

6th



International Chemistry Olympiad

**5 theoretical problems
3 practical problems**

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

THEORETICAL PROBLEMS

PROBLEM 1

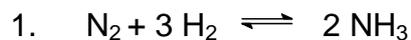
By electrochemical decomposition of water, there are in an electric circuit a voltmeter, platinum electrodes and a battery containing ten galvanic cells connected in series, each of it having the voltage of 1.5 V and internal resistance of 0.4 Ω . The resistance of the voltmeter is 0.5 Ω and the polarisation 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 $^{\circ}\text{C}$ 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.

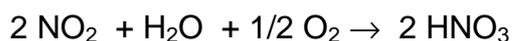
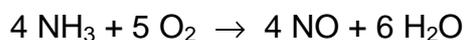
Problems:

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.

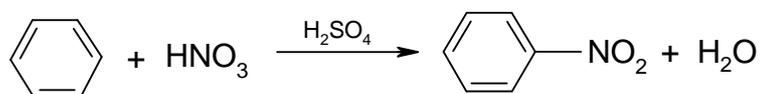
Relative atomic masses: $A_r(\text{N}) = 14$; $A_r(\text{O}) = 16$; $A_r(\text{C}) = 12$; $A_r(\text{H}) = 1$.

SOLUTION

(A)



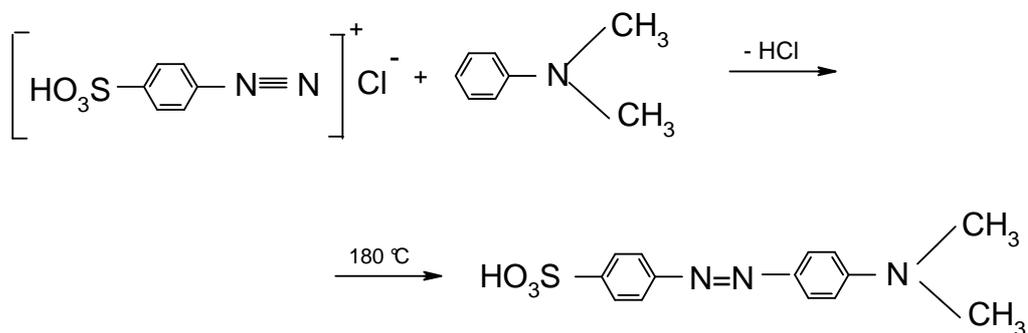
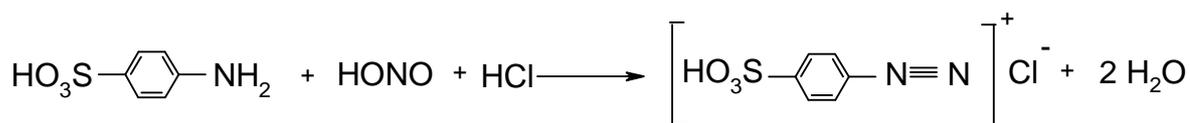
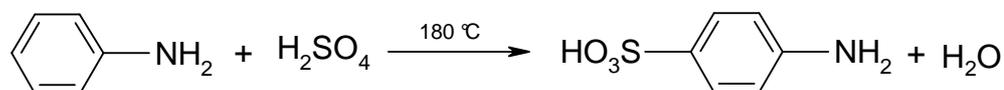
(B)



(C)



(D)



4'-dimethyl amino 4-azo benzene sulphonic acid

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

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

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

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:

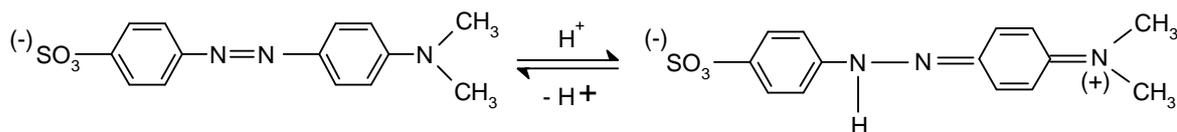
$$1 \text{ g H}_2 \text{ i. e. } 0.5 \text{ mol H}_2 \text{ corresponds } \frac{1}{3} \text{ mol NH}_3 \dots \frac{1}{3} \text{ mol HNO}_3 \dots \frac{1}{3} \text{ mol C}_6\text{H}_5\text{NO}_2$$

$$\dots \frac{1}{3} \text{ mol C}_6\text{H}_5\text{NH}_2 \quad (\mathbf{D})$$

The mass of product **D**:

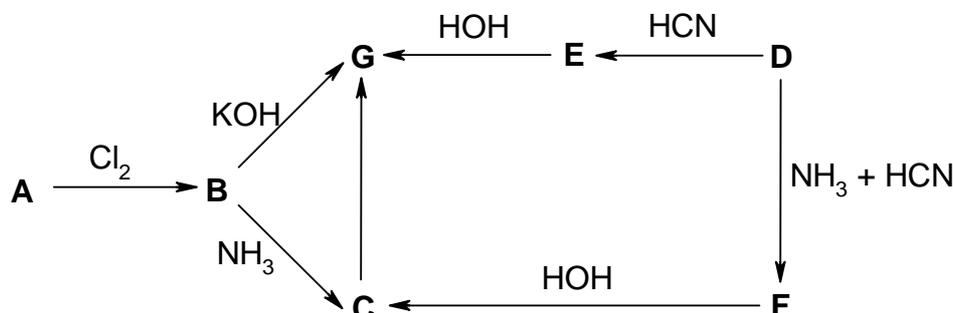
$$m = n M = 31 \text{ g C}_6\text{H}_5\text{NH}_2$$

3.



PROBLEM 2

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



Compound A 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**.

Compound D contains 54.54 mass % of carbon, 9.09 % of hydrogen, and 36.37 % of oxygen. It combines with NaHSO₃ to produce a compound containing 21.6 % of sulphur.

Problems:

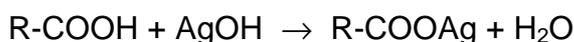
1. Write summary as well as structural formulas of substances **A** and **D**.
2. Write structural formulas of substances **B**, **C**, **E**, **F**, and **G**.
3. Classify the reactions in the scheme marked by arrows and discuss more in detail reactions **B** → **G** and **D** → **E**.
4. Write structural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

Relative atomic masses:

$$A_r(\text{C}) = 12; \quad A_r(\text{H}) = 1; \quad A_r(\text{O}) = 16; \quad A_r(\text{Ag}) = 108; \quad A_r(\text{Na}) = 23; \quad A_r(\text{S}) = 32.$$

SOLUTION

1. Compound A:

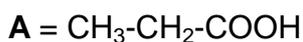


$$\text{A: } (\text{C}_x\text{H}_y\text{O}_z)_n$$

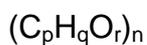
$$x : y : z = \frac{48.60}{12} : \frac{8.10}{1} : \frac{43.30}{16} = 1 : 2 : 0.67$$

If $n = 3$, then the summary formula of substance **A** is: C₃H₆O₂.

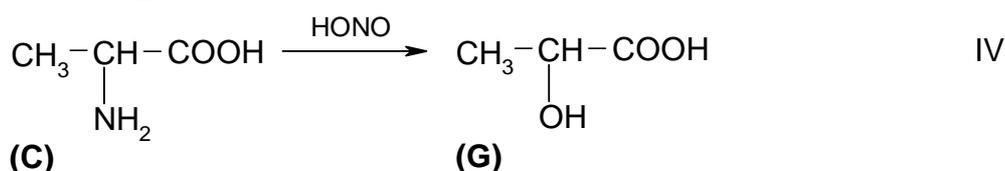
$$M(\mathbf{A}) = 74 \text{ g mol}^{-1}$$



Compound D:

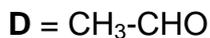
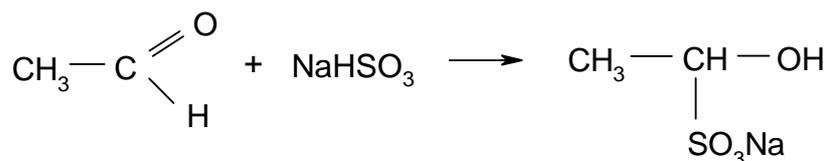


$$p : q : r = \frac{54.54}{12} : \frac{9.09}{1} : \frac{36.37}{16} = 1 : 2 : 0.5$$



If $n = 2$, then the summary formula of substance **D** is: $\text{C}_2\text{H}_4\text{O}$.

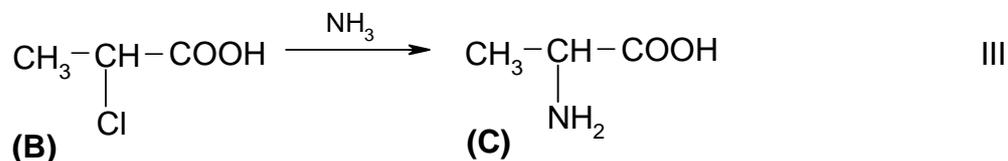
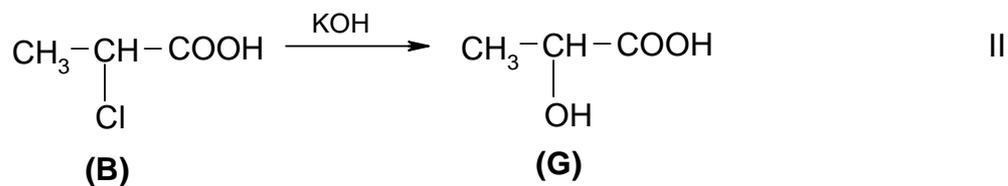
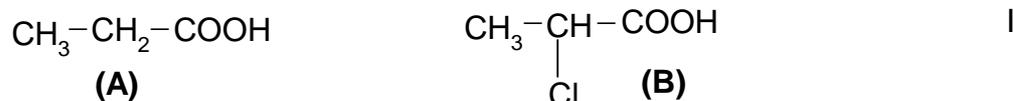
$$M(\mathbf{D}) = 44 \text{ g mol}^{-1}$$

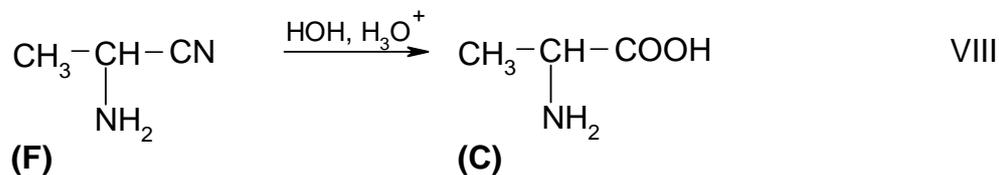
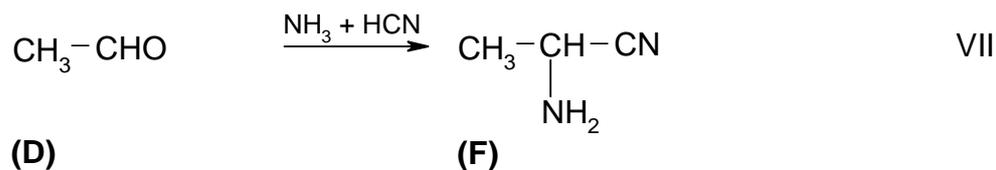
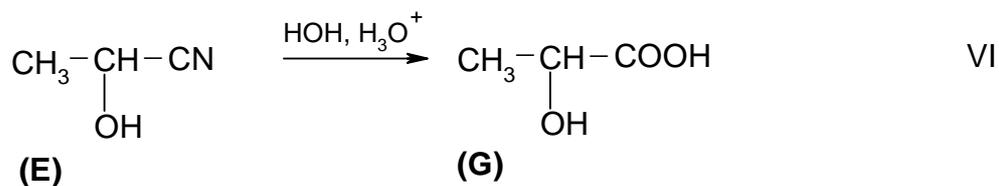
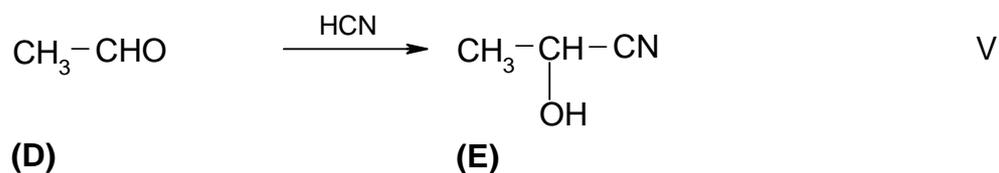
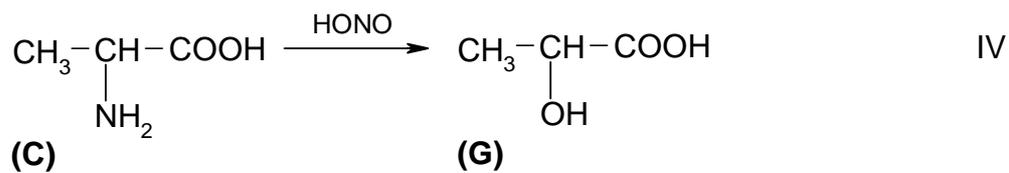


Reaction:

The reduction product contains 21.6 % of sulphur.

