6th

ICHO

International Chemistry Olympiad

5 theoretical problems
3 practical problems

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

THEORETICAL PROBLEMS

PROBLEM 1

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

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

Problems:

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

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

SOLUTION

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

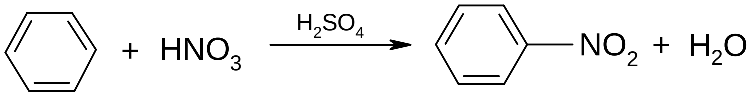
(**A**)

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

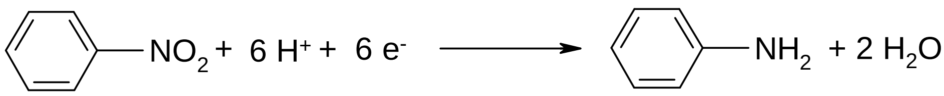
$2\ NO + O_2 \rightarrow 2\ NO_2$

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

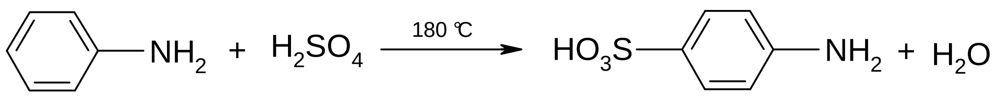
(**B**)

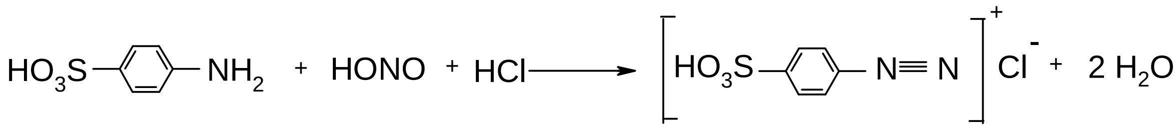


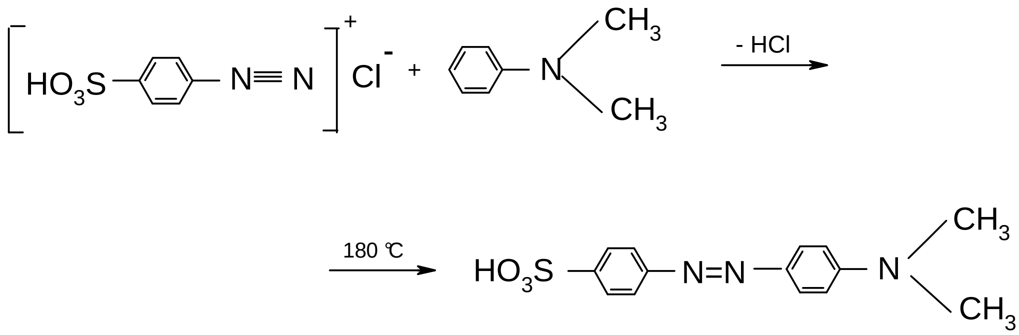
(**C**)



(**D**)







4'-dimethyl amino 4-azo benzene sulphonic acid

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

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

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

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

$$m(H_2) = \frac{1 \text{ g mol}^{-1}}{96500 \text{ C mol}^{-1}} \times 3 \text{ A} \times 32167 \text{ s} = 1 \text{ g}$$

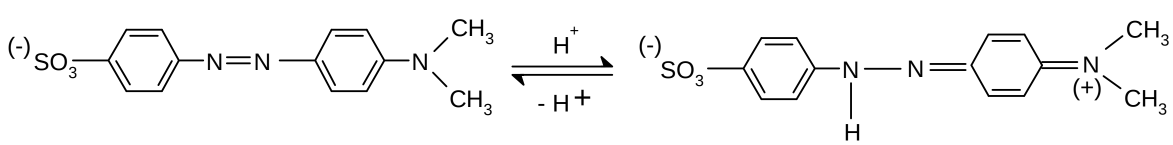
From equations:

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

The mass of product **D**:

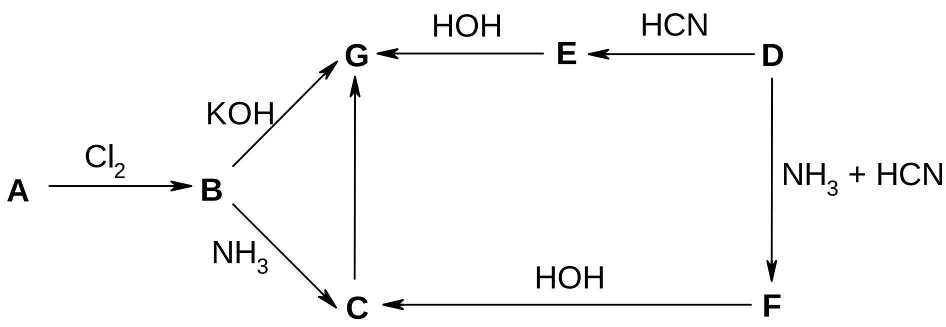
$m = n\,M = 31 \text{ g } C_6H_5NH_2$

3.



PROBLEM 2

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



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

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

Problems:

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

Relative atomic masses:

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

SOLUTION

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

R-COOH + AgOH → R-COOAg + H_2O

A : $(C_xH_yO_z)_n$

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

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

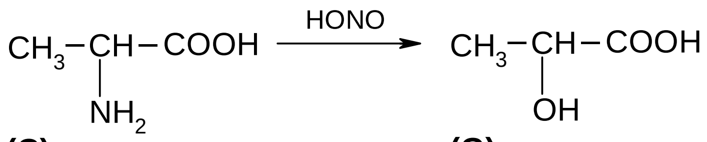
M(**A**) = 74 g mol^{-1}

A = CH_3-CH_2-COOH

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

$(C_pH_qO_r)_n$

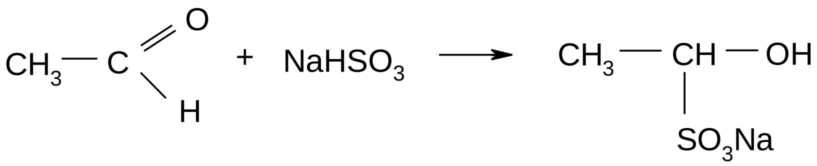
$$p : q : r = \frac{54.54}{12} : \frac{9.09}{1} : \frac{36.37}{16} = 1 : 2 : 0.5$$



(C) **(G)** IV

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

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



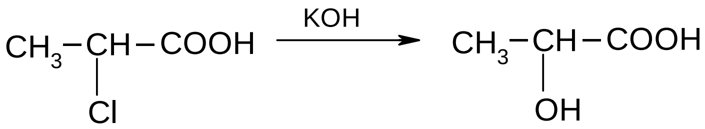
D = CH_3-CHO

Reaction:

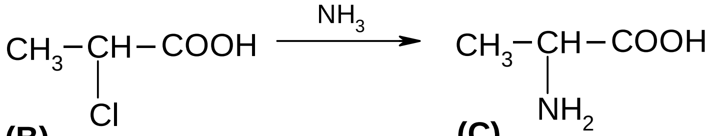
The reduction product contains 21.6 % of sulphur.

2.

(A) **(B)** I



(B) **(G)** II



(B) **(C)** III

$$\underset{\textbf{(C)}}{CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH} \xrightarrow{HONO} \underset{\textbf{(G)}}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH} \qquad \text{IV}$$

$$\underset{\textbf{(D)}}{CH_3-CHO} \xrightarrow{HCN} \underset{\textbf{(E)}}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CN} \qquad \text{V}$$

$$\underset{\textbf{(E)}}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CN} \xrightarrow{HOH,\ H_3O^+} \underset{\textbf{(G)}}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH} \qquad \text{VI}$$

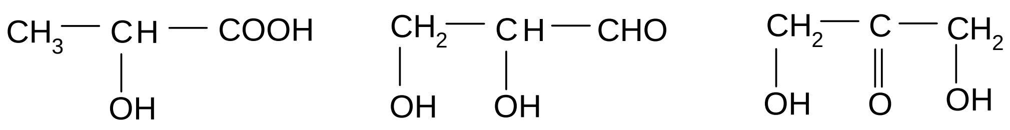
$$\underset{\textbf{(D)}}{CH_3-CHO} \xrightarrow{NH_3\ +\ HCN} \underset{\textbf{(F)}}{CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CN} \qquad \text{VII}$$

$$\underset{\textbf{(F)}}{CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CN} \xrightarrow{HOH,\ H_3O^+} \underset{\textbf{(C)}}{CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH} \qquad \text{VIII}$$

