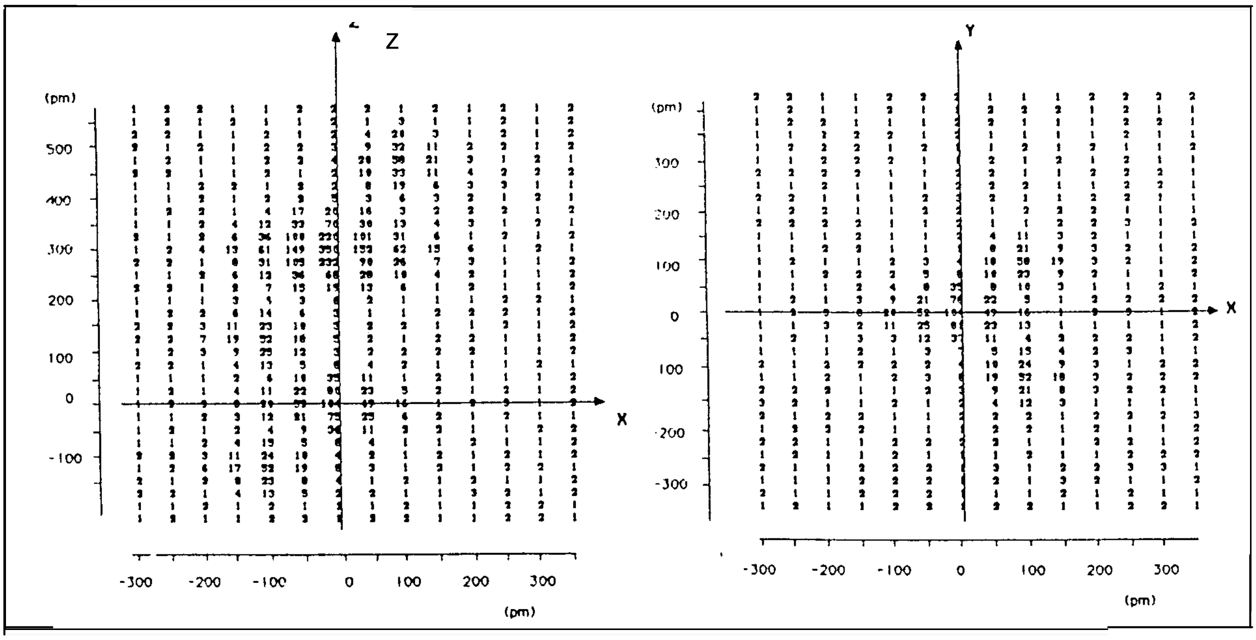
PROBLEM 2

Upon heating of a mixture of **A** and fluorine (molar ratio 1 : 9, pressure approximately 1 MPa) to 900 °C three compounds (**B**, **C** and **D**) are formed. All three products are crystalline solids at ambient temperature with melting points below 150 °C. The fluorine content of **C** is found to be 36.7 % and that of **D** 46.5 % (by weight). When **B** is treated with anhydrous $HOSO_2F$ at -75 °C a compound **E** is formed:

B + $HOSO_2F$ $\rightarrow$ **E** + HF

E is a solid which is stable for weeks at 0 °C, but decomposes in days at room temperature. The electron density distribution of **E** obtained through X-ray diffraction studies is shown on two intersecting, mutually perpendicular planes (see Fig. 1).

Fig. 1



The numbers indicated on the maps relate to the electron density in the neighbourhood of the atoms of **E** as a function of the spatial coordinates. The maxima found in these maps coincide with the locations of the atoms and the values are approximately proportional to the number of electrons in the atom in question.

2.1 Show where the maxima lie by drawing the contour curves around the maxima, connecting points of equal electron densities. Label each maximum to show the identities of the atoms in **E**.

2.2 When 450.0 mg of **C** was treated with an excess of mercury, 53.25 ml of **A** was liberated at a pressure of 101.0 kPa and a temperature of 25 °C. Calculate the relative atomic mass of **A**.

2.3 Identify **A**, **B**, **C**, **D** and **E**.

2.4 Use the valence-shell electron-pair repulsion theory (VSEPR) to propose electron-pair geometries for **B** and **C**. Using the two electron density maps, sketch the molecular geometry of **E**.

The original mixture was hydrolysed in water. **B** reacts to **A** while liberating oxygen and producing aqueous hydrogen fluoride. Hydrolysis of **C** leads to **A** and oxygen (in molar ratio of 4 : 3) and yields an aqueous solution of AO_3 and hydrogen fluoride. **D** hydrolyses to an aqueous solution of AO_3 and hydrogen fluoride.