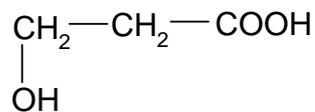
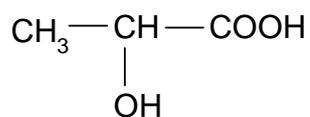
2.



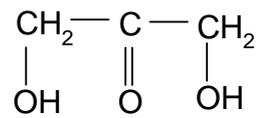
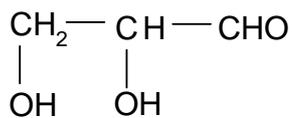
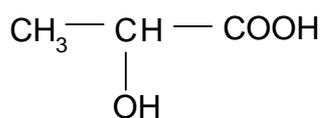


3. I - substitution reaction
 II - substitution nucleophilic reaction
 III - substitution nucleophilic reaction
 IV - substitution reaction
 V - additive nucleophilic reaction
 VI - additive reaction, hydrolysis
 VII - additive reaction
 VIII - additive reaction, hydrolysis

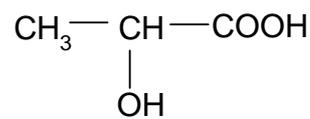
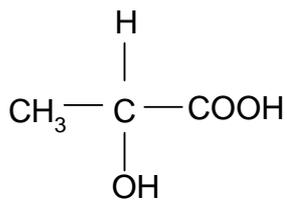
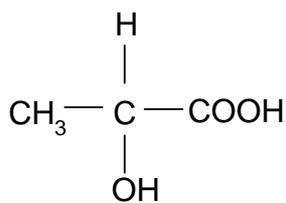
4.



position isomerism



structural isomerism



d(+)
stereoisomerism
(optical isomerism)

l(-)

racemic mixture

PROBLEM 3

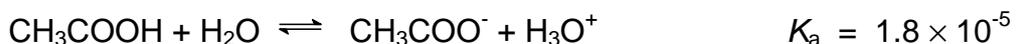
The following 0.2 molar solutions are available:



Problems:

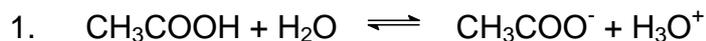
- Determine the concentration of H₃O⁺ ions in solution **C**.
- Determine pH value in solution **A**.
- Write an equation for the chemical reaction that takes place when substances **B** and **E** are allowed to react and mark conjugate acid-base pairs.
- Compare acid-base properties of substances **A**, **B**, and **C** and determine which one will show the most basic properties. Explain your decision.
- Write a chemical equation for the reaction between substances **B** and **G**, and explain the shift of equilibrium.
- Write a chemical equation for the reaction between substances **C** and **E**, and explain the shift of equilibrium.
- Calculate the volume of **D** solution which is required to neutralise 20.0 cm³ of **H** solution.
- 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 °C?

Ionisation constants:



Relative atomic masses:

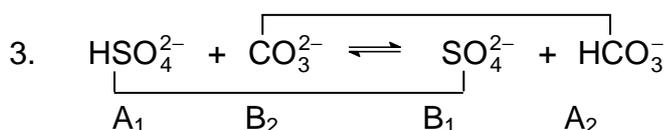
$$A_r(\text{Na}) = 23; \quad A_r(\text{S}) = 32; \quad A_r(\text{O}) = 16.$$

SOLUTION

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}_3\text{O}^+]^2}{c}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a c} = \sqrt{1.8 \times 10^{-5} \times 0.2} = 1.9 \times 10^{-3} \text{ mol dm}^{-3}$$

$$2. \quad \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.2 = 0.7$$

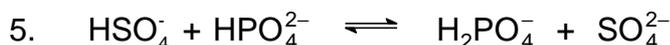


4. By comparison of the ionisation constants we get:

$$K_a(\text{HCl}) > K_a(\text{HSO}_4^-) > K_a(\text{CH}_3\text{COOH})$$

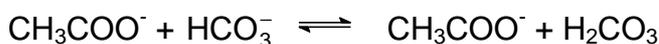
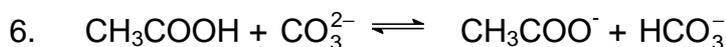
Thus, the strength of the acids in relation to water decreases in the above given order.

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



$$K_a(\text{HSO}_4^-) \gg K_a(\text{HPO}_4^{2-})$$

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



$$K_a(\text{CH}_3\text{COOH}) > K_a(\text{H}_2\text{CO}_3) > K_a(\text{HCO}_3^-)$$

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

$$7. \quad n(\text{H}_2\text{SO}_4) = c V = 0.2 \text{ mol dm}^{-3} \times 0.02 \text{ dm}^3 = 0.004 \text{ mol}$$

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

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

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 $\text{Ba}(\text{OH})_2$ solution, its volume is decreased by 15.46 %.

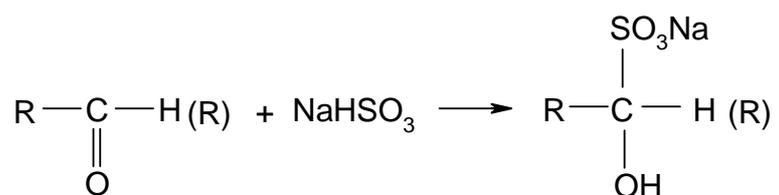
Problems:

- 4.1 Write structural formulas of substance **A** and **B**.
 4.2 Calculate the molar ratio of substances **A** and **B** in the mixture.

$$A_r(\text{C}) = 12; \quad A_r(\text{O}) = 16; \quad A_r(\text{S}) = 32; \quad A_r(\text{Na}) = 23.$$

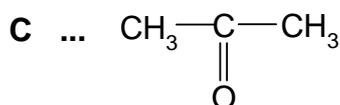
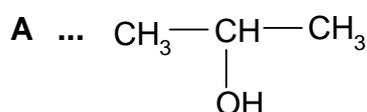
SOLUTION

4.1

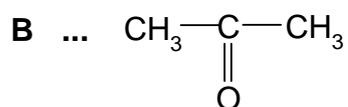


$$M_r(\text{C}) \quad M_r(\text{NaHSO}_3) = 104 \quad M_r(\text{C}) + 104$$

$$\frac{M_r(\text{C}) + 104}{M_r(\text{C})} = 2.7931 \quad M_r(\text{C}) = 58$$

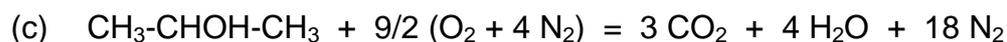


4.2 At STP conditions the gaseous mixture can only contain CO₂ and N₂. Carbon dioxide is absorbed in a barium hydroxide solution and therefore:



(a) $V(\text{CO}_2) = 5.432 \text{ dm}^3 \times 0.1546 = 0.84 \text{ dm}^3$

(b) $V(\text{N}_2) = 5.432 \text{ dm}^3 - 0.84 \text{ dm}^3 = 4.592 \text{ dm}^3$



Let us mark the amounts of substances as:

$$n(\text{CH}_3\text{—CHOH—CH}_3) = x$$

$$n(\text{CH}_3\text{—CO—CH}_3) = y$$

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:

$$x = 0.0025 \text{ mol} \quad y = 0.01 \text{ mol}$$

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

PROBLEM 5

A mixture of two metals found in Mendelejev's periodical table in different groups, reacted with 56 cm³ 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 %.

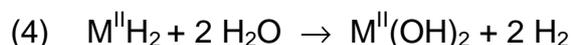
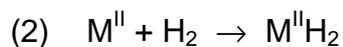
Problem:

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:

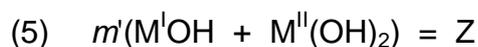


reacted: 0.09 g H₂O, i. e. 0.005 mol

unreacted: 0.18 g H₂O, 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:



Therefore:

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

$$(6) \quad m'(M^I\text{OH} + M^{II}(\text{OH})_2) = 0.077 \text{ g}$$

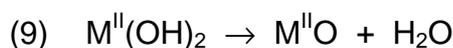
It represents 40.95 % of the total mass of the hydroxides, i. e. the total mass of hydroxides is as follows:

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

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

$$(8) \quad 0.188 \text{ g} - 0.077 \text{ g} = 0.111 \text{ g}$$

Heating:



Decrease of the mass: 0.027 g (H_2O)

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

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

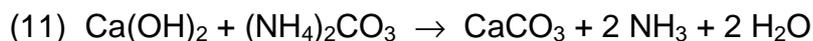
$$\frac{M_r(M^{II}\text{O})}{M_r(M^{II}\text{O}) + 18} = \frac{0.084}{0.111}$$

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

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

$$\underline{M^{II} = \text{Ca}}$$

Precipitation with $(\text{NH}_4)_2\text{CO}_3$:



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

$$0.18 \text{ g} + 0.077 \text{ g} = 0.257 \text{ g}$$

After precipitation with $(\text{NH}_4)_2\text{CO}_3$:

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

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

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

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

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

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

The total amount of substance of Ca(OH)₂ (both in the precipitate and in the solution):

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

According to equations (3) and (4):

$$n(\text{H}_2\text{O}) = 0.004 \text{ mol} \quad (\text{for } \text{M}^{\text{II}}\text{H}_2)$$

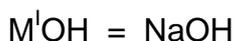
$$n(\text{H}_2\text{O}) = 0.001 \text{ mol} \quad (\text{for } \text{M}^{\text{I}}\text{H})$$

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

According to equations (7) and (11):

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

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



Composition of the mixture:

$$0.002 \text{ mol Ca} + 0.001 \text{ mol Na}$$

or

$$0.080 \text{ g Ca} + 0.023 \text{ g Na}$$

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 $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ are crystallised out from 320 g $\text{KAl}(\text{SO}_4)_2$ 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 $\text{KAl}(\text{SO}_4)_2$ by mass.)

Relative atomic masses:

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

SOLUTION

Let us mark

x - mass of crystallised alum,

y - mass of the saturated solution of $\text{AlK}(\text{SO}_4)_2$ which remains after crystallisation

Mass fraction of $\text{KAl}(\text{SO}_4)_2$ in the crystalhydrate is equal to 0.544.

Then: $320 = x + y + 160$

i. e. $y = 160 - x$

Mass balance equation for $\text{AlK}(\text{SO}_4)_2$:

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

$x = 18.0 \text{ g}$

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 cm³ 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 cm³ 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:

$$A_r(\text{Al}) = 26.98; \quad A_r(\text{Zn}) = 65.37; \quad A_r(\text{Si}) = 28.09; \quad A_r(\text{Cu}) = 63.55.$$

SOLUTION

2.1 HCl dissolves: Al, Zn

NaOH dissolves: Al, Zn, Si

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

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

The difference of 8.52 mmol H₂ corresponds to 4.26 mmol Si

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

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

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

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

$$\% \text{ Cu} = 5.03$$

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

$x \text{ mg Al}$ gives $\frac{3}{2} \times \frac{x}{26.98} \text{ mmol H}_2$

$(830 - x) \text{ mg Zn}$ gives $\frac{830 - x}{65.37} \text{ mmol H}_2$

$$\frac{3}{2} \times \frac{x}{26.98} + \frac{830 - x}{65.37} = 37.61 \text{ mmol H}_2$$

$x = 618.2 \text{ mg Al}$ (in 1000 mg of the alloy)

$\% \text{ Al} = 61.82$

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

$\% \text{ Zn} = 21.18$

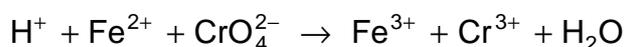
PROBLEM 3

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:

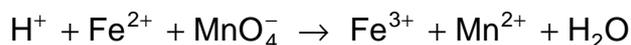
After elimination of silver and copper, chromium is oxidised in it according to the following unbalanced equation:



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:



According to the unbalanced equation:



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.

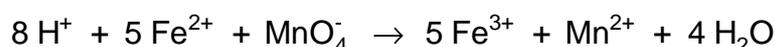
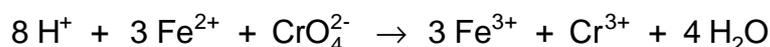
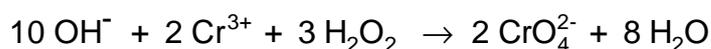
Problem:

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

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

SOLUTION

3.1 Equations:



Content of Cr:

$$17.20 \times 0.020 = 0.344 \text{ mmol KMnO}_4$$

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

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

It corresponds:

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

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

$$\underline{\% \text{ Cr} = 9.013}$$

Content of Cu and Ag:

$$Q = 40.575 \text{ mF} / 1500 \text{ mg} \quad (1087.4 \text{ mAh})$$

$$Q_{\text{Cr}} = 2.6 \times 3 = 7.8 \text{ mF} \quad (209 \text{ mAh})$$

$$Q_{(\text{Cu}+\text{Ag})} = 40.575 - 7.8 = 32.775 \text{ mF} \quad (878.4 \text{ mAh})$$

(F = Faraday's charge)

$$m(\text{Cu} + \text{Ag}) = m(\text{alloy}) - m(\text{Cr}) = 1500 - 135.2 = 1364.8 \text{ mg}$$

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

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

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

$$x = 906.26$$

$$m(\text{Cu}) = 906.26 \text{ mg in 1500 mg of the alloy}$$

$$m(\text{Ag}) = 458.54 \text{ mg in 1500 mg of the alloy}$$

$$\underline{\% \text{ Cu} = 60.4}$$

$$\underline{\% \text{ Ag} = 30.6}$$

PROBLEM 4

The pH value of a solution containing 3 % by mass of formic acid ($\rho = 1.0049 \text{ g cm}^{-3}$) 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: $A_r(\text{H}) = 1.01$; $A_r(\text{C}) = 12.01$; $A_r(\text{O}) = 16$.

