10th

ICHO

International Chemistry Olympiad

**5 theoretical problems
2 practical problems**

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

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THEORETICAL PROBLEMS

PROBLEM 1

a)   A chromium ore which does not contain water, consists of: $Fe(CrO_2)_2$, $Mg(CrO_2)_2$, $MgCO_3$, and $CaSiO_3$.

b)   It was found by analysis the ore contains 45.6 % of Cr_2O_3, 7.98 % of Fe_2O_3, and 16.12 % of MgO.

c)   When the ore was treated with a concentrated hydrochloric acid, chromium compounds being present in the ore did not react with the acid.

d)   When the reaction was finished, the ore was thoroughly washed with water (till the reaction with Cl^- was negative) and the solid residue was dried to a constant mass.

Problems:

1.1   Write stoichiometric and ionic equations for the reactions taking place when the ore is treated with the hydrochloric acid as given in c).

1.2   Calculate:

–   the content of the compounds (in mass %) present in the ore,

–   amounts of substances of the compounds present in the ore.

1.3   Calculate the content of Cr_2O_3 (in mass %) in the dried residue obtained according to d).

1.4   A glass tube was filled with a sufficient amount of granulated CaO, the total mass of the filled tube having been 412.02 g. A gas formed by the reaction as given in c), was dried and then transmitted through the glass tube. Calculate the mass of the glass tube with its filling after the reaction was finished.

Relative atomic masses: $A_r(Cr) = 52.01$; $A_r(Fe) = 55.85$; $A_r(Mg) = 24.32$; $A_r(Ca) = 40.08$;

$A_r(Si) = 28.09$; $A_r(C) = 12.01$; $A_r(O) = 16.00$.

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SOLUTION

1.1 $MgCO_3 + 2\,HCl \rightarrow MgCl_2 + CO_2 + H_2O$

$MgCO_3 + 2\,H^+ \rightarrow Mg^{2+} + CO_2 + H_2O$

$CaSiO_3 + 2\,HCl \rightarrow CaCl_2 + SiO_2 + H_2O$

$CaSiO_3 + 2\,H^+ \rightarrow Ca^{2+} + SiO_2 + H_2O$
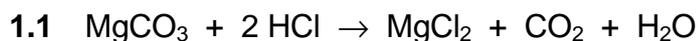
1.2 The total amount of iron is in the form of $Fe(CrO_2)_2$:

Since:

$$Fe_2O_3 \triangleq 2\ Fe(CrO_2)_2$$

$M_r(Fe_2O_3) = 159.70$

$M_r(Fe(CrO_2)_2) = 223.87$ % $Fe_2O_3 = 7.98$

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

The difference between the total amount of Cr_2O_3 and that being contained in $Fe(CrO_2)_2$ corresponds to the amount of Cr_2O_3, having been in the form of $Mg(CrO_2)_2$.

% Cr_2O_3 in $Fe(CrO_2)_2$:

$$Fe(CrO_2)_2 \triangleq Cr_2O_3$$
$$M_r: \quad 223.87 \qquad 152.02$$

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

% Cr_2O_3 in $Mg(CrO_2)_2$: $45.5 - 15.19 = 30.41$

Content of $Mg(CrO_2)_2$:

$$Cr_2O_3 \triangleq Mg(CrO_2)_2$$
$$M_r: \quad 152.02 \qquad 192.34$$

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

The difference between the total amount of MgO in the ore and that corresponding to $Mg(CrO_2)_2$, is contained in $MgCO_3$. % MgO and % $MgCO_3$ can be calculated analogously as it is given above.

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$$Mg(CrO_2)_2 \stackrel{\triangle}{=} MgO$$

M_r: 192.34   40.32
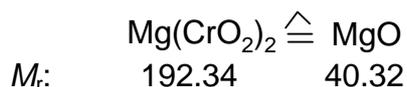
% MgO $= \dfrac{40.32}{192.34} \times 38.47 = \mathbf{8.06}$

$$MgO \stackrel{\triangle}{=} MgCO_3$$

M_r: 40.32   84.32
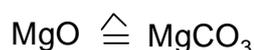
% MgCO$_3$ $= \dfrac{84.32}{40.32} \times 8.06 = \mathbf{16.86}$

Content of CaSiO$_3$ is obtained as complementary value to 100 %.

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

One kilogram of the ore contains:

223.7 g of Fe(CrO$_2$)$_2$ $\stackrel{\triangle}{=}$ 1 mol

384.7 g of Mg(CrO$_2$)$_2$ $\stackrel{\triangle}{=}$ 2 mol

168.6 g of MgCO$_3$ $\stackrel{\triangle}{=}$ 2 mol

223.0 g of CaSiO$_3$ $\stackrel{\triangle}{=}$ 2 mol

1.3 In order to simplify the problem we can assume that the hydrochloric acid reacts with 1 kg of the ore, i. e. with 168.6 g of MgCO$_3$ and with that CaO which is contained in 223.0 g CaSiO$_3$, i. e. with 107.65 of CaO.

Thus, 276.25 g of the ore (168.6 g + 107.65 g) reacted while 723.75 g remain unreacted.

One kilogram of the ore contains 456 g of Cr$_2$O$_3$ (45.6 %) and the same amount remains in the unreacted part that represents:

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

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.

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PROBLEM 2

A sample of water under investigation had 10° of t emporary hardness and 10° of permanent hardness. Hardness of the water was caused by cations Fe^{2+} and Ca^{2+} only.

A volume of 10.00 dm^3 of the water was at disposal. From this volume 100.00 cm^3 were taken for further procedure. The water was oxidised with a H_2O_2 solution and then precipitated with an aqueous ammonia solution. A brown precipitate was dried and after an appropriate heating 0.01432 g of an anhydrous product was obtained.

Problems:

2.1 Calculate the molar ratio of Fe^{2+} : Ca^{2+} in the water under investigation.

2.2 In another experiment, 10.00 dm^3 of the water was used again. The temporary hardness caused by cations Ca^{2+} was removed first and the permanent hardness caused by cations Fe^{2+} was removed by addition of Na_3PO_4. Calculate the mass of the precipitate (in its anhydrous form) on the assumption that only one half of cations Fe^{2+} was oxidised to Fe^{3+} in 10.00 dm^3 of the water analysed. Calculation should be made with an accuracy of one hundredth. Give the molar ratio in integers.