2.5 Write the equations for the three hydrolysis reactions.

2.6 Quantitative hydrolysis of a mixture of **B**, **C** and **D** gives 60.2 ml of gas (measured at 290 K and 100 kPa). The oxygen content of this gas is 40.0% (by volume). The amount of AO_3 dissolved in water is titrated with an aqueous 0.1 molar $FeSO_4$ solution and 36.0 ml used thereby. During the titration Fe^{2+} is oxidized to Fe^{3+} and AO_3 is reduced to **A**. Calculate the composition (% by moles) of the original mixture of **B**, **C** and **D**.

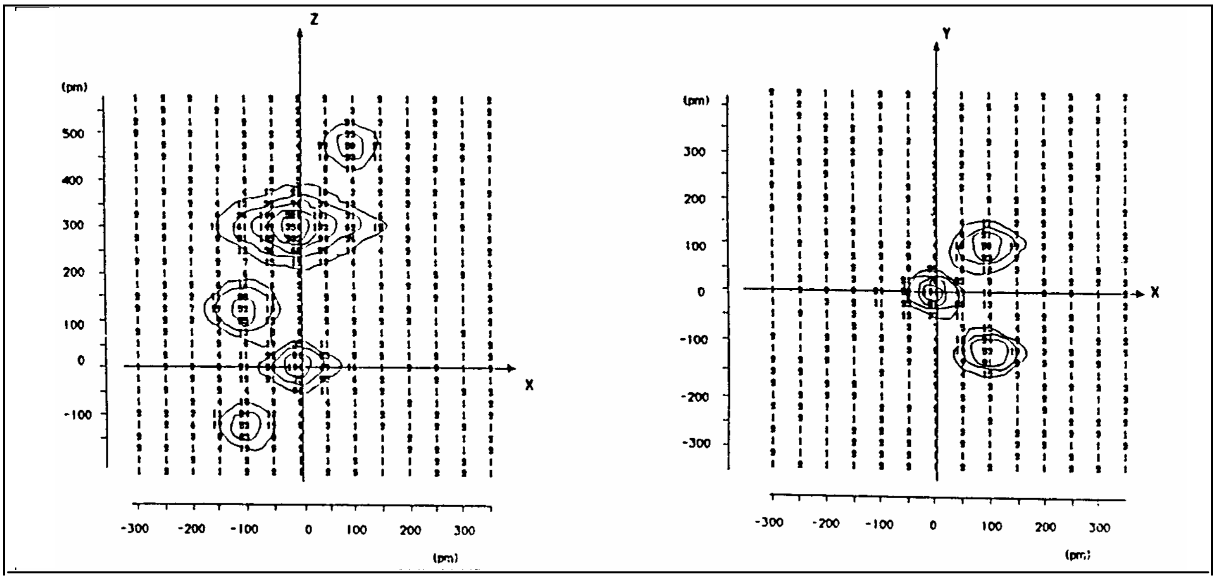
SOLUTION

2.1 Fig. 2 shows the electron densities with maxima 52, 58, 104, and 350. Since compound **E** is supposed to contain the atoms of fluorine, oxygen, sulphur, and **A**, the above maxima can be assign to particular atoms as follows:

Maximum	Element	Atomic number
52	O	8
58	F	9
104	S	16
350	**A**	?

The atomic number of **A** is 54. Thus, the element **A** is xenon.

Fig. 2



2.2 $\mathbf{A}F_n + n/2\ Hg \rightarrow \mathbf{A} + n/2\ HgF_2$

$$n_{gas} = \frac{pV}{RT} = \frac{101\,000\ \text{Pa} \times 53.25 \times 10^{-6}\ \text{m}^3}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}} = 2.17 \times 10^{-3}\ \text{mol} \ = n(\mathbf{A}) = n(\mathbf{A}F_n)$$

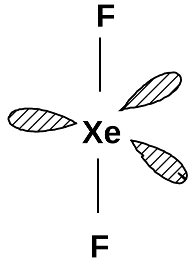
$$\underline{M(\mathbf{A}F_n)} = \frac{0.45}{2.17 \times 10^{-3}} = \underline{\ 207.4\ \text{g mol}^{-1}\ } = M(\mathbf{A}) + n\,M(F)$$

$$n\,M(F) = 0.367\ M(\mathbf{A}F_n) \Rightarrow n = \frac{207 \times 0.367}{19} = 4.0055 \Rightarrow \underline{\mathbf{A}F_4};$$

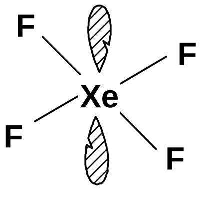
$$\underline{M(\mathbf{A})} = M(\mathbf{A}F_n) - n\,M(F) = 207.4 - 76.1 = \underline{131.3\ \text{g mol}^{-1}}$$