SOLUTION

$$4.1 \quad c_1 = \frac{n_1}{V} = \frac{1004.9 \text{ g} \times 0.03}{45.03 \text{ g mol}^{-1} \times 1 \text{ dm}^3} = 6.55 \times 10^{-1} \text{ mol dm}^{-3}$$

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

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

Calculation of c_2 after dilution (two alternative solutions):

a) α_1 – before dilution; α_2 – after dilution

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

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

From equations (1) and (2):

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

$$b) \quad K_a = \frac{[\text{H}^+]^2}{c - [\text{H}^+]} = \frac{(1.0715 \times 10^{-2})^2}{0.655 - 1.0715 \times 10^{-2}} = 1.78 \times 10^{-4}$$

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

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

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.

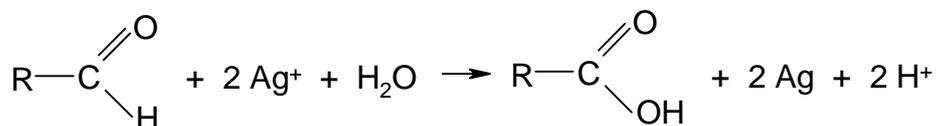
5.2 Give the structural formulas of the aldehydes.

Relative atomic masses:

$$A_r(\text{C}) = 12.01; \quad A_r(\text{O}) = 16.00; \quad A_r(\text{H}) = 1.01; \quad A_r(\text{Ag}) = 107.87$$

SOLUTION

5.1 Equation:



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

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

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

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

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

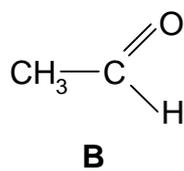
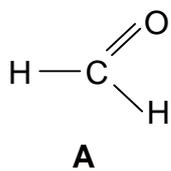
According to equation (1):

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

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

5.2 A = formaldehyde, methanal

B = acetaldehyde, ethanal



PROBLEM 6

The equilibrium constant of the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$ is at 600 °C equal to 70.0

Problems:

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

- 1 : 1 molar ratio at 600 °C;
- 2 : 1 molar ratio at 600 °C (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 °C?

SOLUTION

6.1a) (two alternative solutions)

$$\text{i) } [\text{H}_2] = [\text{I}_2] = c - x$$

$$[\text{HI}] = 2x$$

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{4x^2}{(c-x)^2}$$

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

$$x = \frac{\sqrt{70} \cdot c}{2 + \sqrt{70}} \quad \frac{x}{c} = 0.807 \quad 80.7 \%$$

$$\text{ii) } [\text{H}_2] = [\text{I}_2] = c - c\alpha$$

$$[\text{HI}] = 2c\alpha$$

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

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

$$\alpha = 0.807, \text{ i. e. } 80.7 \%$$

6.1b) (two alternative solutions)

$$\text{i) } [\text{H}_2] = 2c - x \quad [\text{I}_2] = c - x$$

$$[\text{HI}] = 2x$$

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

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

$$\text{ii) } [\text{H}_2] = 2c - c\alpha \quad [\text{I}_2] = c - c\alpha$$

$$[\text{HI}] = 2c\alpha$$

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

$$\alpha = 0.951 \text{ i. e. } 95.1 \%$$

$$\text{6.2 } [\text{H}_2] = xc - 0.99c \quad [\text{I}_2] = c - 0.99c$$

$$[\text{HI}] = 1.98c$$

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

$$x = 6.59 \text{ mol H}_2$$

PROBLEM 7

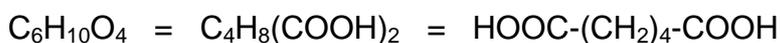
A certain saturated hydrocarbon **A** is transformed by a catalytic oxidation partly into a secondary alcohol **B**, and partly into a ketone **C**. The ketone when oxidised with nitric acid in the presence of catalyst yields a compound **D** with a formula of $C_6H_{10}O_4$. From compound **D** when 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:

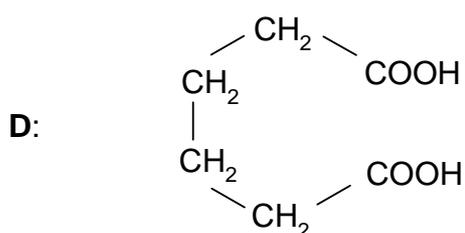
7.1 Write the structural formulas of compounds **A**, **B**, **C**, **D**, and **E**.

SOLUTION

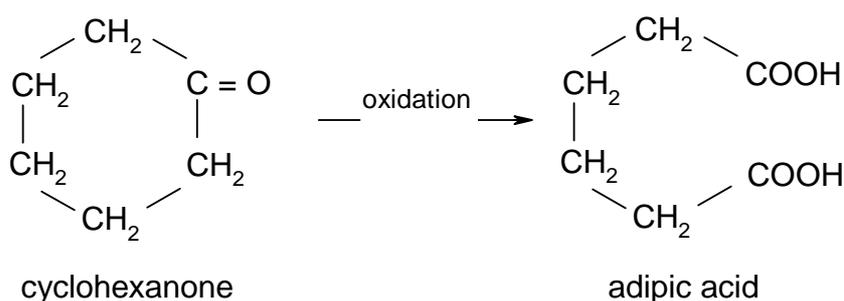
7.1 In general: ketone $\xrightarrow{\text{oxidation}}$ carboxylic acid

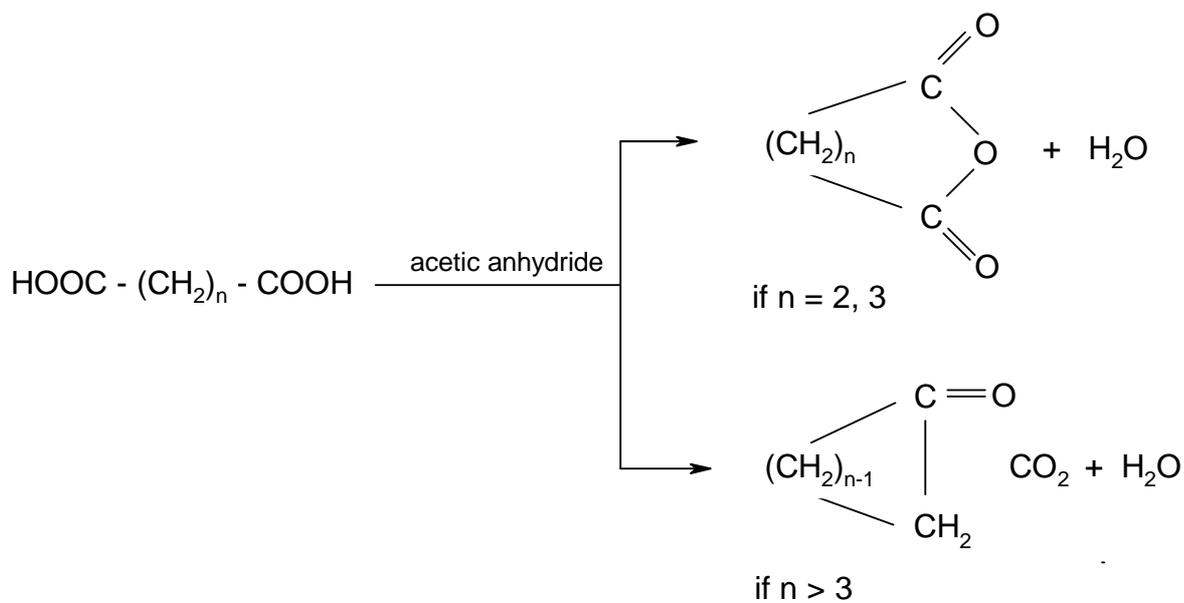
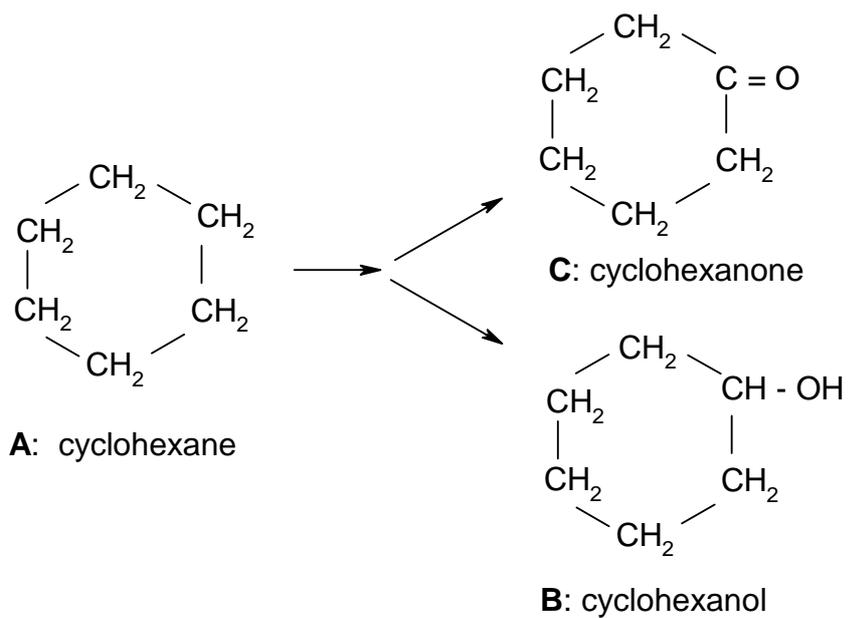


Product **D** is adipic acid which is a basic material in the production of nylon.



Compound C is cyclohexanone, because:





Compound E: cyclopentanone

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 ₂ H ₄	N ₂ H ₄	H ₂ O ₂	H ₂ F 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 ₂ H ₆	CO ₃ ²⁻	C ₂ O ₄ ²⁻
NH ₄ ⁺	N ₂ H ₆ ²⁺	NO ₂ ⁺	N ₂

SOLUTION

a)

Assertion	Molecule			
	C ₂ H ₄	N ₂ H ₄	H ₂ O ₂	H ₂ F 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 ₂ H ₆	CO ₃ ²⁻	CO ₂	C ₂ O ₄ ²⁻	C ₂ ²⁻
NH ₄ ⁺	N ₂ H ₆ ²⁺	NO ₃ ⁻	NO ₂ ⁺	N ₂ O ₄	N ₂

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Aqueous solutions of the following compounds: AgNO_3 , HCl , Ag_2SO_4 , $\text{Pb}(\text{NO}_3)_2$, 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 below the diagonal using the following uniform symbols:

white precipitate : \downarrow

coloured precipitate: $\downarrow\downarrow$

formation of a complex soluble in water: []

evolution of a gas: \uparrow

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 $\text{Na}_2\text{CO}_3 \cdot x \text{H}_2\text{O}$ 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.

$$A_r(\text{Na}) = 22.99; \quad A_r(\text{C}) = 12.01; \quad A_r(\text{O}) = 16.00; \quad A_r(\text{H}) = 1.01.$$

8th



International Chemistry Olympiad

**7 theoretical problems
3 practical problems**

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

<h2>THEORETICAL PROBLEMS</h2>

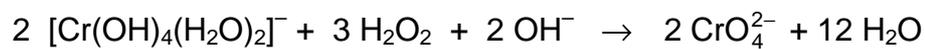
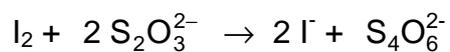
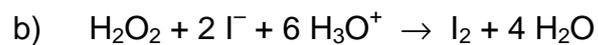
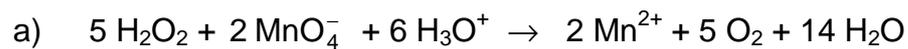
PROBLEM 1

- 1.1 Explain by means of generally used international symbols and formulas which compounds are named as peroxy 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:
- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ dissolved in water, is mixed with an excess of sodium hydroxide solution. A clear green solution is formed. The colour of the solution changes to yellow when an aqueous hydrogen peroxide solution is added.
 - 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 Peroxy compounds contain the functional group: O_2^{2-}
Examples: H_2O_2 , Na_2O_2 , BaO_2 , H_2SO_5 , $\text{H}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{C}_2\text{O}_6$, CrO_5 , $[\text{VO}_2]^{3+}$
- 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:
- manganometric method,
 - iodometric method.

Equations:

b) Equation is given in 2a.