1° of hardness = 10 mg CaO in 1 dm^3 of water.

Relative atomic masses:

$A_r(Ca) = 40.08$; $A_r(Fe) = 55.85$; $A_r(C) = 12.01$;

$A_r(H) = 1.01$; $A_r(P) = 31.00$; $A_r(O) = 16.00$.

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SOLUTION

2.1 Anhydrous product: Fe_2O_3

$m(Fe_2O_3) = 0.01432$ g from 100 cm^3 of water, i. e. 1.432 g from 10 dm^3

1 mol Fe_2O_3 $\Leftrightarrow$ 2 mol FeO

$$n(Fe_2O_3) = \frac{1.432 \text{ g}}{159.7 \text{ g mol}^{-1}} \approx 0.009 \text{ mol}$$

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

1° of hardness = 10 mg CaO / dm^3 of water

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$$1° \text{ of hardness} = \frac{M(FeO)}{M(CaO)} \times 10 \text{ mg} = 12.81 \text{ mg FeO/dm3 of water}$$

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

Since the water has totally 20° of hardness, and 10 ° of hardness fall on FeO, the other 10° of hardness are attributed to CaO which corresponds to 1 g of CaO in 10 dm^3 of the water.

Molar ratio:

$$n(FeO) : n(CaO) = \frac{m(FeO)}{M(FeO)} : \frac{m(CaO)}{M(CaO)} = \frac{1.289 \text{ g}}{71.85 \text{ g mol}^{-1}} : \frac{1 \text{ g}}{56.08 \text{ g mol}^{-1}} = 1 : 1$$

2.2 A volume of 10.00 dm^3 of the water contains so much iron that corresponds to 1.293 g of FeO. 50 % of iron (0.6445 g of FeO) were oxidised to Fe(III), and therefore $Fe_3(PO_4)_2$ as well as $FePO_4$ are formed at the same time.

3 mol FeO   . . . . . .   1 mol $Fe_3(PO_4)_2$

215.55 g   . . . . . .   357.55 g

0.6445 g   . . . . . .   <u>1.0699 g $Fe_3(PO_4)_2$</u>

1 mol FeO   . . . . . .   1 mol $FePO_4$

71.85 g   . . . . . .   150.85 g

0.6445 g   . . . . . .   <u>1.3542 g $FePO_4$</u>
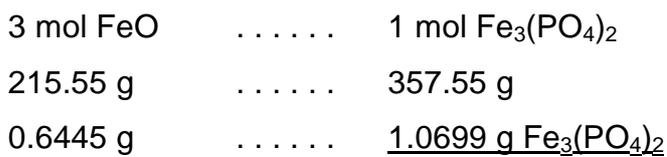
<u>Mass of the precipitate:</u>   1.0699 g + 1.3542 g = <u>2.4241 g</u>

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PROBLEM 3

Chromium plating is usually made by electrolysis in a solution of chromic acid. The chromium plated objects form the cathode. The anode is an alloy that is inert under given conditions, i. e. it does not react either chemically or electrochemically.

An electrolytic cell was filled with 100.0 dm^3 of an aqueous solution which contained 0.230 kg of chromium acid anhydride in 1 dm^3 of the solution.

In electrolysis a current of 1500 A passed through the electrolyte for 10.0 hours. After electrolysis an increase of the mass of the cathode was 0.679 kg.

The ratio of gas volumes

$$\frac{V_C}{V_A} = 1.603$$

where V_C is a volume of gases evolved at the cathode, whereas that marked as V_A is the volume of gases which are evolved at the anode. Both volumes were measured at the same conditions.

Problems

3.1 What part of the total charge (in %) was used for a deposition of 0.679 kg of chromium?

3.2 Calculate:

a) the volume ratio of both gases (at STP) which are evolved as by-products at the cathode and anode,

b) current efficiency for the corresponding reactions taking place separately at the cathode and anode when the gases are evolved.

If you find any disproportion between the data calculated and those given in the task, try to explain what process would take place in the electrolytic cell which has not been considered till now.

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

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SOLUTION

3.1 The total electric charge passed through the electrolyte:

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$$Q = \frac{1500 \times 3600 \times 10}{96500} = 559.6 \ F$$

Reaction at the cathode:

$Cr^{VI} + 6 \ e^- \rightarrow Cr^0$ or

$CrO_4^{2-} + 8 \ H^+ + 6 \ e^- \rightarrow Cr + 4 \ H_2O$
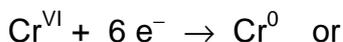
Deposited:

$$\frac{679 \ g}{51.996 \ g \ mol^{-1}} = 13.06 \ mol \ of \ chromium$$

A charge of 78.36 F was required to deposit the above chromium.

Current efficiency:

$$\frac{78.36 \ F}{559.6 \ F} \times 100 = 14.0 \ \%$$

3.2 The simplest assumption: Only hydrogen is evolved at the cathode and at the same time oxygen at the anode. On this assumption the amounts of substances of the evolved oxygen and hydrogen are as follows:

$$n(H_2) = \frac{559.6 \times 0.86}{2} = 240.63 \ mol$$

$$n(O_2) = \frac{559.6}{4} = 139.9 \ mol$$

The molar ratio is:

$$\frac{n(H_2)}{n(O_2)} = \frac{V(H_2)}{V(O_2)} = \frac{240.63 \ mol}{139.9 \ mol} = 1.720$$

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

Balance of the processes:

The main process: $CrO_3 \rightarrow Cr + 3/2 \ O_2$

                                              cathode   anode

$\eta_1 = 14.0 \ \%$

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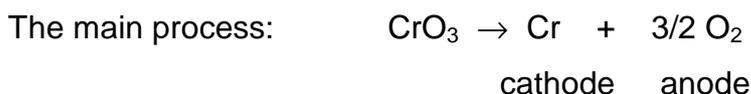
The by process: (electrolysis of water)