2.3 **A**: Xe **B**: XeF_2 **C**: XeF_4 **D**: XeI_6 **E**: $XeF(OSO_2F)$

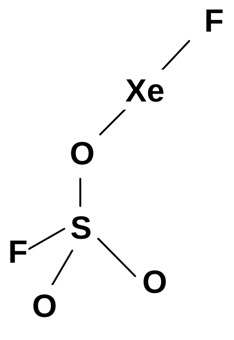
2.4



B



C



E

2.5 $XeF_2 + H_2O \rightarrow Xe + 2\ HF + 0.5\ O_2$

$XeF_4 + 2\ H_2O \rightarrow 2/3\ Xe + 4\ HF + 1/3\ XeO_3 + 0.5\ O_2$

$XeF_6 + 3\ H_2O \rightarrow XeO_3 + 6\ HF$

2.6 $$n_{gas} = \frac{pV}{RT} = \frac{100\ 000\ \text{Pa} \times 60.2 \times 10^{-6}\ \text{m}^3}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 290\ \text{K}} = 2.50 \times 10^{-3}\ \text{mol}$$

$n(O_2) = 0.4 \times n_{gas} = 1.00 \times 10^{-3}$ mol

$n(Xe) = 1.50 \times 10^{-3}$ mol

Assume $n(XeF_2) = a$; $n(XeF_4) = b$; $n(XeF_6) = c$

$n(Xe) = a + 2/3\ b$;

$n(O_2) = 1/2\ a + 1/2\ b$;

$n_{gas} = n(Xe) + n(O_2) = 3/2\ a + 7/6\ b = 2.50 \times 10^{-3}$ mol

$n(O_2) = 1/2\ a + 1/2\ b = 1.00 \times 10^{-3}$ mol

Solution of the equations:

$a = 0.5 \times 10^{-3}$ mol; $b = 1.5 \times 10^{-3}$ mol

$6\ Fe^{2+} + XeO_3 + 3\ H_2O \rightarrow 6\ Fe^{3+} + 6\ OH^- + Xe$

$n(XeO_3) = 1/6\ n(Fe^{2+}) = 1/6\ [c(Fe^{2+})\ V(Fe^{2+})] = 1/6 \times 0.100 \times 36.0 \times 10^{-3}$ mol =

$= 6.00 \times 10^{-4}$ mol $= 1/3\ b + c$

$c = 0.6\ 10^{-3} - 0.5\ 10^{-3} = 1\ 10^{-4}$

<u>molar composition:</u>			
	XeF_2:	0.5×10^{-3} mol	(23.8 %)
	XeF_4:	1.5×10^{-3} mol	(71.4 %)
	XeF_6:	1×10^{-4} mol	(4.8 %)

PROBLEM 3

A typical family car has four cylinders with a total cylinder volume of 1600 cm^3 and a fuel consumption of 7.0 l per 100 km when driving at a speed of 90 km/h. During one second each cylinder goes through 25 burn cycles and consumes 0.4 g of fuel. Assume that fuel consists of 2,2,4-trimethylpentane, C_8H_{18}. The compression ratio of the cylinder is 1:8.

3.1 Calculate the air intake of the engine (m^3/s). The gasified fuel and air are introduced into the cylinder when its volume is largest until the pressure is 101.0 kPa. Temperature of both incoming air and fuel are 100 °C. Air contains 21.0 % (by volume) of O_2 and 79.0 % of N_2. It is assumed that 10.0 % of the carbon forms CO upon combustion and that nitrogen remains inert.

3.2 The gasified fuel and the air are compressed until the volume in the cylinder is at its smallest and then ignited. Calculate the composition (% by volume) and the temperature of the exhaust gases immediately after the combustion (exhaust gases have not yet started to expand). The following data is given:

Compound	ΔH_f (kJ/mol)	C_p (J/mol K)
O_2(g)	0.0	29.36
N_2(g)	0.0	29.13
CO(g)	-110.53	29.14
CO_2(g)	-395.51	37.11
H_2O(g)	-241.82	33.58
2,2,4-trimethylpentane	-187.82	

3.3 Calculate the final temperature of the leaving gases assuming that the piston has moved to expand the gases to the maximum volume of the cylinder and that the final gas pressure in the cylinder is 200 kPa.

3.4 To convert CO(g) into CO_2(g) the exhaust gases are led through a bed of catalysts with the following work function:

$$\frac{n(\text{CO})}{n(\text{CO}_2)} = \frac{1}{4} k \left[\frac{n(\text{CO})}{n(\text{CO}_2)}\right]_1 v e^{-\frac{T}{T_0}}$$

where $[n(\text{CO}) / n(\text{CO}_2)]_1$ is the molar ratio before the catalyst, v is the flow rate in mol/s and *T* the temperature of the gases entering the catalyst (the same as the temperature of the leaving exhaust gases). T_0 is a reference temperature (373 K) and *k* is equal to 3.141 s/mol. Calculate the composition (% by volume) of the exhaust gases leaving the catalyst.