PROBLEM 2

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

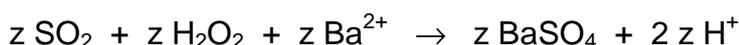
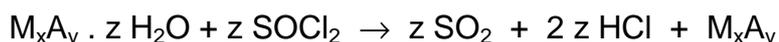
Problems:

- 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:

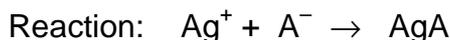


$$n(BaSO_4) = \frac{m(BaSO_4)}{M(BaSO_4)} = \frac{14.004 \text{ g}}{233.4 \text{ g mol}^{-1}} = 0.06 \text{ mol}$$

Amount of substance of H_2O in the hydrate:

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

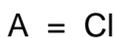
b) Amount of substance of A⁻ in the sample:



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

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

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



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

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

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

The molar ratio of Cl⁻ to H₂O in the hydrate:

$$n(\text{Cl}^-) : n(\text{H}_2\text{O}) = 0.02 : 0.06 = 1 : 3$$

Assumption:

i) MCl₃ · 3 H₂O

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

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

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

$$\begin{aligned} M(\text{M}) &= M(\text{MCl}_3 \cdot 3 \text{ H}_2\text{O}) - M(\text{Cl}) - 3 M(\text{H}_2\text{O}) = \\ &= 118.965 - 35.453 - 54.046 = 29.466 \text{ g mol}^{-1} \end{aligned}$$

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

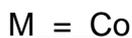
ii) MCl₂ · 6 H₂O

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

$$n(\text{MCl}_2 \cdot 6 \text{ H}_2\text{O}) = 0.01 \text{ mol}$$

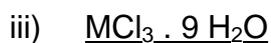
$$M(\text{MCl}_2 \cdot 6 \text{ H}_2\text{O}) = \frac{2,3793 \text{ g}}{0,01 \text{ mol}} = 237.93 \text{ g mol}^{-1}$$

$$\begin{aligned} M(\text{M}) &= M(\text{MCl}_2 \cdot 6 \text{ H}_2\text{O}) - 2 M(\text{Cl}) - 6 M(\text{H}_2\text{O}) = \\ &= 237.93 - 70.906 - 108.092 = 58.932 \text{ g mol}^{-1} \end{aligned}$$



The second assumption satisfies the conditions of the task.

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



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

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

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

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

M = Y

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

PROBLEM 3

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

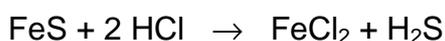
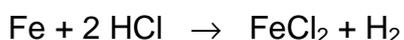
Problems:

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:



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

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

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

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

3.2 Composition of the gaseous mixture:

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

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

PROBLEM 4

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



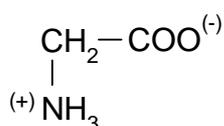
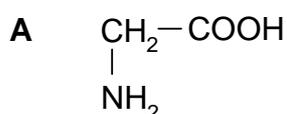
The given substances when allowed to react with an alkali hydroxide solution yield alkali salts. However, in a neutral or acidic solution the reaction takes place on the nitrogen atom.

Problems:

- 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



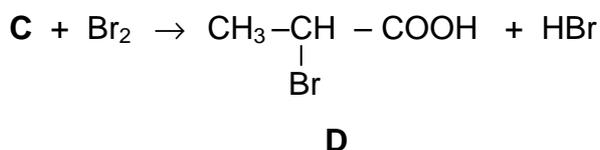
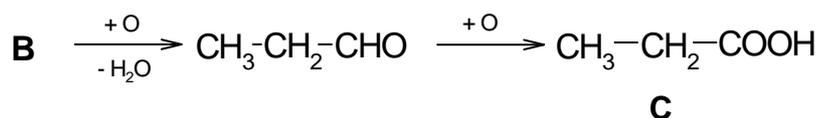
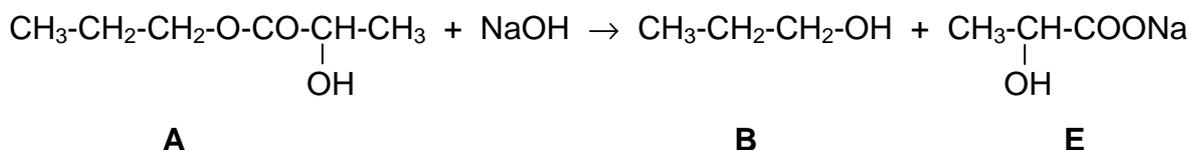
PROBLEM 5

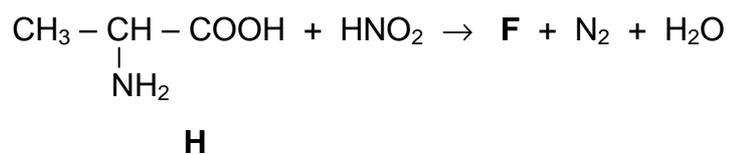
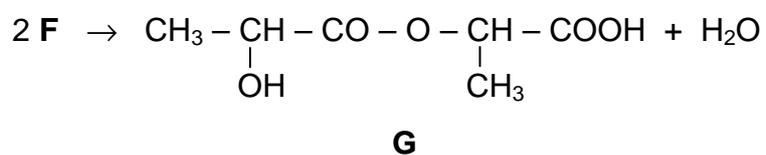
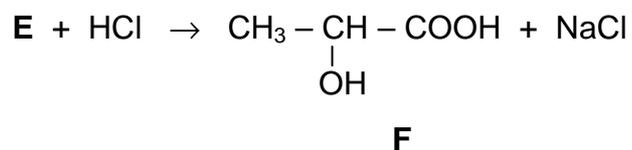
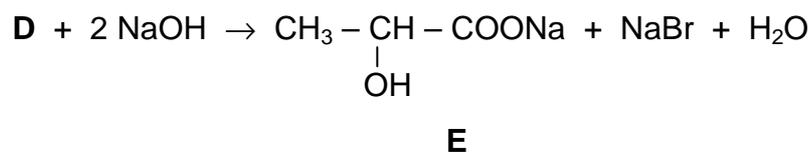
- a) Compounds **B** and **E** are formed when an organic substance **A** (summary formula $C_6H_{12}O_3$) reacts with a sodium hydroxide solution (saponification).
- b) Substance **B** can be oxidised in a two-step process to a substance **C**.
- c) Substance **C** when reacted with bromine yields a 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



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 cm³ 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 cm³ 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:

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

6.2 Escaped from the tube:

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

Remained in the tube:

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

- 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):

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

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

6.4 No change can occur in comparison with the preceding experiment.

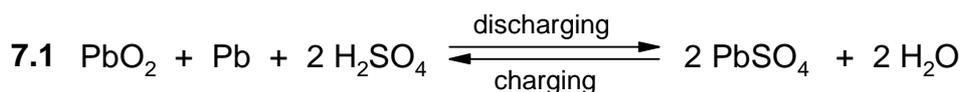
PROBLEM 7

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

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

Problems:

- 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

$$7.2 \quad n(\text{H}_2\text{SO}_4) = 2 \text{ mol} \qquad n(\text{H}_2\text{O}) = 2 \text{ mol}$$

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

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

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

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

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

7.3 The mass of H_2SO_4 required:

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

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

Analogously:

26.8 Ah corresponds to 18 g H₂O

120 Ah corresponds to 80.6 g H₂O

Discharged lead accumulator:

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

Charged lead accumulator:

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

Because:

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

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

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

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

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

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 , $\text{KNO}_3/\text{Na}_2\text{CO}_3$, NH_4SCN , $\text{Na}_2\text{B}_4\text{O}_7$, NaF, $\text{C}_2\text{H}_5\text{OH}$, BaCl_2 , AgNO_3 , NH_4Cl , $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, alizarin B.

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

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

PROBLEM 2 (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 ($c = 0.01972 \text{ mol dm}^{-3}$), NaOH ($c = 0.1019 \text{ mol dm}^{-3}$), 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



International Chemistry Olympiad

**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:

- The O–O bond is characteristic for the anion.
- The S–S bond is characteristic for the anion.
- The S–O–S bond is characteristic for the anion.
- It is formed by thermal decomposition of hydrogen sulphate.
- It is formed by anodic oxidation of hydrogen sulphate.
- It is formed by the reaction of an aqueous solution of sulphite with sulphur.
- Its aqueous solution dissolves silver bromide.
- Neutralisation of its aqueous solution with hydroxide MOH yields sulphate M_2SO_4 .
- 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:

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

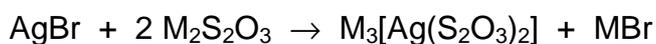
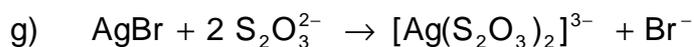
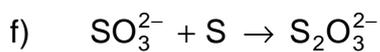
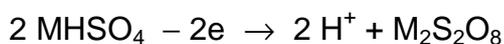
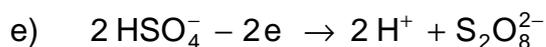
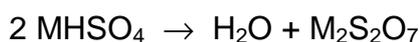
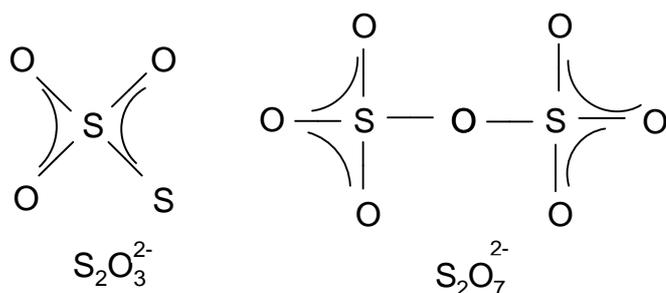
- 1.2 Write structural formulas of the anions of the above three salts and assign σ -bonds and π -bonds in them.
- 1.3 Write the chemical equations expressing the processes involved in the assertions under the letters d, e, f, g, h, i.

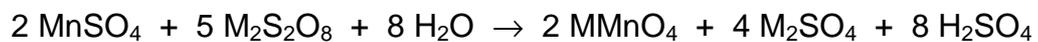
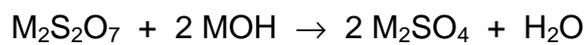
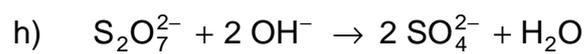
SOLUTION

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





PROBLEM 2a

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

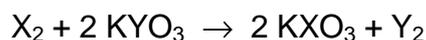
A t t e n t i o n

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 KYO₃ according to the equation:



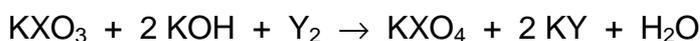
1. The atomic number of halogen X is greater than that of halogen Y. (If you find this answer correct open envelope 1.)
2. The atomic number of halogen X is smaller than that of halogen Y. (If you find this assertion correct open envelope 2.)

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 KXO₃ is oxidised in alkaline solution by halogen Y forming a compound KX^{VII}O₄ whereas halogen Y is reduced to halide KY:



An aqueous solution of potassium halide KY yields with AgNO₃ 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:



Text in envelope 5:

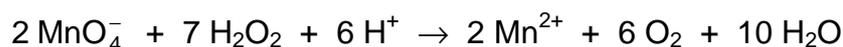
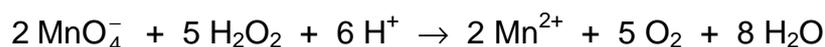
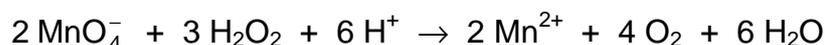
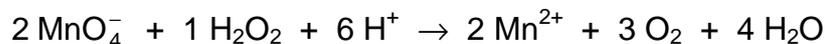
Your answer is incorrect. Choose answers 3 or 4.

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:



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

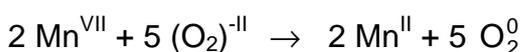
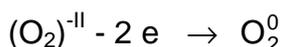
Indicate the correct assertion by a cross in the corresponding square and explain your decision.

