4th

ICHO

International Chemistry Olympiad

6 theoretical problems
2 practical problems

THE FOURTH
INTERNATIONAL CHEMISTRY OLYMPIAD

MOSCOW 1972
SOVIET UNION

THEORETICAL PROBLEMS

PROBLEM 1

A mixture of two solid elements with a mass of 1.52 g was treated with an excess of hydrochloric acid. A volume of 0.896 dm^3 of a gas was liberated in this process and 0.56 g of a residue remained which was undissolved in the excess of the acid.

In another experiment, 1.52 g of the same mixture were allowed to react with an excess of a 10 % sodium hydroxide solution. In this case 0.896 dm^3 of a gas were also evolved but 0.96 g of an undissolved residue remained.

In the third experiment, 1.52 g of the initial mixture were heated to a high temperature without access of the air. In this way a compound was formed which was totally soluble in hydrochloric acid and 0.448 dm^3 of an unknown gas were released. All the gas obtained was introduced into a one litre closed vessel filled with oxygen. After the reaction of the unknown gas with oxygen the pressure in the vessel decreased by approximately ten times (T = *const*).

Problem:

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

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

SOLUTION

a) Reaction with hydrochloric acid:

1.52 g – 0.56 g = 0.96 g of a metal reacted and 0.896 dm^3 of hydrogen (0.04 mol) were formed.

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

Possible solutions:

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

Reaction: $Mg + 2\,HCl \rightarrow MgCl_2 + H_2$

b) Reaction with sodium hydroxide:

1.52 g – 0.96 g = 0.56 g of an element reacted, 0.896 dm^3 (0.04 mol) of hydrogen were formed.

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

Possible solutions:

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

Reaction: $Si + 2\,NaOH + H_2O \rightarrow Na_2SiO_3 + 2\,H_2$

c) Combining of both elements:

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

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

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

silicide: Mg_2Si

d) Reaction of the silicide with acid:

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

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

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

e) Reaction of silane with oxygen:

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

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

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

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

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

The remainder of oxygen in the closed vessel:

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

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

PROBLEM 2

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

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

Problems:

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

Relative atomic masses:

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

SOLUTION

1. a) Reduction by hydrogen:

$FeO + H_2 \rightarrow Fe + H_2O$

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

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

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

The mass of iron after reduction: 3.92 g

The total amount of substance of iron after reduction:

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

b) Reaction with copper(II) sulphate:

$Fe + CuSO_4 \rightarrow Cu + FeSO_4$

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

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

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

Amount of substance of iron in the mixture:

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

c) Formation of water after reduction:

0.90 g H_2O, i.e. 0.05 mol

0.05 mol = n(Fe) + 3 n(Fe_2O_3) (3)

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

n(FeO) = 0.02 mol

n(Fe_2O_3) = 0.01 mol

d) Consumption of acid:

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

$FeO + 2\ HCl \rightarrow FeCl_2 + H_2O$

$Fe_2O_3 + 6\ HCl \rightarrow 2\ FeCl_2 + 3\ H_2O$

n(HCl) = 2 n(Fe) + 2 n(FeO) + 6 n(Fe_2O_3) =

= 0.06 mol + 0.04 mol + 0.06 mol = 0.16 mol

A part of iron reacts according to the equation:

$Fe + 2\ FeCl_3 \rightarrow 3\ FeCl_2$

n(Fe) = 0.5 × n($FeCl_3$) = n(Fe_2O_3)

n(Fe) = 0.01 mol

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

The total consumption of acid: n(HCl) = 0.14 mol

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

2. Volume of hydrogen:

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

Iron in the mixture: 0.03 mol

Iron reacted with $FeCl_3$: 0.01 mol

Iron reacted with acid: 0.02 mol

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

PROBLEM 3

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

Problem:

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

Relative atomic masses:

A_r(H) = 1; A_r(O) = 16; A_r(Na) = 23; A_r(Cl) = 35.5; A_r(Cu) = 64.

SOLUTION

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

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

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

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

$$Cl_2 + Cu \rightarrow CuCl_2$$

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

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

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

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

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

The amount of water is decreased in the solution by:

$n(H_2O)$ = 2 mol

$m(H_2O)$ = 36 g

Before electrolysis:

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

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

After electrolysis:

m(solution NaCl) = 220 g – 36 g = 184 g

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

PROBLEM 4

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

Problems:

1. Calculate the final temperature of the resulting solution.
2. Determine the amount of a dry residue that remains after evaporation of the solution.

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

Relative atomic masses:

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

SOLUTION

1. a) NaOH + HCl $\rightarrow$ NaCl + H_2O

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

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

unreacted: n(NaOH) = 0.025 mol

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

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

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

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

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

$c_1 = c_2 = c$

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

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

d) The temperature increase due to the reaction of NaOH with H_2SO_4 is as follows:

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

The final temperature of the solution: t = 22 + 2 = 24 °C

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

$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$

Na_2SO_4 is the dry residue.

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

PROBLEM 5

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

Problem:

1. Determine the structural formula of the unknown hydrocarbon.

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

SOLUTION

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

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

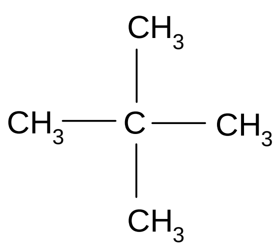
   Monobromo derivative can only come into consideration because the relative molecular mass of dibromo derivative should be greater:

   $M_r(RBr_2) > 160$

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

   The corresponding summary formula: C_5H_{12}

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



PROBLEM 6

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

The initial compound **A** when allowed to react with hydrobromide yields product **C** which on boiling in water gives substance **D** containing 35.82 % carbon, 4.48 % hydrogen, and oxygen. An amount of 2.68 g of substance **D** required reacting with 20 cm^3 of a 2 N solution of potassium hydroxide.

Problems:

1. Determine structural formulas of all the above mentioned substances **A**, **B**, **C** and **D**. Use the finding that compound **A** splits off water when heated.
2. Write chemical equations for the above reactions.

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

SOLUTION

1. Stoichiometric formulas of compounds:

A : $C_xH_yC_z$

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

B : $C_mH_nO_p$

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

D : $C_aH_bO_c$

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

20 cm^3 of 2 N KOH correspond 0.04 / v mol of substance **D** and it corresponds to 2.68 g of substance **D**

v = 1, 2, 3, ...

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

M_r(**D**) = 67 or 134 or 201, etc.

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

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

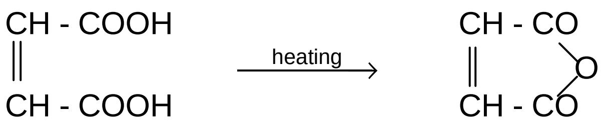
A: $C_4H_4O_4$ **B**: $C_8H_{12}O_4$ **C**: $C_4H_5O_4Br$

2. Equations:

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

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

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



Compound **A**: maleic acid

PRACTICAL PROBLEMS

PROBLEM 1

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

PROBLEM 2

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