SOLUTION

3.1 $M_r(C_8H_{18}) = 114.0$,

Cylinder volume (V_0) = 4.00×10^{-4} m^3, p_0 = 101 000 Nm^{-2}, T_0 = 373 K

Considering one cylinder during one burn cycle one obtains (f = fuel):

$m_f = 0.400 / 25$ g = 0.0160g, $n_f = 1.4004 \times 10^{-4}$ mol

(m_f = mass of fuel, n_f = amount of substance of fuel)

$n_G = n_f + n_A = p_0V_0 / (RT_0) = 0.0130$ mol

(n_G = number of moles of gases, n_A = moles of air)

$\Rightarrow$ n_A = 0.0129 mol

$\Rightarrow$ Air intake of one cylinder during 25 burn cycles:

$V_A = 25\, n_A R\, T_0 / p_0 = 9.902 \times 10^{-3}$ m^3/s

$\Rightarrow$ The air intake of the whole engine is therefore: $V_{total} = 4\, V_A = 0.0396$ m^3/s

3.2 The composition of the exhaust gases of one cylinder during one burn cycle is considered:

before: $n_{O_2} = 0.21\, n_A = 2.709$ mmol

$n_{N_2} = 0.79\, n_A = 10.191$ mmol

$0.1 \text{ x } C_8H_{18} + 8.5\, O_2 \rightarrow 8\, CO + 9\, H_2O$ (10% C)

$0.9 \text{ x } C_8H_{18} + 12.5\, O_2 \rightarrow 8\, CO_2 + 9\, H_2O$ (90% C)

$C_8H_{18} + 12.1\, O_2 \rightarrow 0.8\, CO + 7.2\, CO_2 + 9\, H_2O$

Amounts of substances (in mol) before and after combustion:

	C_8H_{18}	O_2	CO	CO_2	H_2O
before	1.404×10^{-4}	2.709×10^{-3}	0	0	0
after	0	10.10×10^{-4}	1.123×10^{-4}	10.11×10^{-4}	12.63×10^{-4}

The composition of the gas after combustion is therefore:

Component	N_2	O_2	CO	CO_2	H_2O	Total
mol × 10^4	101.91	10.10	1.12	10.11	12.63	135.87
%	75.0	7.4	0.8	7.5	9.3	100

From thermodynamics the relation between the enthalpy and temperature change is given by

$$\Delta H = \int_{T_1}^{T_2} \sum_{i=1}^{i=k} c_{pi}\, n_i\, dT = \sum_{i=1}^{i=k} c_{pi} n_i \,(T_2 - T_1)$$

$\Delta H = n_f\,[0.8\,\Delta H_f(CO) + 7.2\,\Delta H_f(CO_2) + 9\,\Delta H_f(H_2O) - \Delta H_f(C_8H_{18})] = -\,0.6914$ kJ

This yields to: 691.4 = 0.4097 (T_2 – 373) and T_2 = 2 060 °C

3.3 The final temperature of the leaving gases from one cylinder:

p_2 = 200 000 Pa, $V_0 = 4.00 \times 10^{-4}\ m^3$,

n_G = moles of exhaust gases in one cylinder = 0.01359 mol

$$T_2 = \frac{p_2 V_0}{n_G R} = 708\ K$$

3.4 The flow from all four cylinders is given: v = 4 × 25 × n_G = 1.359 mol/s, so that

$$\frac{n(CO)}{n(CO)_2} = 0.25 \times 3.141 \times \frac{1.12 \times 10^4}{10.11 \times 10^4} \times 1.359 \times e^{\frac{708}{373}} = 0.01772$$

During catalysis:	CO +	$0.5\ O_2$	→ CO_2
moles × 10^4 (4 cylinders):			
initial	4.48	40.40	40.44
final	4.48 - x	40.40 - 0.5 x	40.44 + x

0.01772 (40.44 + x) = 4.48 + x ⇒ x = 3.70

Thus, the composition of the gas after the catalyst is:

Component	N_2	O_2	CO	CO_2	H_2O	Total
mol × 10^4	407.64	40.40 - 0.5x	4.48 - x	40.44 + x	50.52	541.63
		38.55	0.78	44.14		
%	75.26	7.12	0.15	8.14	9.33	100

PROBLEM 4

Chloride ions are analytically determined by precipitating them with silver nitrate. The precipitate is undergoing decomposition in presence of light and forms elemental silver and chlorine. In aqueous solution the latter disproportionates to chlorate(V) and chloride. With excess of silver ions, the chloride ions formed are precipitated whereas chlorate(V) ions are not.