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 cm³ 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:



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

Reducing agent: H_2O_2 or $(\text{O}_2)^{-\text{II}}$

3. $V(\text{O}_2) = 112 \text{ cm}^3$

$$n(\text{O}_2) = \frac{0.112 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.005 \text{ mol}$$

$$n(\text{KMnO}_4) = 0.005 \text{ mol} \times \frac{2}{5} = 0.002 \text{ mol}$$

$$m(\text{KMnO}_4) = 0.316 \text{ g}$$

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:

- only compound **C** forms a cyclic anhydride easily,
- B** yields an cyclic anhydride only at higher temperatures,
- of all the acids under investigation, only **A** releases carbon dioxide when heated,
- D** and **E** do not change at higher temperatures,
- 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 (CH₂I₂) yields a tetraester C₁₅H₂₄O₈. This new ester gives a tetraester C₁₆H₂₄O₈ 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 \blacktriangleleft , that under the plane with \cdots

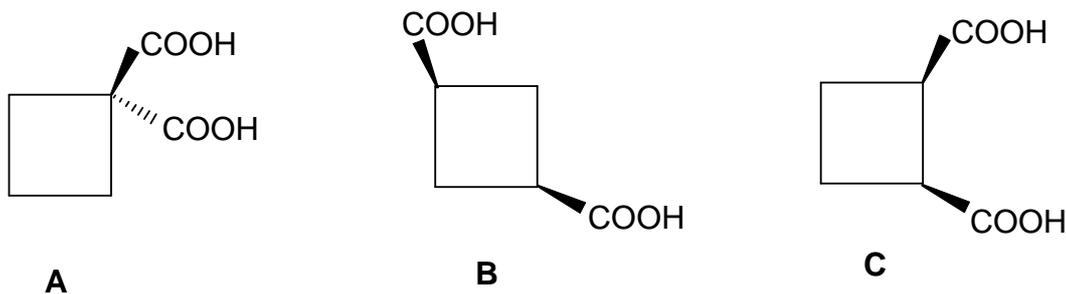
For example:

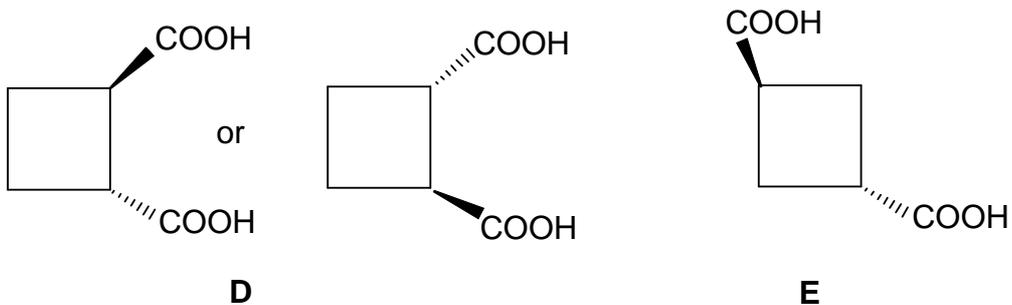


- 3.2** Express processes a), b), and c) by chemical equations.
- _____

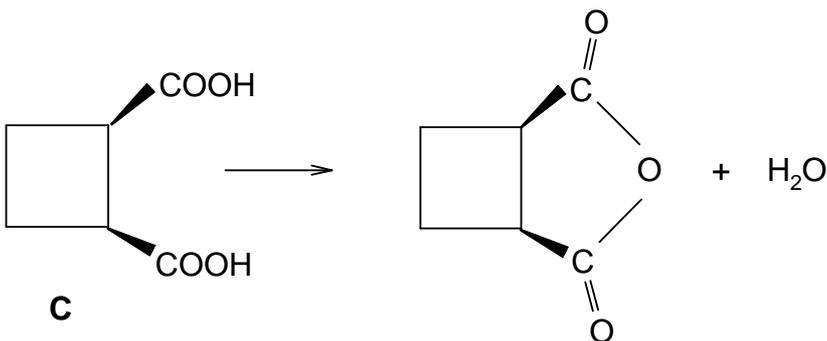
SOLUTION

3.1

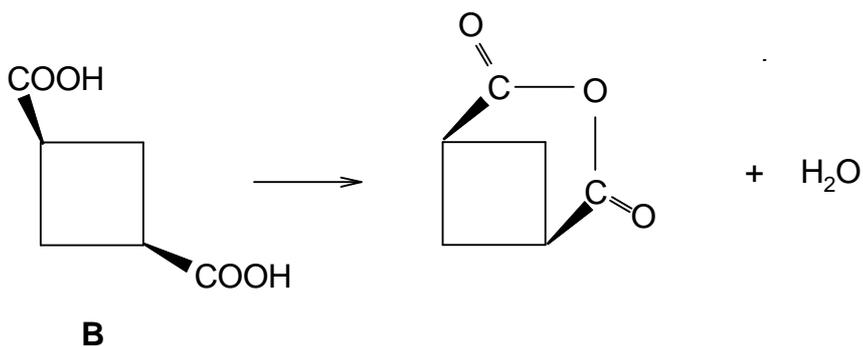




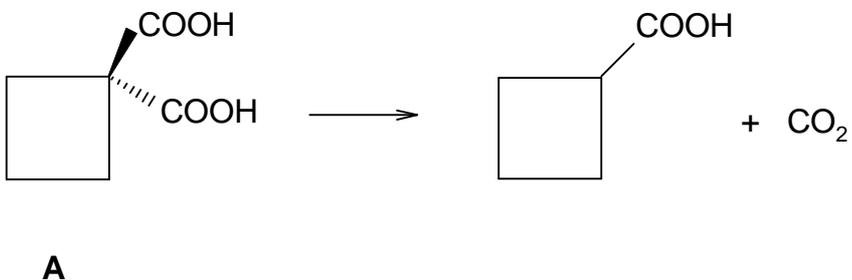
3.2 a)



b)



c)



PROBLEM 4a

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

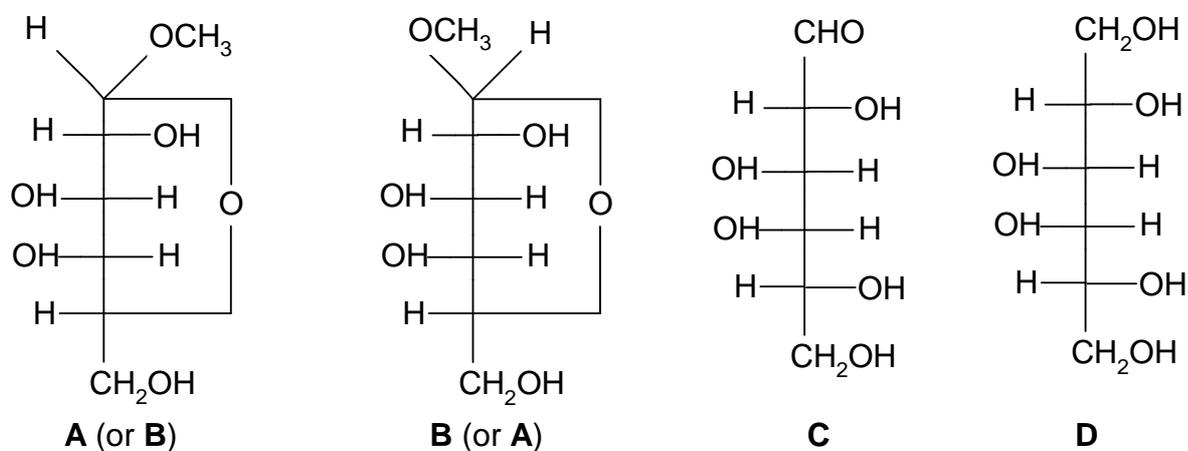
Compounds **A** and **B**, having the same summary formula $C_7H_{14}O_6$ but different physical properties (for example melting point and specific optical rotation), belong to the group of saccharides containing six-member heterocycles. When 1 % solution of sulphuric acid is added to compound **A** 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:

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

SOLUTION

1.



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

PROBLEM 4b

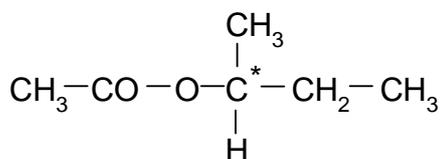
An optically active ester (11.6 g) having the summary formula $C_6H_{12}O_2$, was hydrolysed by heating with an excess of aqueous sodium hydroxide solution. After terminating the hydrolysis the alkaline reaction mixture was several times extracted with ether. The aqueous solution was not optically active. 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 °C was obtained.

Problems:

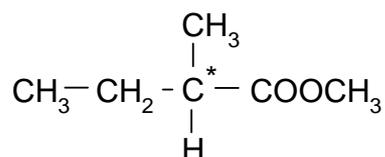
1. Write the structural formula of the ester.
2. What would be the structure of an ester with identical summary formula, i. e. $C_6H_{12}O_2$, if the aqueous solution after the alkaline hydrolysis obtained in the above mentioned way, were optically active?
3. Write down equations for the alkaline hydrolysis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

SOLUTION

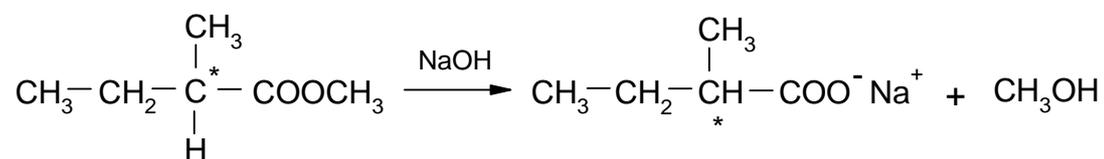
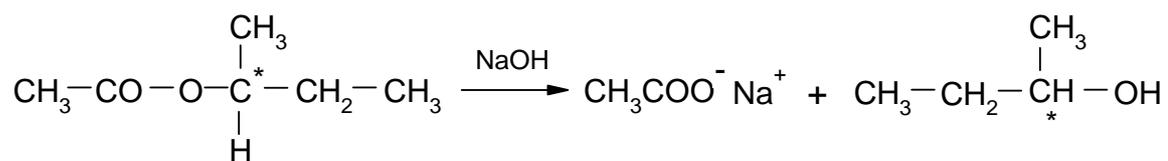
1.



2.



3.



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 $K_s(\text{CuA})$ and $K_s(\text{CuB})$ and the ionisation constants of the acids are $K_a(\text{HA})$ and $K_a(\text{HB})$?

SOLUTION

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

$$a = n(\text{A}^-) + n(\text{HA}) + n(\text{CuA})$$

$$b = n(\text{B}^-) + n(\text{HB}) + n(\text{CuB})$$

$$m = n(\text{Cu}^+) + n(\text{CuA}) + n(\text{CuB})$$

The amounts of precipitates are eliminated from the equations:

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

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:

$$[\text{A}^-] + [\text{HA}] + [\text{B}^-] + [\text{HB}] = [\text{Cu}^+] \quad (1)$$

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

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

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

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

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

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

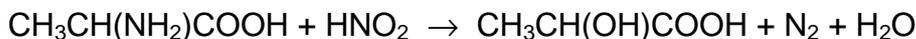
By substituting (2) and (3) into (6):

$$[\text{Cu}^+] = \frac{K_s(\text{CuA})}{[\text{Cu}^+]} \left(1 + \frac{[\text{H}^+]}{K_a(\text{HA})} \right) + \frac{K_s(\text{CuB})}{[\text{Cu}^+]} \left(1 + \frac{[\text{H}^+]}{K_a(\text{HB})} \right) \quad (7)$$

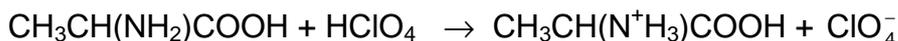
$$[\text{Cu}^+] = \sqrt{K_s(\text{CuA}) \left(1 + \frac{[\text{H}^+]}{K_a(\text{HA})} \right) + K_s(\text{CuB}) \left(1 + \frac{[\text{H}^+]}{K_a(\text{HB})} \right)}$$

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:



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



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 cm³ 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 cm³.

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

$$\mathbf{6.1} \quad n(\text{HClO}_4) = Vc = 0.0500 \text{ dm}^3 \times 0.100 \text{ mol dm}^{-3} = 0.00500 \text{ mol}$$

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

Consumed in the reaction:

$$n(\text{HClO}_4) = (0.00500 - 0.00240) \text{ mol} = 0.00260 \text{ mol}$$

$$V(\text{HClO}_4) = 0.0260 \text{ dm}^3$$

Since:

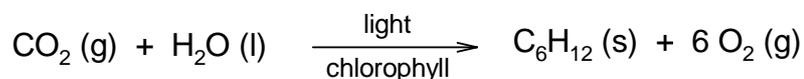
$$n(\text{HClO}_4) = n(\text{glycine}) = n(\text{N}_2) = 0.0260 \text{ mol}$$

then:

$$V(\text{N}_2) = \frac{nRT}{p} = \frac{0.0260 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 293.1 \text{ K}}{102.658 \text{ kPa}} = 0.617 \text{ dm}^3$$

PROBLEM 7

Photosynthesis can be summarised by the overall equation:



for which values of ΔH and ΔS at 25 °C are as follows:

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

$\Delta H = 2.816 \times 10^6 \text{ J mol}^{-1}$, $\Delta S = -182 \text{ J K}^{-1} \text{ mol}^{-1}$ if ΔH and ΔS 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 cm².

SOLUTION

7.1 Two alternative solutions:

a) By means of quantities related to one mole of reaction changes.

For the reaction taking place in the cell it would correspond:

$$\Delta G = -2.87 \times 10^6 \text{ J mol}^{-1}$$

b) By means of quantities related to the given reaction.