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

cathode   anode

$$\eta_2 = ?$$
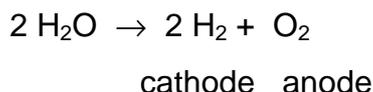
The amount of substance of the hydrogen evolved at the cathode is equal to:

$$n(H_2) = \frac{Q \cdot \eta_2}{2}$$

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

$$n(O_2) = \frac{Q \cdot (\eta_1 + \eta_2)}{4}$$

According to the data given in the task:

$$\frac{V(H_2)}{V(O_2)} = \frac{n(H_2)}{n(O_2)} = \frac{\dfrac{Q \cdot \eta_2}{2}}{\dfrac{Q \cdot (\eta_1 + \eta_2)}{4}} = 1.603$$

In solving the equation for η_2 we get a value:

$\eta_2 = 0.565$ (56.5 %)

Volumes of the hydrogen and oxygen evolved:

$$n(H_2) = \frac{559.6 \times 0.565}{2} = 158.1\,mol$$

$V(H_2) = 22.41\ dm^3\ mol^{-1} \times 158.1\ mol = 3543\ dm^3$

$$n(O_2) = \frac{559.6 \times (0.140 + 0.565)}{4} = 98.6\ mol$$

$V(O_2) = 22.41\ dm^3\ mol^{-1} \times 98.6\ mol = 2210\ dm^3$

The current efficiency when the hydrogen is evolved at the cathode is equal to 56.5 %. The current efficiency when the oxygen is evolved at the anode is equal to 70.5 %.

Thus, 29.5 % of the electric charge is used without an apparent effect. Therefore some cyclic process is taking place in the electrolytic cell which causes that anion CrO_4^{2-} is reduced incompletely. One of the reactions which causes a decrease of the current efficiency value, is the following:

$$CrO_4^{2-} + 8\,H^+ + 3\,e^- \underset{anode}{\overset{cathode}{\rightleftharpoons}} Cr^{3+} + 4\,H_2O$$

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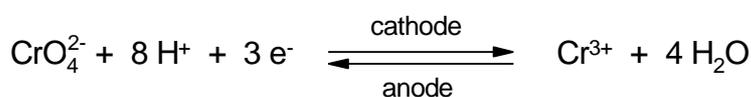
PROBLEM 4

A vessel of a volume of 5.0 dm^3 was filled with ethane at a temperature of 300 K and normal pressure and sealed. The vessel with the gas was then heated and the pressure in it was measured at distinct temperatures. The following data were found:

T (K)	Pressure p, measured (kPa)	Pressure p', calculated (kPa)
300	101.25	
500	169.20	
800	276.11	
1000	500.48	

Problems:

4.1 Calculate the pressure p' of ethane in the vessel according to the ideal gas law equation and fill in the values in a free column in the above table.

(R = 8.314 J mol^{-1} K^{-1})

4.2 Explain the differences between theoretical value p' and those (p) obtained by measurements.

4.3 Write the chemical equation for the reaction which takes place probably in the vessel at higher temperatures.

4.4 Calculate the value for the conversion degree α of ethane and that for equilibrium constant K_p of the reaction that takes place at temperatures of 800 and 1000 K.

4.5 The ratio of equilibrium constant K_p at two different temperatures is according to van't Hoff's equation equal to:

$$\ln\frac{K_1}{K_2} = \frac{\overline{\Delta H}}{R} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(ln = 2.303 log)

Calculate the mean value $\overline{\Delta H}$ for reaction heat in the temperature range of 800 – 1000 K.

4.6 What influence will have an elevation of temperature and pressure on the conversion degree of ethane?

4.7 Calculate the relative error of the calculation.

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SOLUTION

4.1 The complete table contains the following data:

T (K)	Pressure p, measured (kPa)	Pressure p', calculated (kPa)
300	101.325	101.325
500	169.820	168.706
800	276.111	269.930
1000	500.748	337.412

4.2 The p values at higher temperatures are greater than those calculated (p'). Hence, the number of molecules (moles) in the system increases. Apparently, there occurs a thermal decomposition of ethane.

4.3 Alkanes are thermally decomposed to produce alkenes and hydrogen:

$C_2H_6 \rightleftharpoons C_2H_4 + H_2$
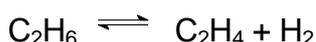
4.4 Clapeyron's equation for the substances undergoing thermal decomposition into two other gaseous substances, has the form:

$p V = n(1 + \alpha) R T$

where α is degree of decomposition.

From one mole of C_2H_6:

α moles of C_2H_4 and α moles of H_2 are obtained, and $(1 - \alpha)$ moles of C_2H_6 remain unreacted.

From n moles of C_2H_6:

$n\alpha$ moles of C_2H_4 and $n\alpha$ moles of H_2 are obtained, and $n(1 - \alpha)$ moles of C_2H_6 remain unreacted.

Hence, the total amounts of substances of compounds in the gaseous mixture will be:

$\Sigma n = 2n\alpha + n(1 - \alpha) = n(1 + \alpha)$

In comparing the theoretical and experimental values of pressure we obtain:

$p' V = n R T \implies p' = \dfrac{n}{V} R T$

$p V = n(1 + \alpha) R T \implies p = \dfrac{n(1 + \alpha)}{V} R T$

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

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

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

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

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

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

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

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

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

4.5   According to van't Hoff's equation:

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

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-Bronw's principle in the sense of forward reaction when the temperature rises and on the contrary, the equilibrium is shifted in the sense of reverse reaction when the pressure is elevated.

4.7   If the correct value is ΔH_1 and ΔH_2 is a calculated one then the relative error is calculated according to the relation:

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

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PROBLEM 5

A certain liquid organic compound **X** (being present in coal tar) with a mass of 1.06 g was burned to produce 0.90 g of water and 3.52 g of carbon dioxide. Its vapours were 3.79 times as dense as nitrogen.

The compound **X** was oxidised by a hot mixture of $CrO_3 + H_2SO_4$. A colourless crystalline substance **A** was isolated from the reaction mixture. It was soluble in an aqueous solution of NaOH or $NaHCO_3$.