4.1 Write the balanced equations of the reactions mentioned above.

4.2 The gravimetric determination yielded a precipitate of which 12 % by mass was decomposed by light. Determine the size and direction of the error caused by this decomposition.

4.3 Consider a solution containing two weak acids HA and HL, 0.020 molar and 0.010 molar solutions, respectively. The acid constants are 1×10^{-4} for HA and 1×10^{-7} for HL. Calculate the pH of the solution.

4.4 M forms a complex ML with the acid H_2L with the formation constant K_1. The solution contains another metal ion N that forms a complex NHL with the acid H_2L. Determine the conditional equilibrium constant, K'_1 for the complex ML in terms of $[H^+]$ and K values.

$$K_1 = \frac{[ML]}{[M][L]}$$

$$K_{1'} = \frac{[ML]}{[M'][L']}$$

[M'] = total concentration of M not bound in ML

[L'] = the sum of the concentrations of all species containing L except ML

In addition to K_1, the acid constants K_{a1} and K_{a2} of H_2L as well as the formation constant K_{NHL} of NHL are known.

$$K_{NHL} = \frac{[NHL]}{[N]\,[L]\,[H^+]}$$

You may assume that the equilibrium concentration $[H^+]$ and [N] are known, too.

SOLUTION

4.1 $Ag^+ + Cl^- \rightarrow AgCl\downarrow$

$2\ AgCl \rightarrow 2\ Ag + Cl_2$

$3\ Cl_2 + 3\ H_2O \rightarrow ClO_3^- + 5\ Cl^- + 6\ H^+$

Total:

$6\ AgCl + 3\ H_2O \rightarrow 6\ Ag + ClO_3^- + 5\ Cl^- + 6\ H^+$ or

$3\ Cl_2 + 5\ Ag^+ + 3\ H_2O \rightarrow ClO_3^- + 5\ AgCl + 6\ H^+$

4.2 From 100 g AgCl 12 g decompose and 88 g remain. 12 g equals 0.0837 mol and therefore, 0.04185 mol Cl_2 are liberated. Out of that (12 × 107.9) / 143.3 = 9.03 g Ag remain in the precipitate. 5/6 × 0.837 mol AgCl are newly formed (= 10.0 g), so that the total mass of precipitate (A) yields:

A = 88 g + 9.03 g + 10.0 g = <u>107.03 g</u>; relative error = <u>7.03 %</u>

4.3 $[H^+] = [A^-] + [L^-] + [OH^-]$

$[HA] + [A^-] = 0.02\ mol\ dm^{-3}$ $pK(HA) = pH + p[A-] - p[HA] = 4$

$[HL] + [L^-] = 0.01\ mol\ dm^{-3}$ $pK(HL) = pH + p[L-] - p[HL] = 7$

For problems like these, where no formal algebraic solution is found, only simplifications lead to a good approximation of the desired result, e.g.

1. $[H^+] = [A^-]$ (since HA is a much stronger acid than HL then $[A^-] \gg [L^-] + [OH^-]$)

   $[H^+]^2 + K_{(HA)}[H^+] - K_{(HA)}0.02 = 0$

   $[H^+] = 1.365 \times 10^{-3}\ mol\ dm^{-3}$

   pH = <u>2.865</u>

2. Linear combination of the equations

   $$[H+] = K_{(HA)} \frac{[HA]}{[A^-]} = K_{(HL)} \frac{[HL]}{[L^-]};$$

   $[HA] = 0.02 - [A^-]$;

   $[HL] = 0.01 - [L^-]$;

   $[H^+] = [A^-] + [L^-] + [OH^-]$

   yields:

$$[A] = \frac{0.02 \times K_{(HA)}}{[H^+] + K_{(HA)}}$$

$$[L] = \frac{0.01 \times K_{(HL)}}{[H^+] + K_{(HL)}}$$

$$[H^+] = \frac{0.02 \times K_{(HA)}}{[H^+] + K_{(HA)}} + \frac{0.01 \times K_{(HL)}}{[H^+] + K_{(HL)}} + \frac{K_w}{[H^+]}$$

The equation above can only be solved by numerical approximation methods. The result is pH = 2.865. We see that it is not necessary to consider all equations. Simplifications can be made here without loss of accuracy. Obviously it is quite difficult to see the effects of a simplification - but being aware of the fact that already the so-called exact solution is not really an exact one (e.g. activities are not being considered), simple assumption often lead to a very accurate result.