For the reaction taking place in the cell it would correspond:

$$\Delta G = -2.87 \times 10^6 \text{ J}$$

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:



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

Since one voltcoulomb is one joule, then:

$$E = \frac{-(-2.87 \times 10^6) \text{ V C mol}^{-1}}{24 \times 96\,487 \text{ C mol}^{-1}} = 1.24 \text{ V}$$

$$E = \frac{-(-2.87 \times 10^6) \text{ V C}}{24 \text{ mol} \times 96\,487 \text{ C mol}^{-1}} = 1.24 \text{ V}$$

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 $2.87 \times 10^6 \text{ J}$. Thus:

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

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

$$= \frac{2.87 \times 10^6 \text{ J} \times 500.10^{-9} \text{ m}}{6.6256 \cdot 10^{-34} \text{ Js} \times 2.9979 \cdot 10^8 \text{ ms}^{-1} \times 6.022 \cdot 10^{23} \text{ mol}^{-1}} =$$

$$= 11.99 \approx 12 \text{ mol of photons}$$

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

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 $1.013 \cdot 10^5$ 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

$$8.1 \quad n(\text{N}_2) = \frac{m(\text{N}_2)}{M(\text{N}_2)} = \frac{0.652 \text{ g}}{28 \text{ g mol}^{-1}} = 0.0233 \text{ mol}$$

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:

$$n(\text{N}_2) = n(\text{A}) = n(\text{B}) = n(\text{C}) = n(\text{D})$$

$$M(\mathbf{A}) = \frac{m(\mathbf{A})}{n(\mathbf{A})}$$

$$M(\mathbf{B}) = \frac{m(\mathbf{B})}{n(\mathbf{B})}$$

$$M(\mathbf{C}) = \frac{m(\mathbf{C})}{n(\mathbf{C})}$$

$$M(\mathbf{D}) = \frac{m(\mathbf{D})}{n(\mathbf{D})}$$

The mass of element **X** in one mole of **A**, **B**, **C** or **D**:

A: $M(\mathbf{A}) \times 0.973 = 35.45 \text{ g mol}^{-1}$

B: $M(\mathbf{B}) \times 0.689 = 70.91 \text{ g mol}^{-1}$

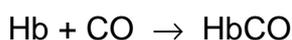
C: $M(\mathbf{C}) \times 0.851 = 177.17 \text{ g mol}^{-1}$

D: $M(\mathbf{D}) \times 0.922 = 141.78 \text{ g mol}^{-1}$

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):



The chemical bond in carbonyl haemoglobin is about 200 times stronger than that in oxyhaemoglobin (HbO₂) 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 $1.6 \times 10^{-6} \text{ mol dm}^{-3}$ by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to $8 \times 10^{-6} \text{ mol dm}^{-3}$

Problems:

- 8.1** Calculate the rate of oxyhaemoglobin formation if the rate constant is $k = 2.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (at 37 °C – normal body temperature).
- 8.2** In some cases (carbon monoxide poisoning) an increase of the rate of oxyhaemoglobin formation up to $1.1 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ is needed.
- Calculate the required concentration of oxygen assuming that the concentration of haemoglobin in blood is constant.
 - 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

$$8.1 \quad v = k[\text{Hb}][\text{O}_2]$$

$$k = 2.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$[\text{Hb}] = 8 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[\text{O}_2] = 1.6 \times 10^{-6} \text{ mol dm}^{-3}$$

$$v = \underline{2.688 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}}$$

Because 1 mole of oxygen (O₂) is needed to form 1 mole of oxyhaemoglobin, the rate of oxygen consumption is the same as the of oxyhaemoglobin formation.

$$8.2 \quad [\text{O}_2] = \frac{v}{k [\text{Hb}]}$$

$$v = 1.1 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$k = 2.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$[\text{Hb}] = 8 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\underline{[\text{O}_2] = 6.5 \times 10^{-6} \text{ mol dm}^{-3}}$$

The oxygen concentration must increase up to $6.5 \times 10^{-6} \text{ mol dm}^{-3}$. 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 cm³; 2nd – 9.0 cm³; 3rd – 8.0 cm³, 9th – 2.0 cm³; into the tenth one – 1.0 cm³. Then add to all the test-tubes (except the first one) distilled water to reach a total volume of 10.0 cm³ 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 cm³ of bromine solution with 1.0 cm³ of 1.00-molar solution of formic acid. Immediately after mixing transfer 10.0 cm³ 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 Br₂.

Task:

Plot the bromine concentration in dependence on time and read the half-time of the reaction from the diagram.

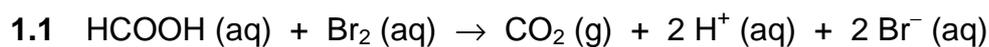
Questions:

- 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:



PROBLEM 2 (practical)

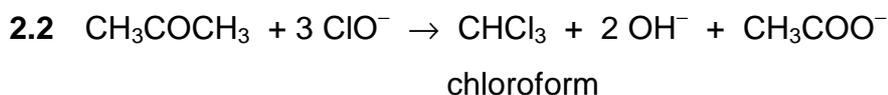
By thermometric titration of a hypochlorite solution with a solution of propanone you will find the equivalent amounts of the reactants and consequently, the reaction products.

Procedure:

For the reaction of a hypochlorite solution with a propanone use solutions tempered at laboratory temperature (check). Put 100,0 cm³ of a hypochlorite solution into a thermobeker, insert a thermometer and keep adding a 4-molar solution of propanone in 1,0 cm³ 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 be 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

2.3 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 cm³ of the 4-molar propanone solution),

products – CHCl₃, OH⁻, CH₃COO⁻.

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 $2 \text{ClO}^- \rightarrow \text{O}_2$

$$2 \text{ mol} \rightarrow 1 \text{ mol} = 22.4 \text{ dm}^3$$

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 cm³ Erlenmeyer flask. Add 50.0 cm³ 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.
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10th



International Chemistry Olympiad

**5 theoretical problems
2 practical problems**

THE TENTH INTERNATIONAL CHEMISTRY OLYMPIAD 3–13 JULY 1978, TORUN, POLAND

THEORETICAL PROBLEMS

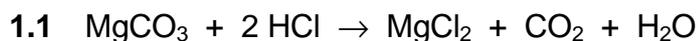
PROBLEM 1

- a) A chromium ore which does not contain water, consists of: $\text{Fe}(\text{CrO}_2)_2$, $\text{Mg}(\text{CrO}_2)_2$, 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: $A_r(\text{Cr}) = 52.01$; $A_r(\text{Fe}) = 55.85$; $A_r(\text{Mg}) = 24.32$; $A_r(\text{Ca}) = 40.08$;
 $A_r(\text{Si}) = 28.09$; $A_r(\text{C}) = 12.01$; $A_r(\text{O}) = 16.00$.

SOLUTION

1.2 The total amount of iron is in the form of $\text{Fe}(\text{CrO}_2)_2$:

Since:



$$M_r(\text{Fe}_2\text{O}_3) = 159.70$$

$$M_r(\text{Fe}(\text{CrO}_2)_2) = 223.87 \quad \% \text{Fe}_2\text{O}_3 = 7.98$$

$$\% \text{Fe}(\text{CrO}_2)_2 = \frac{2 \times 223.87}{159.70} \times 7.98 = \mathbf{22.37}$$

The difference between the total amount of Cr_2O_3 and that being contained in $\text{Fe}(\text{CrO}_2)_2$ corresponds to the amount of Cr_2O_3 , having been in the form of $\text{Mg}(\text{CrO}_2)_2$.

% Cr_2O_3 in $\text{Fe}(\text{CrO}_2)_2$:

$$M_r: \quad \begin{array}{ccc} \text{Fe}(\text{CrO}_2)_2 & \hat{=} & \text{Cr}_2\text{O}_3 \\ 223.87 & & 152.02 \end{array}$$

$$\% \text{Cr}_2\text{O}_3 = \frac{152.02}{223.87} \times 22.37 = \mathbf{15.19}$$

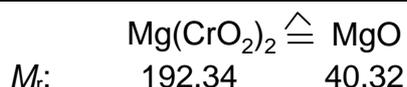
$$\% \text{Cr}_2\text{O}_3 \text{ in } \text{Mg}(\text{CrO}_2)_2 : 45.5 - 15.19 = 30.41$$

Content of $\text{Mg}(\text{CrO}_2)_2$:

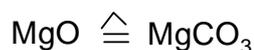
$$M_r: \quad \begin{array}{ccc} \text{Cr}_2\text{O}_3 & \hat{=} & \text{Mg}(\text{CrO}_2)_2 \\ 152.02 & & 192.34 \end{array}$$

$$\% \text{Mg}(\text{CrO}_2)_2 = \frac{192.34}{152.02} \times 30.41 = \mathbf{38.47}$$

The difference between the total amount of MgO in the ore and that corresponding to $\text{Mg}(\text{CrO}_2)_2$, is contained in MgCO_3 . % MgO and % MgCO_3 can be calculated analogously as it is given above.



$$\% \text{MgO} = \frac{40.32}{192.34} \times 38.47 = \mathbf{8.06}$$



$$\% \text{MgCO}_3 = \frac{84.32}{40.32} \times 8.06 = \mathbf{16.86}$$

Content of CaSiO_3 is obtained as complementary value to 100 %.

$$\% \text{CaSiO}_3 = 100 - (22.37 + 38.47 + 16.86) = \mathbf{22.30}$$

One kilogram of the ore contains:

$$223.7 \text{ g of } \text{Fe}(\text{CrO}_2)_2 \hat{=} 1 \text{ mol}$$

$$384.7 \text{ g of } \text{Mg}(\text{CrO}_2)_2 \hat{=} 2 \text{ mol}$$

$$168.6 \text{ g of } \text{MgCO}_3 \hat{=} 2 \text{ mol}$$

$$223.0 \text{ g of } \text{CaSiO}_3 \hat{=} 2 \text{ mol}$$

- 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:

$$\% \text{Cr}_2\text{O}_3 = \frac{456}{723.75} \times 100 = \mathbf{63.0}$$

- 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 Fe²⁺ and Ca²⁺ only.

A volume of 10.00 dm³ of the water was at disposal. From this volume 100.00 cm³ were taken for further procedure. The water was oxidised with a H₂O₂ 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 Fe²⁺ : Ca²⁺ in the water under investigation.
- 2.2** In another experiment, 10.00 dm³ of the water was used again. The temporary hardness caused by cations Ca²⁺ was removed first and the permanent hardness caused by cations Fe²⁺ was removed by addition of Na₃PO₄. Calculate the mass of the precipitate (in its anhydrous form) on the assumption that only one half of cations Fe²⁺ was oxidised to Fe³⁺ in 10.00 dm³ 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 dm³ of water.

Relative atomic masses:

$A_r(\text{Ca}) = 40.08$; $A_r(\text{Fe}) = 55.85$; $A_r(\text{C}) = 12.01$;

$A_r(\text{H}) = 1.01$; $A_r(\text{P}) = 31.00$; $A_r(\text{O}) = 16.00$.

SOLUTION

2.1 Anhydrous product: Fe₂O₃

$m(\text{Fe}_2\text{O}_3) = 0.01432 \text{ g}$ from 100 cm³ of water, i. e. 1.432 g from 10 dm³

1 mol Fe₂O₃ ⇔ 2 mol FeO

$$n(\text{Fe}_2\text{O}_3) = \frac{1.432 \text{ g}}{159.7 \text{ g mol}^{-1}} \approx 0.009 \text{ mol}$$

$$m(\text{FeO}) = n M = 2 \times 0.009 \text{ mol} \times 71.85 \text{ g mol}^{-1} \approx 1.293 \text{ g}$$

1° of hardness = 10 mg CaO / dm³ of water

$$1^\circ \text{ of hardness} = \frac{M(\text{FeO})}{M(\text{CaO})} \times 10 \text{ mg} = 12.81 \text{ mg FeO/dm}^3 \text{ of water}$$

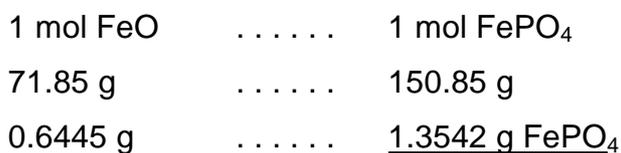
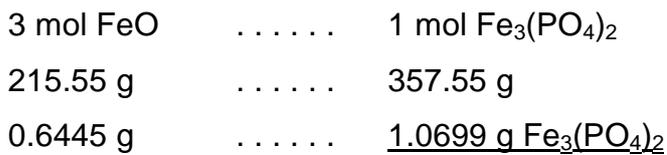
$$\frac{1.293 \text{ g FeO}}{0.1281 \text{ g FeO}} \approx 10^\circ \text{ of hardness}$$

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 dm³ 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 dm³ 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 Fe₃(PO₄)₂ as well as FePO₄ are formed at the same time.



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 dm³ of an aqueous solution which contained 0.230 kg of chromium acid anhydride in 1 dm³ 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:
- the volume ratio of both gases (at STP) which are evolved as by-products at the cathode and anode,
 - 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.

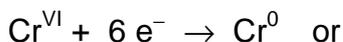
Write the corresponding summary equation for the reactions at electrodes and correct your previous calculations if possible.

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:



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:

$$n(\text{H}_2) = \frac{559.6 \times 0.86}{2} = 240.63 \text{ mol}$$

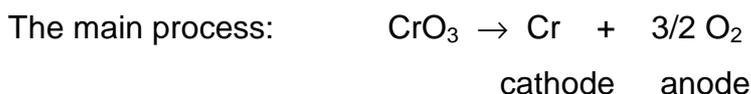
$$n(\text{O}_2) = \frac{559.6}{4} = 139.9 \text{ mol}$$

The molar ratio is:

$$\frac{n(\text{H}_2)}{n(\text{O}_2)} = \frac{V(\text{H}_2)}{V(\text{O}_2)} = \frac{240.63 \text{ mol}}{139.9 \text{ mol}} = 1.720$$

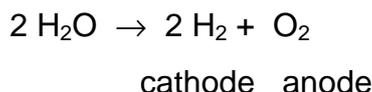
This value is different from that given in the task. Thus, beyond the mentioned reactions also other processes take place at the electrodes. The current efficiency may be calculated from the volume ratio of gases evolved, without making any investigation of what kind the processes are.