Compound **A** when heated loses water and converts to compound **B**. Condensation of compound **B** with phenol in the presence of H_2SO_4 or $ZnCl_2$ yields a substance **Y** which is very often used as an acid-base indicator.

Both compound **A** and compound **B** when heated with an access of 1-butanol (some drops of a concentrated H_2SO_4 solution are added) gives the same liquid compound **C**.

If accepted that a carbon atom shows a tendency to form four bonds in organic compounds, it is possible to write <u>formally</u> 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 cm³ 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.

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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:

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

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SOLUTION

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

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

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

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

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

X: C_xH_y $x : y = \dfrac{90.6}{12} : \dfrac{9.4}{1} = 4 : 5$

Empirical formula: C_4H_5

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Molecular formula: $(C_4H_5)_n$

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

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

<u>Molecular formula of the compound **X** is C_8H_{10}.</u>

5.2 The information given in the task and concerning compound **X** supports the assumption that compound **X** is o-xylene.

X	**A**	**B**
o-xylene	phthalic acid	phthalic anhydride
1,2-dimetylbenzene	1,2-benzene-dicarboxylic acid	
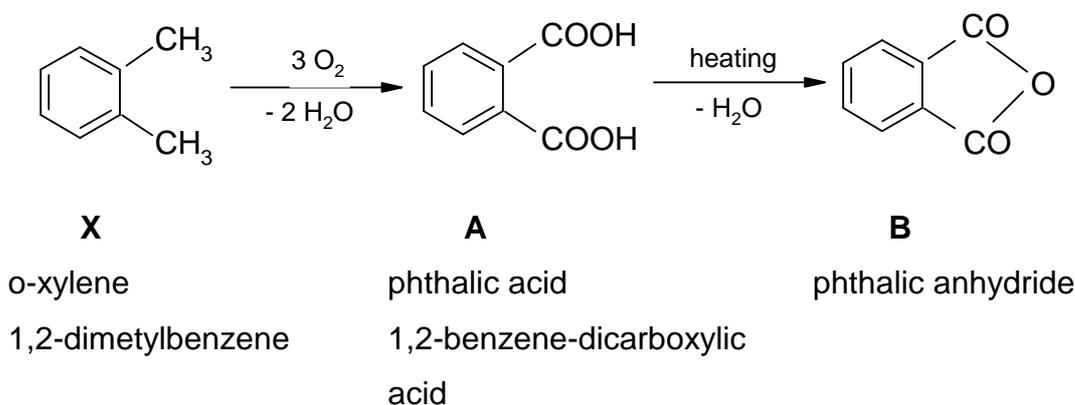
Phthalic acid (**A**) or its anhydride (**B**) when heated with an excess of 1-butanol with addition of a certain amount of mineral acid as a catalyst, yield dibutyl ester of phthalic acid – **C**:
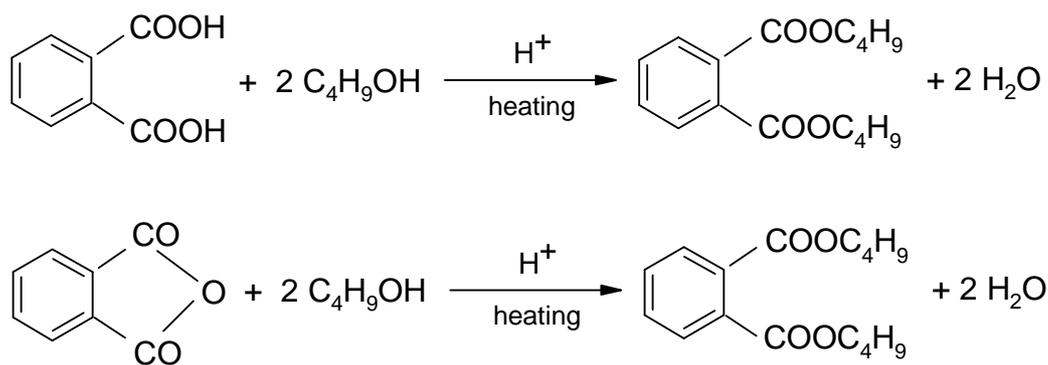
C : dibutyl phthalate

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

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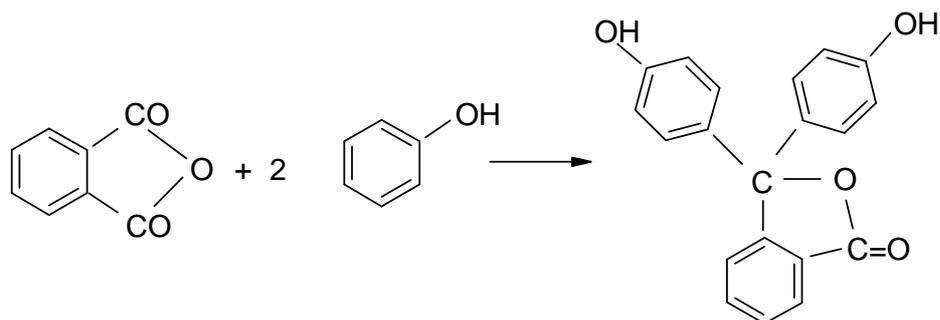
Y : phenolphthalein

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

colourless   red
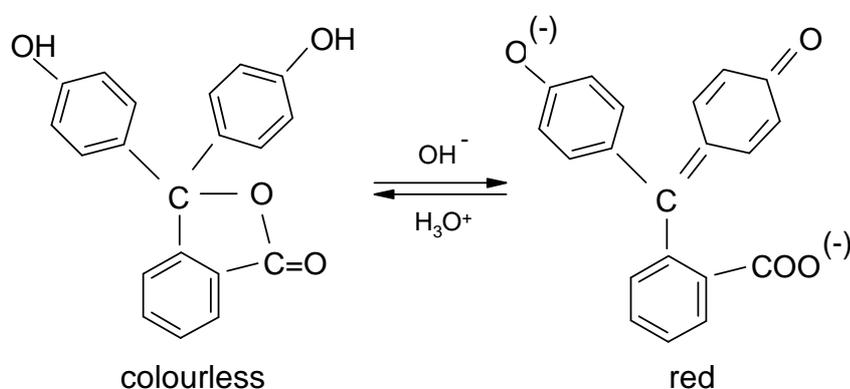
5.4   Kekule's formulas for o-xylene:
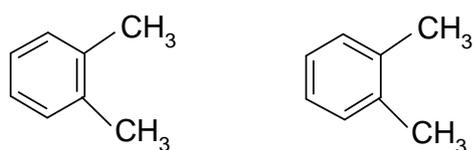
would allow to suggest that this compound does exist in two isomeric forms. Nobody, however, has succeeded in obtaining the two isomers of o-disubstituted benzene. At present it is already known that all bonds C-C as well as C-H in benzene and its derivatives are equivalent. Therefore, the formula for o-xylene can be written in the following way:

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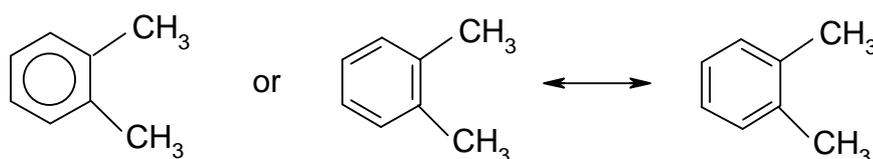
This kind of writing of the formulas expresses that the π-bonds are equally divided on the whole benzene ring. Of course, such formulas no longer support the existence of two isomeric forms of o-xylene.

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

5.5

   D   ethanedial, glyoxal

   E   propanonal, methylglyoxal

   F   butanedion, diacetyl

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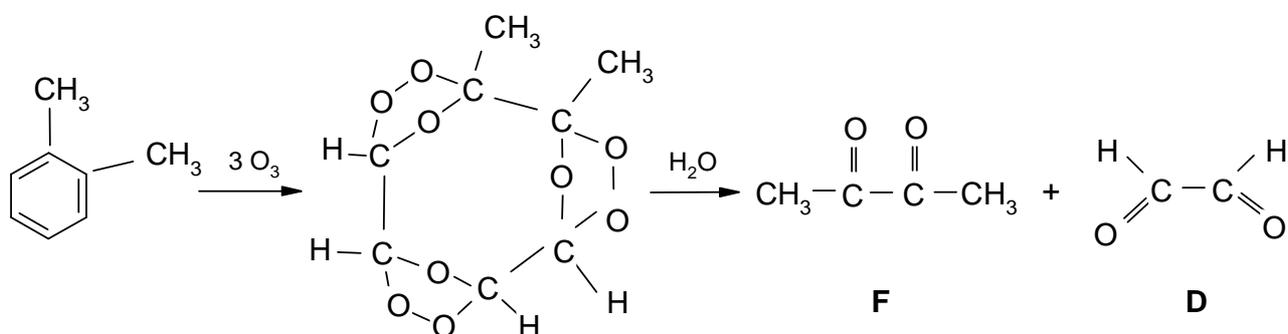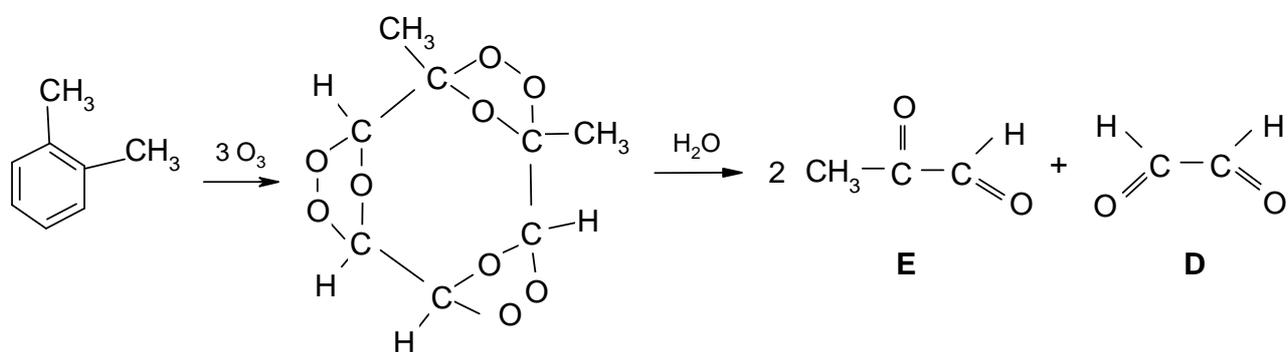
Products in the resulting mixture after hydrolysis of ozonides are in a molar ratio 3 : 2 : 1 and it proves the equivalence of C-C bonds in the benzene ring.

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

glyoxalic acid

oxalic acid

H pyruvic acid
alpha-ketopropionic acid
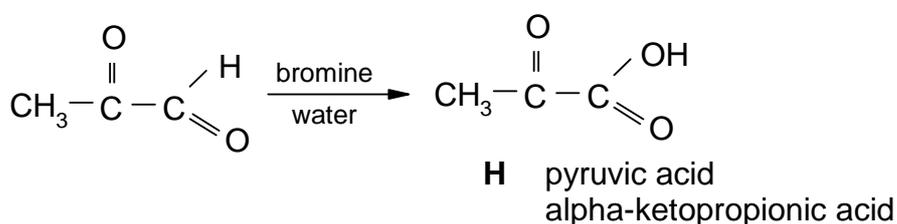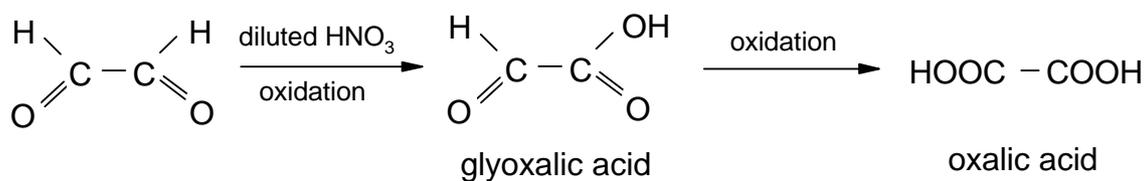
Compound **F** requires a stronger oxidising agents, such as aqueous solutions of H_2O_2, HIO_4, etc.