4.4

$$K_{1'} = \frac{[ML]}{[M]([L] + [HL] + [NHL] + [H_2L])} = \frac{K_1 [L]}{([L] + [HL] + [NHL] + [H_2L])}$$

$$[HL] = \frac{K_{a1} [H_2L]}{[H]}$$

$$[HL] = \frac{[L]\,[H]}{K_{a2}}$$

$$[L] = \frac{K_{a2}\,[HL]}{[H]} = \frac{K_{a1} K_{a2}\,[H_2L]}{[H]^2}$$

$$[NHL] = K_{NHL}\,[N]\,[L]\,[H]$$

$$K_{1'} = \frac{K_1}{\left[1 + \frac{[H]}{K_{a1}} + \frac{[H]^2}{K_{a1}\,K_{a2}} + K_{NHL}[N][H]\right]}$$

PROBLEM 5

A common compound **A** is prepared from phenol and oxidized to compound **B**. Dehydration of **A** with H_2SO_4 leads to compound **C** and treatment of **A** with PBr_3 gives **D**. In the mass spectrum of **D** there is a very strong peak at m/e = 83 (base peak) and two molecular ion peaks at m/e 162 and 164. The ratio of intensities of the peaks 162 and 164 is 1.02. Compound **D** can be converted to an organomagnesium compound **E** that reacts with a carbonyl compound **F** in dry ether to give **G** after hydrolysis. **G** is a secondary alcohol with the molecular formula $C_8H_{16}O$.

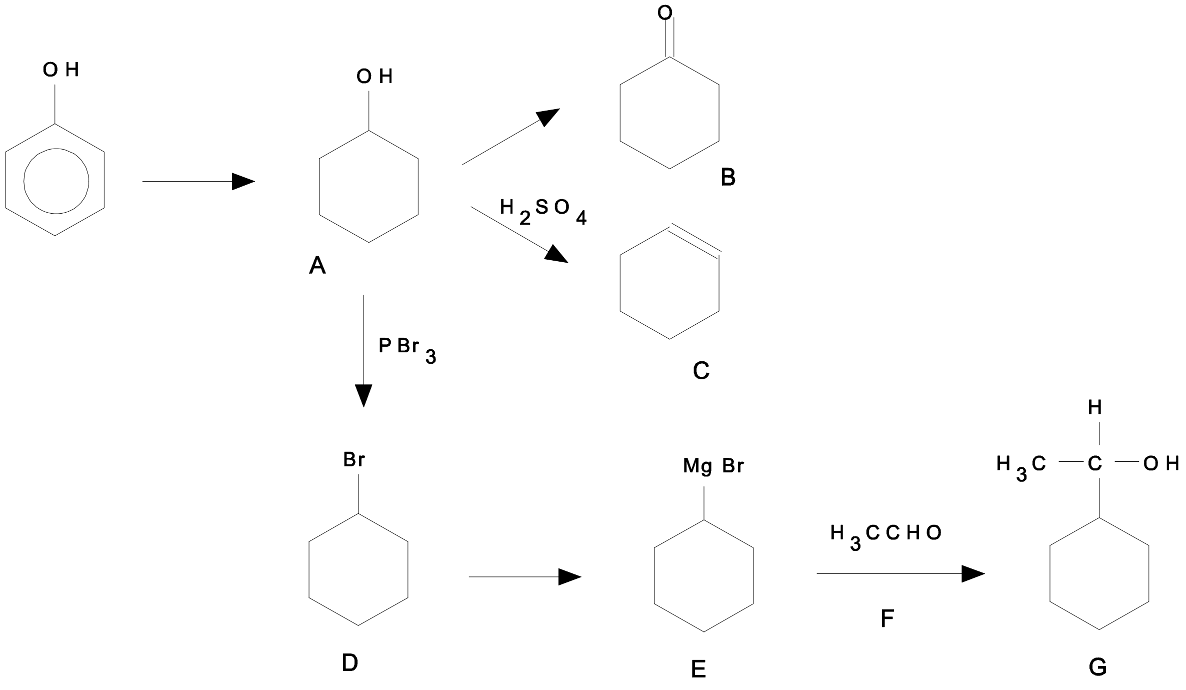
5.1 Outline all steps in the synthesis of **G** and draw the structural formulae of the compounds **A** – **G**.