Balance of the processes:



$$\eta_1 = 14.0 \%$$

The by process: (electrolysis of water)



$$\eta_2 = ?$$

The amount of substance of the hydrogen evolved at the cathode is equal to:

$$n(\text{H}_2) = \frac{Q \cdot \eta_2}{2}$$

The amount of substance of the oxygen evolved at the anode is equal to:

$$n(\text{O}_2) = \frac{Q \cdot (\eta_1 + \eta_2)}{4}$$

According to the data given in the task:

$$\frac{V(\text{H}_2)}{V(\text{O}_2)} = \frac{n(\text{H}_2)}{n(\text{O}_2)} = \frac{\frac{Q \cdot \eta_2}{2}}{\frac{Q \cdot (\eta_1 + \eta_2)}{4}} = 1.603$$

In solving the equation for η_2 we get a value:

$$\eta_2 = 0.565 \quad (56.5 \%)$$

Volumes of the hydrogen and oxygen evolved:

$$n(\text{H}_2) = \frac{559.6 \times 0.565}{2} = 158.1 \text{ mol}$$

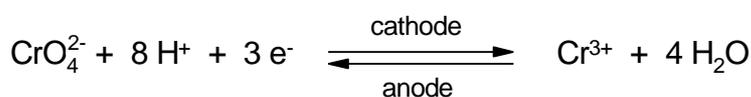
$$V(\text{H}_2) = 22.41 \text{ dm}^3 \text{ mol}^{-1} \times 158.1 \text{ mol} = 3543 \text{ dm}^3$$

$$n(\text{O}_2) = \frac{559.6 \times (0.140 + 0.565)}{4} = 98.6 \text{ mol}$$

$$V(\text{O}_2) = 22.41 \text{ dm}^3 \text{ mol}^{-1} \times 98.6 \text{ mol} = 2210 \text{ dm}^3$$

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:



PROBLEM 4

A vessel of a volume of 5.0 dm³ 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.
($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
- 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.

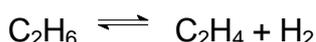
SOLUTION

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:



4.4 Clapeyron's equation for the substances undergoing thermal decomposition into two other gaseous substances, has the form:

$$pV = n(1 + \alpha)RT$$

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:

$$p'V = nRT \Rightarrow p' = \frac{n}{V}RT$$

$$pV = n(1 + \alpha)RT \Rightarrow p = \frac{n(1 + \alpha)}{V}RT$$

$$\frac{p'}{p} = \frac{n}{n(1 + \alpha)} \Rightarrow \alpha = \frac{p - p'}{p'}$$

$$\alpha_{800} = \frac{276.111 - 269.930}{269.930} = 0.023$$

$$\alpha_{1000} = \frac{500.748 - 337.412}{337.412} = 0.484$$

The reaction takes place in gaseous phase and thus, the equilibrium constant K_p is calculated according to the relation:

$$K_p = \frac{p_{C_2H_4} p_{H_2}}{p_{C_2H_6}}$$

$$p_{C_2H_4} = p_{H_2} = p' \alpha \quad p_{C_2H_6} = p' (1 - \alpha)$$

$$K_p = \frac{\alpha^2 p'}{1 - \alpha}$$

$$T = 800 \text{ K} \quad K_p = \frac{0.023^2 \times 269.930}{0.977} = 0.146 \text{ kPa}$$

$$T = 1000 \text{ K} \quad K_p = \frac{0.484^2 \times 337.412}{0.516} = 153.18 \text{ kPa}$$

4.5 According to van't Hoff's equation:

$$\overline{\Delta H} = \frac{2.303 \log \frac{K_1}{K_2} R}{\frac{1}{T_2} - \frac{1}{T_1}}$$

After substituting the known values:

$$\overline{\Delta H} = 231.36 \text{ kJ mol}^{-1}$$

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-Brow'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:

$$\frac{\Delta H_1 - \Delta H_2}{\Delta H_1} \times 100 \text{ (\%)}$$

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 $\text{CrO}_3 + \text{H}_2\text{SO}_4$. 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 excess 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:

$$M(\text{C}) = 12 \text{ g mol}^{-1}; \quad M(\text{O}) = 16 \text{ g mol}^{-1}; \quad M(\text{H}) = 1 \text{ g mol}^{-1}; \quad M(\text{KMnO}_4) = 158 \text{ g mol}^{-1}.$$

SOLUTION

- 5.1 The empirical formula of the compound **X** can be calculated from the composition of combustion products of this compounds:

$$n(\text{H}_2\text{O}) = \frac{0.9 \text{ g}}{18 \text{ g mol}^{-1}} = 0.05 \text{ mol} \Rightarrow n(\text{H}) = 0.1 \text{ mol}$$

$$\% \text{H} = \frac{0.1 \text{ g}}{1.06 \text{ g}} \cdot 100 = 9.4$$

$$n(\text{CO}_2) = \frac{3.52 \text{ g}}{44 \text{ g mol}^{-1}} = 0.08 \text{ mol} \Rightarrow n(\text{C}) = 0.8 \text{ mol i. e. } 0.96 \text{ g}$$

$$\% \text{C} = \frac{0.96 \text{ g}}{1.06 \text{ g}} \times 100 = 90.6$$

$$\text{X: } \text{C}_x\text{H}_y \quad x : y = \frac{90.6}{12} : \frac{9.4}{1} = 4 : 5$$

Empirical formula: C_4H_5

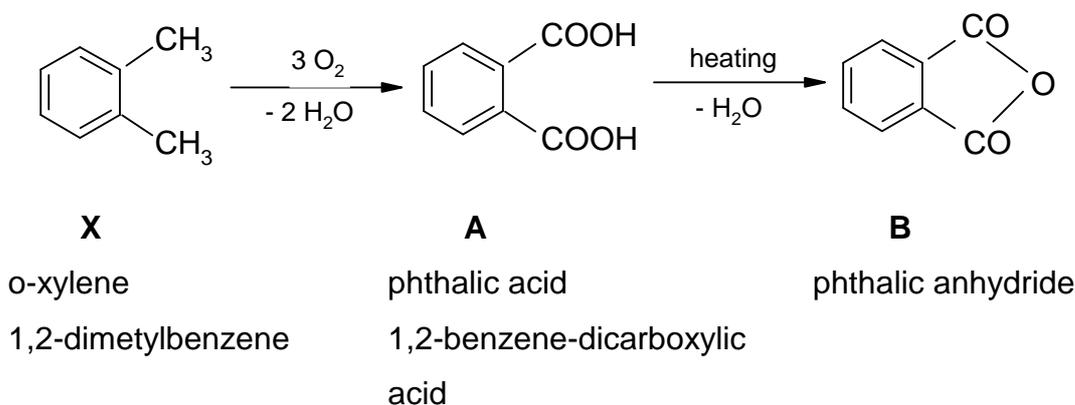
Molecular formula: $(C_4H_5)_n$

Molar mass of **X** is calculated in the following way:

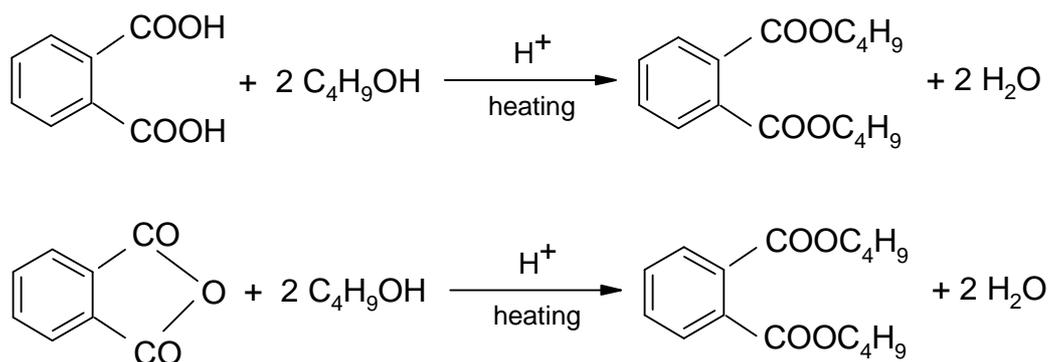
$$M(\mathbf{X}) = M(N_2) \frac{\rho(\mathbf{X})}{\rho(N_2)} = 28 \text{ g mol}^{-1} \times 3.79 = 106 \text{ g mol}^{-1}$$

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.

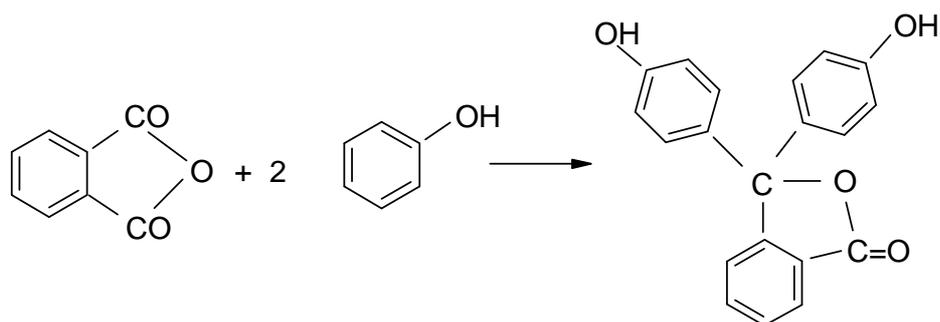


Phthalic acid (**A**) or its anhydride (**B**) when heated with an excess of 1-butanol with addition of a certain amount of mineral acid as a catalyst, yield dibutyl ester of phthalic acid – **C**:



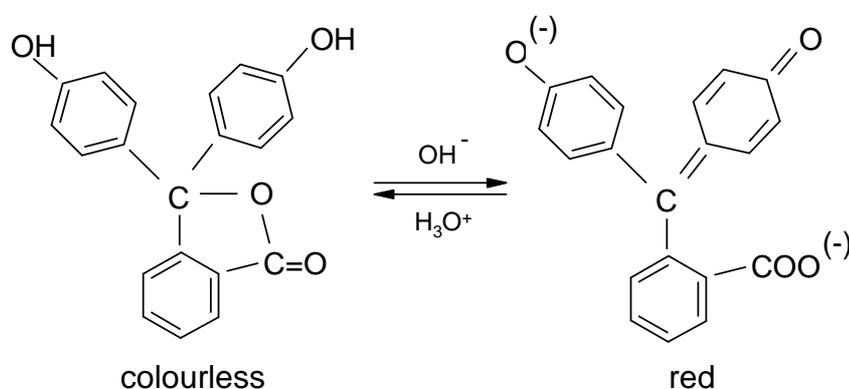
C : dibutyl phthalate

5.3 Condensation of the anhydride of phthalic acid with phenol in the presence of H_2SO_4 or anhydrous ZnCl_2 :

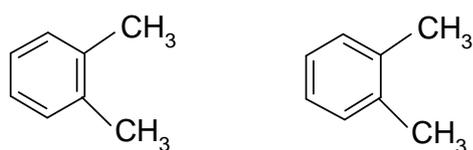


Y : phenolphthalein

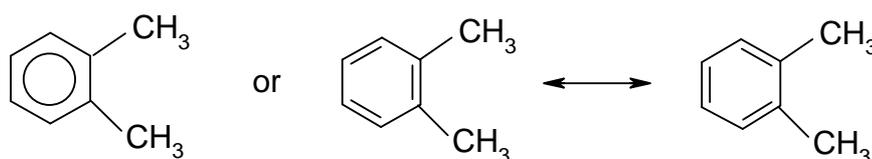
Phenolphthalein is used as acid-base indicator which is colourless in an acidic solution but purple red in an alkaline solution.