ethanoic acid, acetic acid
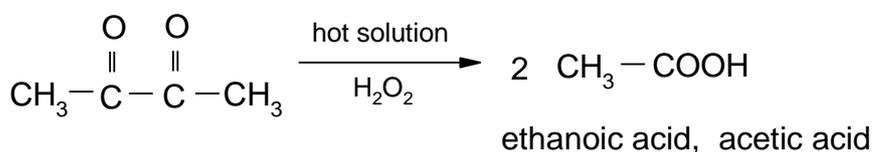
Oxalic acid is used as a standard substance in preparation of volumetric $KMnO_4$ solutions:

$$2\ KMnO_4\ +\ 5\ (COOH)_2\ +\ 3\ H_2SO_4\ \rightarrow\ 2\ MnSO_4\ +\ K_2SO_4\ +\ 10\ CO_2\ +\ 8\ H_2O$$
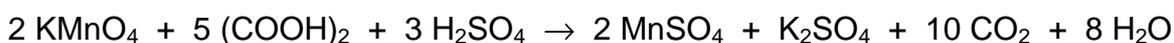
Experimental data on determination of compound **G** by titration with a 0.05-molar $KMnO_4$ solution show that compound **G** is oxalic acid, and thus they do confirm the correctness of the solution.

$n(KMnO_4)\ =\ c\ V\ =\ 0.05\ mol\ dm^{-3} \times 0.0256\ dm^3\ =\ 0.00128\ mol$

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

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

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5.7 In 1865 Kekulé suggested a cyclic formula for benzene:
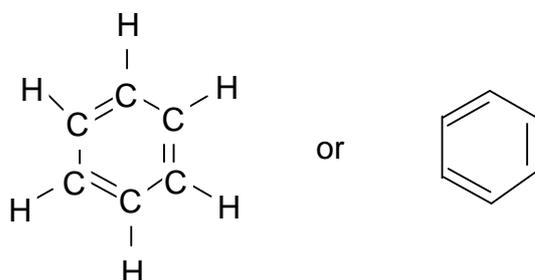
It was, however, proved by experiments that all atoms of carbon and hydrogen are in the benzene molecule equivalent. For the same reason as given under 4, the formula of benzene is at present written in the form:

Ozonolysis of benzene yields a triozonide which after hydrolysis gives glyoxal:

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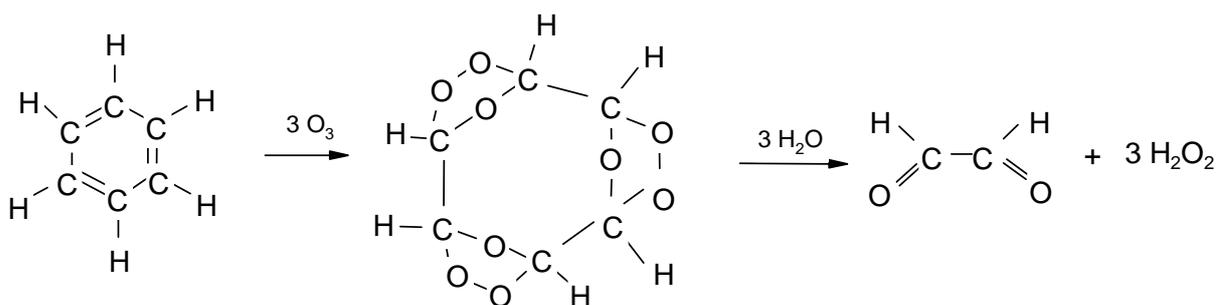
PRACTICAL PROBLEMS

PROBLEM 1   (practical)

Four aqueous solutions are available on the laboratory desk. These are solutions of HCl, NaOH, NH$_3$, and CH$_3$COOH whose concentrations are approximately 1 mol dm^{-3}. The concentration of HCl solution is the only one that is exactly determined and known.

Using the volumetric solution of HCl, determine the exact concentrations of the other solutions. A burette, pipette, titration flasks and indicators methyl orange and phenolphthalein are at your disposal. Perform twice each titration and calculate the mean value for concentration. The third determination is needed to be carried out only in such a case when the results of the previous two titrations differ more than by 2 %.

Now you will perform the following thermochemical measurements of neutralisation heat evolved in the reactions of the above given solutions of acids and bases:

a) Measure quantitatively exactly 50.0 cm^3 of the hydrochloric acid solution into a beaker. Measure into another equal beaker a volume of NaOH solution that contains such a number of moles of NaOH as that of HCl being present in the first beaker. Then measure the temperatures of both solutions with a precision of 0.2 K. Pour quickly the content of the first beaker into the other using the thermometers as a glass stick and stir the resulting solution with the thermometer. Determine the final highest temperature of the mixture.

b) Perform analogous measurement with the following pairs of acids and bases:

HCl – NH$_3$, CH$_3$COOH – NaOH, CH$_3$COOH – NH$_3$.

Problems:

1.1 What indicators have been used for the individual determinations? Give approximately pH regions in which the mentioned indicators show colour transitions. Give reasons for the use of the individual indicators using only ionic equations for the reactions which are characteristic of specific properties of salts being formed in the individual neutralisation reactions. Calculate the concentrations of all solutions under investigations.

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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:

ρ(HCl) = 1.02 g cm^{-3}

ρ(NaOH) = 1.04 g cm^{-3}

ρ(NH$_3$) = 0.99 g cm^{-3}

ρ(CH$_3$COOH) = 1.01 g cm^{-3}

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

1.3. Have you obtained equal results in all four cases? If not, order the particular reaction systems according to the decreasing value of reaction heat. What reactions cause the above mentioned differences? Express the reactions by means of chemical equations.

1.4 The exact methods showed that neutralisation heat in the reaction of the strong acid with a strong base (i. e. the reaction heat when 1 mole of water is formed from H^{+} and OH^{-} ions) is equal to 57.57 kJ mol^{-1}. Calculate the relative error of your determination.