5.2 Which of the products **A** – **G** consist of configurational stereoisomeric pairs?

5.3 Identify the three ions in the mass spectrum considering isotopic abundances given in the text.

SOLUTION

5.1

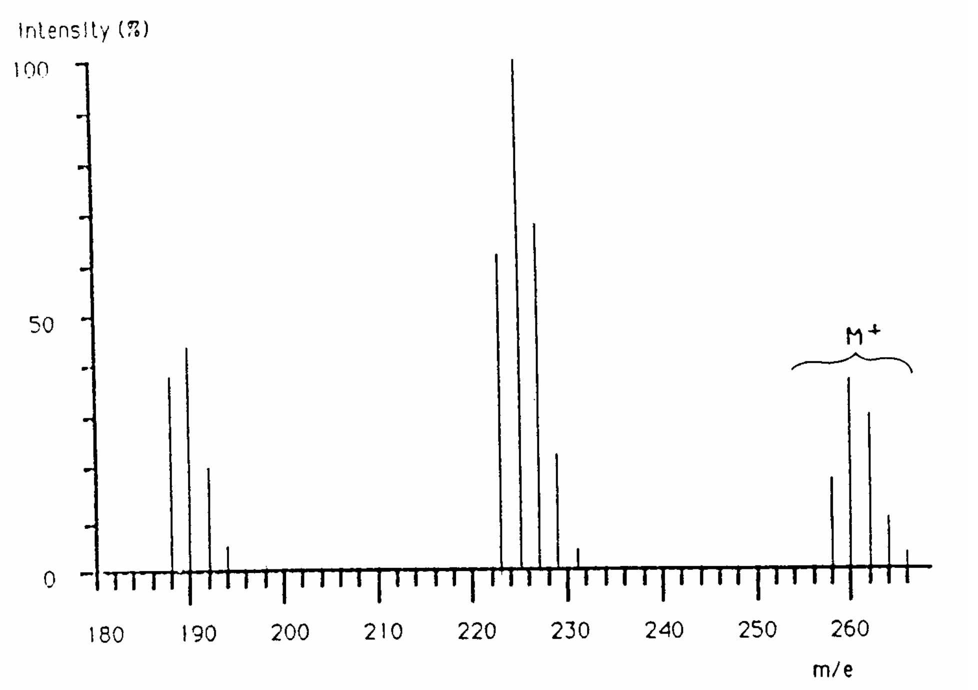


5.2 **G** has two stereoisomeric pairs since it has a chiral carbon.

5.3 The base peak at m/e = 83 is due to the cyclohexyl-cation, $C_6H_{11}^+$, the peaks at m/e = 162 and 164 show the same ratio as the abundance of the two bromine isotopes. Therefore, they are the molecular peaks of bromocyclohexane.

PROBLEM 6

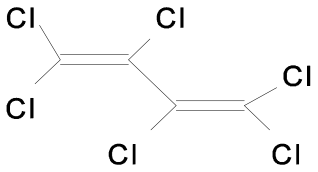
Upon analyzing sea mussels a new bio-accumulated pollutant **X** was found as determined by mass spectroscopy coupled to a gas chromatograph. The mass spectrum is illustrated in figure. Determine the structural formula of **X** assuming that it is produced out of synthetic rubber used as insulation in electrolysis cells that are used for the production of chlorine. Give the name of the compound **X**. The isotopic abundances of the pertinent elements are shown in the figure and table below. Intensities of the ions m/e = 196, 233, 268 and 270 are very low and thus omitted. Peaks of the ^{13}C containing ions are omitted for simplicity.



Elemen	Mas	Norm.abundanc	Mass	Norm.abundanc	Mas	Norm.abundanc
H	1	100.0	2	0.015		
C	12	100.0	13	1.1		
N	14	100.0	15	0.37		
O	16	100.0	17	0.04	18	0.20
P	31	100.0				
S	32	100.0	33	0.80	34	4.4
Cl	35	100.0			37	32.5
Br	79	100.0			81	98.0

SOLUTION

The molecule **X** is hexachlorobutadiene. Butadiene is the monomer of synthetic rubber and freed by decomposition:



PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Synthesis of a derivative (NaHX) of the sodium salt of an organic acid

Apparatus:

1 beaker (250 cm^3), 2 beakers (50 cm^3), 1 pipette (10 cm^3; graduated at intervals of 0.1 cm^3), 1 measuring cylinder (50 cm^3), 1 capillary pipette (Pasteur pipette), 1 thermometer, 1 filter crucible (G4), apparatus for suction filtering, 1 glass rod.

Reagents:

Sodium salt of 1-naphtol-4-sulfonic acid (S), (sodium 1-naphtol-4-sulfonate), (M = 246.22 g mol^{-1}), sodium nitrite (M = 69.00 g mol^{-1}), aqueous solution of HCl (2 mol dm^{-3}), deionised water, absolute ethanol.

Procedure:

Mix the given lot of technical grade starting material, labelled I, (contains 1.50 g of sodium 1-naphtol-4-sulfonate, S) and 0.6 g of $NaNO_2$ with about 10 cm^3 of water in 50 cm^3 beaker. Cool in ice bath (a 250 cm^3 beaker) to the temperature 0 – 5 °C. Keeping the temperature in the 0 – 5 °C range, add dropwise 5 cm^3 of 2 M HCl (aq) to the reaction mixture. Stir for ten more minutes in an ice bath to effect the complete precipitation of the yellow-orange salt NaHX . n H_2O. Weigh the filter crucible accurately (± 0.5 mg). Filter the product with suction in the crucible and wash with a small amount (ca. 5 cm^3) of cold water and then twice (about 10 cm^3) with ethanol. Dry the product in the filter crucible at 110 °C for 30 minutes. Weigh the air-cooled anhydrous material together with the crucible and present it to the supervisor.