5.4 Kekule's formulas for o-xylene:



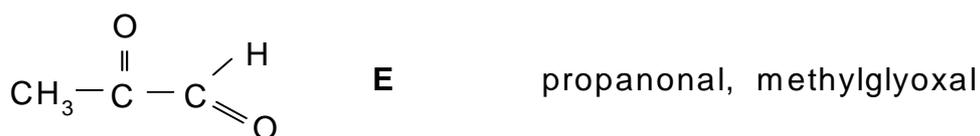
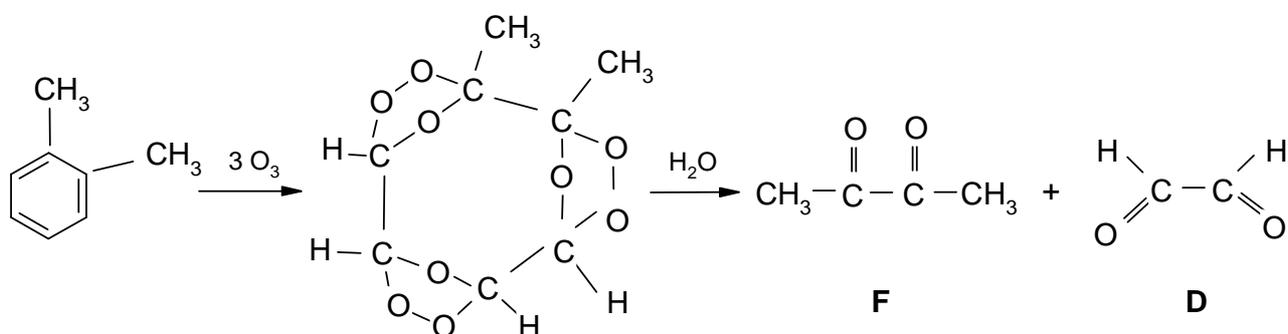
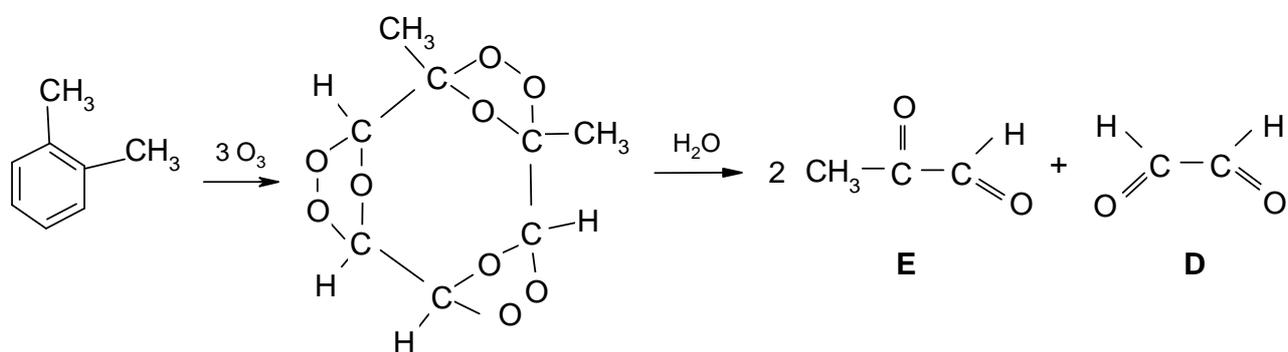
would allow to suggest that this compound does exist in two isomeric forms. Nobody, however, has succeeded in obtaining the two isomers of o-disubstituted benzene. At present it is already known that all bonds C-C as well as C-H in benzene and its derivatives are equivalent. Therefore, the formula for 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.

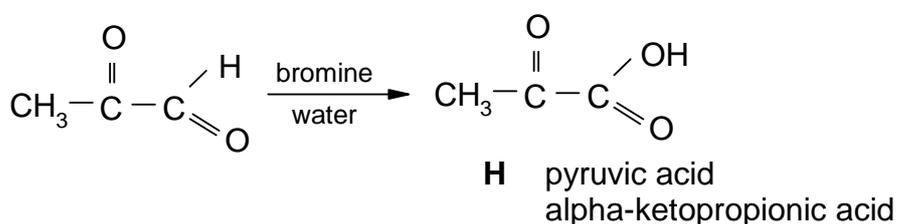
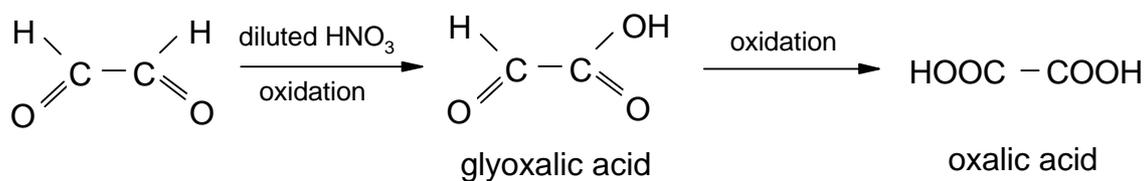
In 1941 Haayman and Witbaut provided further chemical evidence for the equivalence of the six C-C bonds in the benzene ring. They allowed to react o-xylene with ozone and obtained two different triozonides in a molar ratio of 1 : 1. Products of ozonolysis were decomposed by water to form three different substances:

5.5

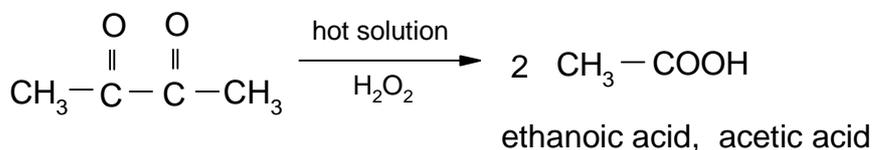


Products in the resulting mixture after hydrolysis of ozonides are in a molar ratio 3 : 2 : 1 and it proves the equivalence of C-C bonds in the benzene ring.

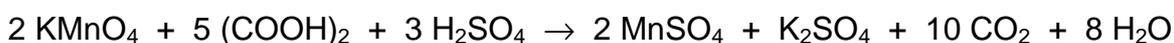
5.6 From the three above obtained compounds **D**, **E**, and **F** only the first two are easily oxidized to the corresponding acids:



Compound **F** requires a stronger oxidising agents, such as aqueous solutions of H₂O₂, HIO₄, etc.



Oxalic acid is used as a standard substance in preparation of volumetric KMnO₄ solutions:



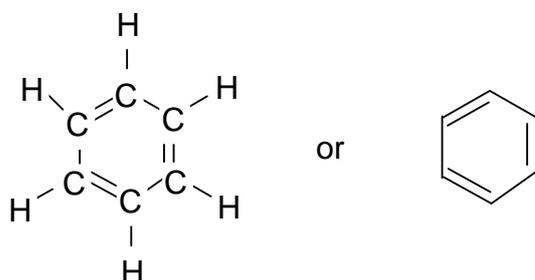
Experimental data on determination of compound **G** by titration with a 0.05-molar KMnO₄ solution show that compound **G** is oxalic acid, and thus they do confirm the correctness of the solution.

$$n(\text{KMnO}_4) = c V = 0.05 \text{ mol dm}^{-3} \times 0.0256 \text{ dm}^3 = 0.00128 \text{ mol}$$

$$n((\text{COOH})_2) = 5/2 \times 0.00128 \text{ mol} = 0.0032 \text{ mol}$$

It corresponds to 0.288 g of substance **G** what is in agreement with the result given in the task.

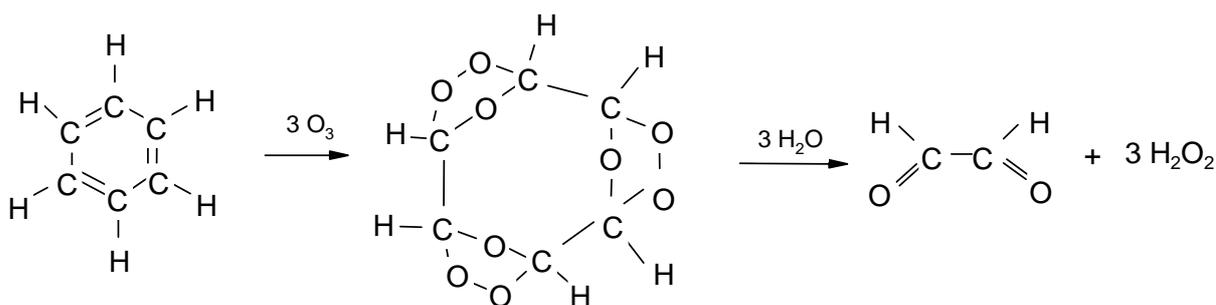
5.7 In 1865 Kekulé suggested a cyclic formula for benzene:



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, NH₃, and CH₃COOH 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 cm³ 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 – NH₃, CH₃COOH – NaOH, CH₃COOH – NH₃.

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:

$$\rho(\text{HCl}) = 1.02 \text{ g cm}^{-3}$$

$$\rho(\text{NaOH}) = 1.04 \text{ g cm}^{-3}$$

$$\rho(\text{NH}_3) = 0.99 \text{ g cm}^{-3}$$

$$\rho(\text{CH}_3\text{COOH}) = 1.01 \text{ g cm}^{-3}$$

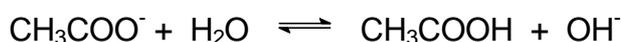
In the calculations consider the specific heat capacity value for the solutions equal to $4.19 \text{ J g}^{-1} \text{ K}^{-1}$ whereas the heat capacity of glass and thermometer may be neglected.

- 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 $57.57 \text{ kJ mol}^{-1}$. Calculate the relative error of your determination.

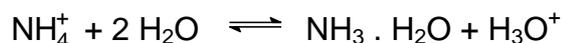
SOLUTION

- 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 $\text{pH} = 8 - 10$). A salt formed undergoes hydrolysis (more precisely its anion) and the solution exhibits a basic reaction:



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:



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:

$$\Delta H_{\text{neutr.}} = (m_1 + m_2) c (T_2 - T_1)$$

m_1 – mass of the first solution,

m_2 – mass of the second solution,

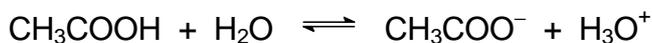
c – specific heat capacity of the solutions,

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:



A similar equation can be written for $\text{NH}_3 \cdot \text{H}_2\text{O}$.

PROBLEM 2 (practical)

The values of standard reduction potentials are given for the following redox systems:

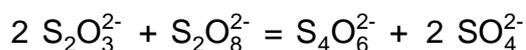
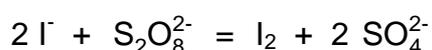
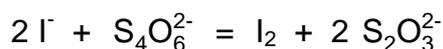


Problems:

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).



2.3 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 cm³ of a 0.10-molar solution of Na₂S₂O₃ into an Erlenmeyer flask and quickly add under intense stirring 1.0 cm³ of a 0.10-molar iodine solution.

Experiment 2

Measure 20.0 cm³ of a 0.10-molar solution of (NH₄)₂S₂O₈ into an Erlenmeyer flask and quickly add under intense stirring 4.0 cm³ of a 0.10-molar potassium iodide solution.

Experiment 3

Put 20.0 cm³ of a 0.10-molar solution of (NH₄)₂S₂O₈ into an Erlenmeyer flask and then quickly add under intense stirring 2.0 cm³ 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 $\text{Na}_2\text{S}_2\text{O}_3$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 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 $\text{S}_2\text{O}_8^{2-}$ ions.

Perform experiment No 4 according to the following instructions:

Experiment 4

- Measure successively into a 250 cm³ Erlenmeyer flask: 25.0 cm³ of a 0.20-molar potassium iodide solution, 10.0 cm³ of a 0.01-molar sodium thiosulphate solution, 5.0 cm³ of a starch paste, and stir the content of the flask.
- Measure 25.0 cm³ of a 0.20-molar $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution into a 100 cm³ 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 $\text{Na}_2\text{S}_2\text{O}_3$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 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 cm³ 0.20-molar KI + 10.0 cm³ 0.20-molar KNO_3

4 (iii): 10.0 cm³ 0.20-molar KI + 15.0 cm³ 0.20-molar KNO_3

4 (iv): 5.0 cm³ 0.20-molar KI + 20.0 cm³ 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:

$$v = \frac{\Delta c(\text{S}_2\text{O}_8^{2-})}{\Delta \tau} \quad (\text{mol dm}^{-3} \text{ s}^{-1})$$

$\Delta c(\text{S}_2\text{O}_8^{2-})$ - concentration change of $\text{S}_2\text{O}_8^{2-}$ in a time interval.

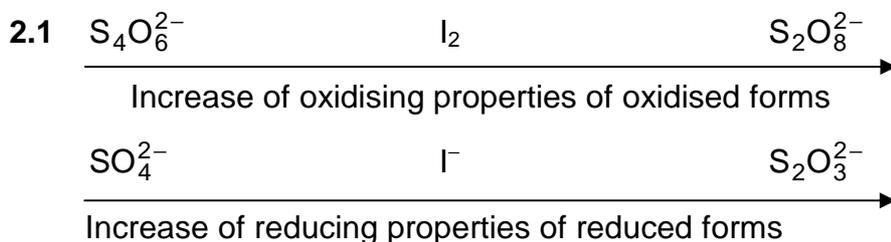
Plot (on the attached mm-paper) the dependence of reaction rate on the concentration of I^- anions at a constant concentration of $\text{S}_2\text{O}_8^{2-}$ anions in the solution.

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 $\text{S}_2\text{O}_8^{2-}$ anions at a constant concentration of I^- anions in the solution.

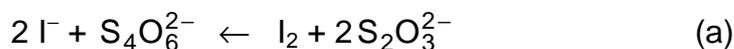
Considering Table 3, fill in Table 4. Mark the columns in the Table, suggest a plan of the experiment and list experimental results as well as the calculated values. Similarly as before, plot the dependence under investigation on a mm-paper.

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



2.2 The expected course of the chemical reactions:





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 $\text{S}_2\text{O}_8^{2-}$ 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 $[\text{I}^-]^2$ (at the constant concentration of $\text{S}_2\text{O}_8^{2-}$ 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 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $(\text{NH}_4)_2\text{SO}_4$ 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 $\text{S}_2\text{O}_8^{2-}$ 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:

$$v = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]^2$$

a) $[\text{I}^-] = \text{const} \Rightarrow v = k'[\text{S}_2\text{O}_8^{2-}]$

$$k = \frac{k'}{[\text{I}^-]^2}$$

k' is the slope of the straight line.

b) $[\text{S}_2\text{O}_8^{2-}] = \text{const} \quad v = k''[\text{I}^-]^2$

$$k'' = k[\text{S}_2\text{O}_8^{2-}]$$

$$k = \frac{k''}{[\text{S}_2\text{O}_8^{2-}]}$$

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.