_____

SOLUTION

1.1. In titrating a strong acid with a strong base, both phenolphthalein and methyl orange can be used as acid-base indicators. The drop on the titration curve covers the colour changes of both indicators (pH values from 4 – 10).

Only phenolphthalein can be used in the case when a weak acid is titrated with a strong base because the neutralisation occurs at higher pH values (the colour transition of phenolphthalein is in the region of pH = 8 – 10). A salt formed undergoes hydrolysis (more precisely its anion) and the solution exhibits a basic reaction:

CH$_3$COO^{-} + H$_2$O $\rightleftharpoons$ CH$_3$COOH + OH^{-}

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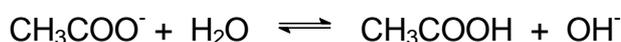
In titrating a strong acid with a weak base or vice versa, methyl orange is used (pH = 3 − 4.5) and due to hydrolysis the resulting solution shows an acidic reaction:

$$NH_4^+ + 2\,H_2O \;\rightleftharpoons\; NH_3 . H_2O + H_3O^+$$
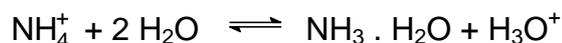
The exact concentrations of the aqueous solutions of sodium hydroxide and ammonia are determined by titrations with the volumetric solution of hydrochloric acid. The exact concentration of the acetic acid solution is then determined by a titration with the sodium hydroxide solution.

1.2 When the specific heat capacities of glass and thermometer are neglected the neutralisation heat can be then calculated according to a simple relation:

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

m_1 – mass of the first solution,

m_2 – mass of the second solution,

c – specific heat capacity of the solutions,

T_1 – temperatures of the solutions before mixing,

T_2 – temperatures of the solutions after mixing.

If the temperatures of the solutions before mixing are not equal then T_1 will be the mean temperature of both. Finally, the neutralisation heat value should be related to 1 mole of water formed.

1.3 The results obtained for the neutralisation of a strong base with a weak acid and vice versa, as well as for the reaction of a weak acid with a weak base, are lower than those obtained for the neutralisation of a strong acid with a strong base. A part of the heat is consumed for ionisation of a weak electrolyte:

$$CH_3COOH + H_2O \;\rightleftharpoons\; CH_3COO^- + H_3O^+$$

A similar equation can be written for $NH_3.H_2O$.

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PROBLEM 2 (practical)

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

$2\ S_2O_3^{2-}/S_4O_6^{2-}$ $\qquad\qquad E_1^0 = 0.17\ V$

$2\ I^-/I_2$ $\qquad\qquad\qquad E_2^0 = 0.535\ V$

$2\ SO_4^{2-}/S_2O_8^{2-}$ $\qquad\qquad E_3^0 = 2.05\ V$

Problems:

2.1 Set in order the oxidation forms of the above given redox systems from the weakest to the strongest oxidising agent (write into Table 1)

In a similar way order the reduction forms from the weakest to the strongest reducing agent.

2.2 In the bellow given equations mark by arrows the expected possible course (direction) of the chemical reaction (Table 1).

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

$2\ I^- + S_2O_8^{2-} = I_2 + 2\ SO_4^{2-}$

$2\ S_2O_3^{2-} + S_2O_8^{2-} = S_4O_6^{2-} + 2\ SO_4^{2-}$
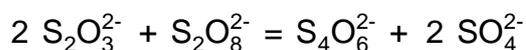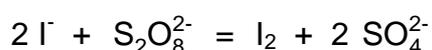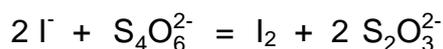
2.3 On the assumption that solutions of the same concentration are used, is it possible to tell without making any experiment which of the given reactions would run at a higher rate and which ones at a lower rate?

In order to confirm your hypothesis given under 3, perform the following three qualitative experiments:

Experiment 1

Pour 20.0 cm^3 of a 0.10-molar solution of Na$_2$S$_2$O$_3$ into an Erlenmeyer flask and quickly add under intense stirring 1.0 cm^3 of a 0.10-molar iodine solution.

Experiment 2

Measure 20.0 cm^3 of a 0.10-molar solution of (NH$_4$)$_2$S$_2$O$_8$ into an Erlenmeyer flask and quickly add under intense stirring 4.0 cm^3 of a 0.10-molar potassium iodide solution.

Experiment 3

Put 20.0 cm^3 of a 0.10-molar solution of (NH$_4$)$_2$S$_2$O$_8$ into an Erlenmeyer flask and then quickly add under intense stirring 2.0 cm^3 of a 0.10-molar sodium thiosulphate solution.

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Since both the reactants and reactant products are colourless, the course of the reaction can be followed indirectly. For that purpose, add to the solution after 1 – 2 minutes two or three drops of a 0.10-molar iodine solution. If the result of your experiment is surprising, perform experiment No 3 again but allow solutions of $Na_2S_2O_3$ and $(NH_4)_2S_2O_8$ to react for 10 minutes.

Order the reactions from experiments No 1 – 3 (into Table 3) according to their increasing reaction rate and then answer the question whether it is possible on the basis of known values of the standard reduction potentials to guess, at least qualitatively, the reaction rate for the reaction mixture containing two pairs of redox systems.

Conclusions made on the above experiments make it possible to investigate the influence of concentration of each of the starting substances on the rate of the reaction between I^- and $S_2O_8^{2-}$ ions.

Perform experiment No 4 according to the following instructions:

<u>Experiment 4</u>

a) Measure successively into a 250 cm^3 Erlenmeyer flask: 25.0 cm^3 of a 0.20-molar potassium iodide solution, 10.0 cm^3 of a 0.01-molar sodium thiosulphate solution, 5.0 cm^3 of a starch paste, and stir the content of the flask.

b) Measure 25.0 cm^3 of a 0.20-molar $(NH_4)_2S_2O_8$ solution into a 100 cm^3 beaker. Pour the content of the beaker quickly into the flask, press a stop-watch and stir the content of the flask. Measure the time till the moment when the solution becomes blue.