Calculate the percentage yield of NaHX (M = 275.20 g mol^{-1}).

The purity of the product NaHX influences your results in Problem 2!

Question:

Write the reaction equation using structural formulae.

PROBLEM 2 (practical)

The spectrophotometric determination of the concentration, acid constant K_{a2} and pK_{a2} of H_2X

Apparatus:

7 volumetric flasks (100 cm^3), 2 beakers (50 cm^3), 1 capillary pipette (Pasteur), 1 pipette (10 cm^3; graduated in intervals of 0.1 cm^3), 1 washing bottle, 1 glass rod, 1 container for waste materials, funnel.

Reagents:

Compound NaHX, aqueous stock solution of Na_2X (0.00100 mol dm^{-3}), aqueous solution of sodium perchlorate (1.00 mol dm^{-3}), aqueous solution of HCl (0.1 mol dm^{-3}), aqueous solution of NaOH (0.1 mol dm^{-3}).

Procedure:

a) Weigh accurately 183.5 ± 0.5 mg of NaHX and dissolve it in water in a volumetric flask and dilute up to the 100 cm^3 mark. Pipette 15.0 cm^3 of this solution into another 100 cm^3 volumetric flask and fill up to the mark with water to obtain the stock solution of NaHX. If you do not use your own material, you will get the NaHX from the service desk.

b) Prepare 5 solutions, numbered 1-5, in the remaining five 100 cm^3 volumetric flasks. These solutions have to fulfil the following requirements:

- The total concentration of ($[X^{2-}] + [HX^-]$) in each solution must be exactly 0.000100 mol dm^{-3}.
- The concentration of sodium perchlorate in each solution must be 0.100 mol dm^{-3} to maintain constant ionic strength. The solutions are prepared by pipetting into each volumetric flask 1-5 the accurate volumes of the NaHX and Na_2X stock solutions, adding a required volume of sodium perchlorate solution and filling up to the mark with water.

- Solution 1 is prepared by pipetting the required amount of the stock solution of NaHX. Add ca. 3 cm^3 of HCl (aq) with the pipette to ensure that the anion is completely in the form HX^-, before adding the sodium perchlorate solution.

- Solution 5 is prepared by pipetting the required amount of the stock solution of Na_2X which is provided for you. Add ca. 3 cm^3 of the NaOH(aq) to ensure that the anion is completely in the form X^{2-}, before adding the sodium perchlorate solution.

- The three remaining solutions 2-4 are prepared by pipetting the stock solutions of NaHX and Na_2X in the following ratios before adding the sodium perchlorate solution:

Solution No.	Ratio NaHX(aq) : Na_2X(aq)
2	7 : 3
3	1 : 1
4	3 : 7

c) Take the five volumetric flasks to the service centre where their UV-vis spectra will be recorded in the region 300-500 nm for you. In another service centre the accurate pH of each solution will be recorded. You may observe the measurements.

d) From the plot of absorbance vs. wavelength, select the wavelength most appropriate for the determination of pK_{a2} of H_2X, and measure the corresponding absorbance of each solution.

e) Calculate the pK_{a2} of H_2X from the pH-absorbance data when the ionic strength I = 0.1 and the temperature is assumed to be ambient (25 °C). Note that:

$$K_{a2} = \frac{[H^+][X^-]}{[HX^-]} = \frac{c_{H^+} \times c_{X^{2-}}}{c_{HX^-}}$$

$$K_{a2} = \frac{(A\ A_{HX^-})[H^+]}{(A_{X^{2-}} - A)} \quad or \quad A = A_{X^{2-}} - (AA_{HX^-})\frac{[H^+]}{K_{a2}}$$

$$pf_{H^+} = \frac{0.509 \times \sqrt{I}}{1 + \sqrt{I}}$$

f) Which of your prepared solutions shows the largest buffer capacity? Calculate this buffer capacity, P, by any suitable method. You may use the equations given:

$$P = 2.3 \times \left([OH^-] + [H^+] + \frac{K_a [H^+] C}{(K_a + [H^+])^2} \right)$$

$$P = 2.3 \times \left(\frac{K_w}{[H^+]} + [H^+] + \frac{[X^{2-}][HX^-]}{C} \right)$$

C is the total concentration of the acid.

$K_w = 2.0 \times 10^{-14}$ at $I = 0.1$ and 25 °C.