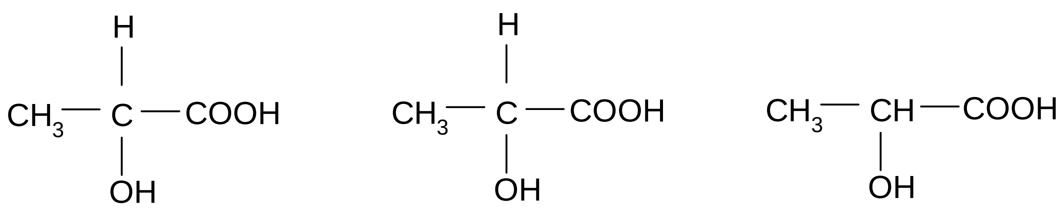
3. I - substitution reaction
   II - substitution nucleophilic reaction
   III - substitution nucleophilic reaction
   IV - substitution reaction
   V - additive nucleophilic reaction
   VI - additive reaction, hydrolysis
   VII - additive reaction
   VIII - additive reaction, hydrolysis

4.

position isomerism



structural isomerism



d(+) l(-)

stereoisomerism
(optical isomerism)

racemic mixture

PROBLEM 3

The following 0.2 molar solutions are available:

A: HCl	**B**: HSO_4^-	**C**: CH_3COOH	**D**: $NaOH$
E: CO_3^{2-}	**F**: CH_3COONa	**G**: HPO_4^{2-}	**H**: H_2SO_4

Problems:

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

Ionisation constants:

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

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

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

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

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

Relative atomic masses:

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

SOLUTION

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

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

$$[H_3O^+] = \sqrt{K_a\ c} = \sqrt{1.8\times10^{-5}\times 0.2} = 1.9\times10^{-3}\ \text{mol dm}^{-3}$$

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

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

4. By comparison of the ionisation constants we get:

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

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

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

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

$K_a(HSO_4^-) >> K_a(HPO_4^{2-})$

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

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

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

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

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

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

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

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

PROBLEM 4

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

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

Problems:

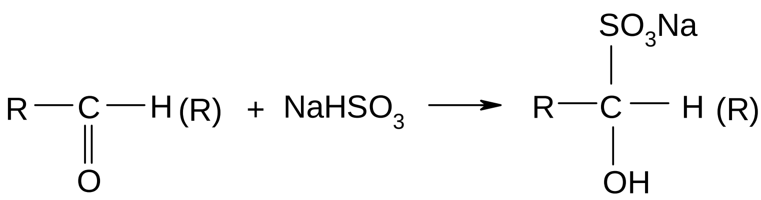
4.1 Write structural formulas of substance **A** and **B**.

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

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

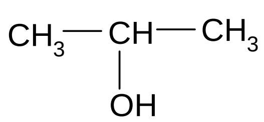
SOLUTION

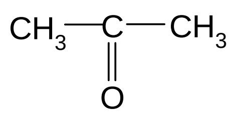
4.1



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

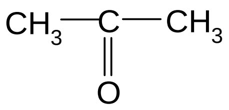
$$\frac{M_r(\mathbf{C}) + 104}{M_r(\mathbf{C})} = 2.7931 \qquad M_r(\mathbf{C}) = 58$$

A ... 

C ... 

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

B ...



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

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

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

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

Let us mark the amounts of substances as:

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

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

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

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

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

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

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

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

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

PROBLEM 5

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

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

Problem:

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

SOLUTION

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

Equations:

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

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

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

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

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

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

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

Thus, the mass of hydroxides dissolved in the solution:

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

Therefore:

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

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

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

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

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

(8) 0.188 g – 0.077 g = 0.111 g

Heating:

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

Decrease of the mass: 0.027 g (H_2O)

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

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

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

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

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

M^{II} = Ca

Precipitation with (NH_4CO_3):

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

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

0.18 g + 0.077 g = 0.257 g

After precipitation with $(NH_4)_2CO_3$:

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

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

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

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

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

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

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

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

According to equations (3) and (4):

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

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

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

According to equations (7) and (11):

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

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

$M^{I}OH = NaOH$

Composition of the mixture:

0.002 mol Ca + 0.001 mol Na

or

0.080 g Ca + 0.023 g Na

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Test tubes with unknown samples contain:

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

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

PROBLEM 2 (practical)

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

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

SOLUTION

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

PROBLEM 3 (practical)

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

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

SOLUTION

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