Perform analogously experiment No 4 three times over, using the bellow given volumes of the 0.20-molar potassium iodide solution, while the volumes of $Na_2S_2O_3$ and $(NH_4)_2S_2O_8$ solutions as well as that of the starch paste remain unchanged. Moreover, add to the solution the bellow given volumes of a 0.20-molar potassium nitrate solution so that the volume of the resulting solution is always the same. Explain the use of potassium nitrate in this case.

4 (ii): 15.0 cm^3 0.20-molar KI + 10.0 cm^3 0.20-molar KNO$_3$

4 (iii): 10.0 cm^3 0.20-molar KI + 15.0 cm^3 0.20-molar KNO$_3$

4 (iv):   5.0 cm^3 0.20-molar KI + 20.0 cm^3 0.20-molar KNO$_3$

2.4 List the results of experiments No 1-4 briefly and clearly in the attached Tables.

Write formulas of the corresponding substances above the arrows in Table 1 (as required under 2.1) and mark the expected course of the mentioned chemical reactions by arrows in the equations.

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For a qualitative evaluation of reaction rate (Table 2) use terms such as: very rapid, rapid, slow, very slow.

Fill in Table 3 exactly according to the titles of the columns.

2.5 Calculate the reaction rate according to the formula:

$$v = \frac{\Delta c(S_2O_8^{2-})}{\Delta \tau} \ (\text{mol dm}^{-3} \text{ s}^{-1})$$

$\Delta c(S_2O_8^{2-})$ -   concentration change of $S_2O_8^{2-}$ in a time interval.

Plot (on the attached mm-paper) the dependence of reaction rate on the concentration of I$^-$ anions at a constant concentration of $S_2O_8^{2-}$ anions in the solution.

2.6 Making use of the knowledge gained from the preceding experiment and the solutions which are at your disposal, suggest another experiment which would make it possible to investigate the reaction rate dependence on concentration of $S_2O_8^{2-}$ anions at a constant concentration of I$^-$ anions in the solution.

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

2.7 Write a general relation for the reaction rate dependence on the concentration of reactants and then using the diagrams attached, calculate the values for the reaction rate constant for both cases and determine their mean value.

_____

SOLUTION

2.1 $S_4O_6^{2-}$ I_2 $S_2O_8^{2-}$
          ⟶

Increase of oxidising properties of oxidised forms

SO_4^{2-} I^- $S_2O_3^{2-}$
          ⟶

Increase of reducing properties of reduced forms
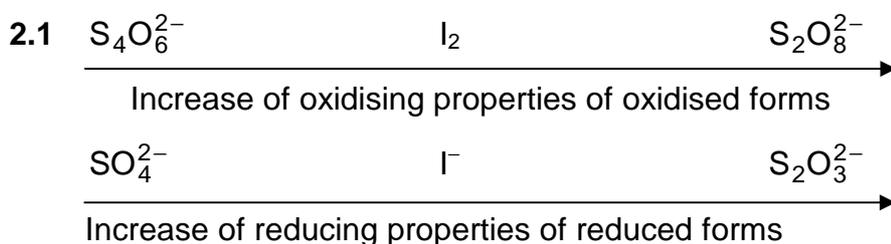
2.2 The expected course of the chemical reactions:

$$2\,I^- + S_4O_6^{2-} \ \leftarrow \ I_2 + 2\,S_2O_3^{2-} \qquad\qquad \text{(a)}$$

$$2\,I^- + S_2O_8^{2-} \ \rightarrow \ I_2 + 2\,SO_4^{2-} \qquad\qquad \text{(b)}$$

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$$2\ S_2O_3^{2-} + S_2O_8^{2-} \rightarrow S_4O_6^{2-} + 2\ SO_4^{2-} \qquad\qquad (c)$$
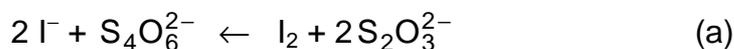
2.3 The formulation of any hypothesis either supporting or neglecting the possibility of predicting the reaction rate, should be accepted as correct.

Results of experiments Nos 1-3:

1 - reaction (a) is very rapid;

2 - reaction (b) is slow;

3 - reaction (c) is very slow, its course can hardly be observed.

Conclusion: The known differences between the values of standard reduction potentials of two pairs of redox systems do not allow to guess even qualitatively the proper relations between the rates of the corresponding reactions.

2.4 You are required to fill in the following data into Table 3:

- volumes of individual solutions,

- the total volume of the solution (65 cm^3),

- calculated values for I^- and $S_2O_8^{2-}$ concentrations,

- reaction time,

- calculated values for the reaction rate.

The addition of 0.20-molar KNO_3 solution is needed to keep the constant ionic strength of the resulting solution.

In plotting the reaction rate in dependence on the values of $[I^-]^2$ (at the constant concentration of $S_2O_8^{2-}$ anions) we get a straight line crossing the beginning of the coordinate system.

Table 4 should be filled in analogously as Table 3 where, moreover, the individual columns should be specified.

Solutions for the experiment are prepared in the same way but the solution of KI (25 cm^3) will form a constant addition, whereas those of $(NH_4)_2S_2O_8$ and $(NH_4)_2SO_4$ will form a changeable addition in the resulting solution and the other conditions are equal. Ammonium sulphate plays the same role in the solution as potassium nitrate in the preceding experiment.

In this case the reaction rate versus the concentration of $S_2O_8^{2-}$ anions is plotted (at a constant concentration of I^- anions) to give also a straight line crossing the beginning of the coordinate system.

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2.5 The rate of the reaction:

$v = k\,[S_2O_8^{2-}]\,[I^-]^2$

a) $[I^-] = \text{const} \;\Rightarrow\; v = k'\,[S_2O_8^{2-}]$

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

k' is the slope of the straight line.

b) $[S_2O_8^{2-}] = \text{const}$ $\qquad v = k''\,[I^-]^2$

$k'' = k\,[S_2O_8^{2-}]$

$$k = \frac{k''}{[S_2O_8^{2-}]}$$

k'' is the slope of the straight line.

The values of the rate constants obtained from the procedures a) and b) should be theoretically equal. If they partly differ, calculate the mean value of the rate constant.

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