

**7<sup>th</sup>**



**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 cm<sup>3</sup> of hydrogen (0 °C, 101.325 kPa) are evolved and 170 mg of an undissolved residue remain. A sample of 500 mg of the alloy when reacted with a NaOH solution produces 517 cm<sup>3</sup> 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 H<sub>2</sub> 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)

$\% \text{ Zn} = 21.18$

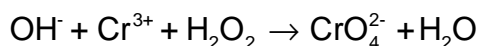
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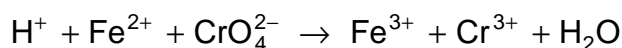
**PROBLEM 3**

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

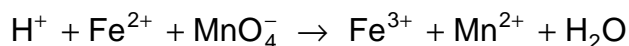
After elimination of silver and copper, chromium is oxidised in it according to the following unbalanced equation:



Then 25.00  $\text{cm}^3$  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  $\text{cm}^3$  of a 0.020-molar  $\text{KMnO}_4$  solution is required for an oxidation of the Fe(II) salt which remains unoxidized in the solution.

In another experiment, a volume of 200  $\text{cm}^3$  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.

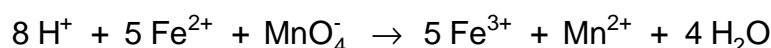
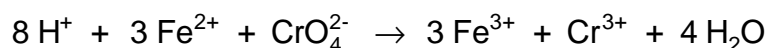
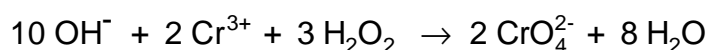
Problem:

**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)

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

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

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

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

$$x = 906.26$$

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

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

$$\underline{\% \text{ Cu} = 60.4} \quad \underline{\% \text{ Ag} = 30.6}$$

**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)  $\alpha_1$  – before dilution;  $\alpha_2$  – 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):

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

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

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

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

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**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  $\text{AgNO}_3$  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.

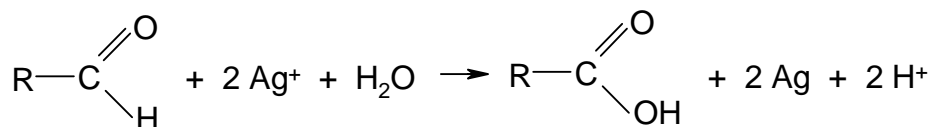
5.2 Give the structural formulas of the aldehydes.

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:



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

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

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

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

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

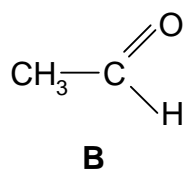
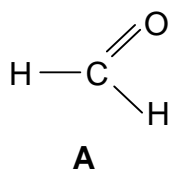
According to equation (1):

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

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

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**

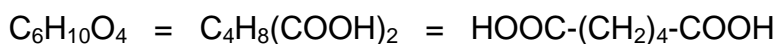
A certain saturated hydrocarbon **A** is transformed by a catalytic oxidation partly into a secondary alcohol **B**, and partly into a ketone **C**. The ketone when oxidised with nitric acid in the presence of catalyst yields a compound **D** with a formula of  $C_6H_{10}O_4$ . From compound **D** when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

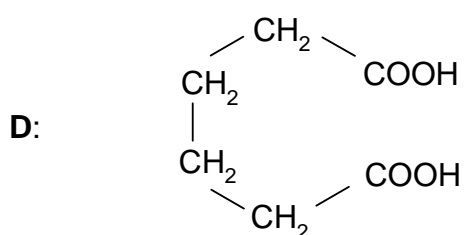
7.1 Write the structural formulas of compounds **A**, **B**, **C**, **D**, and **E**.

**SOLUTION**

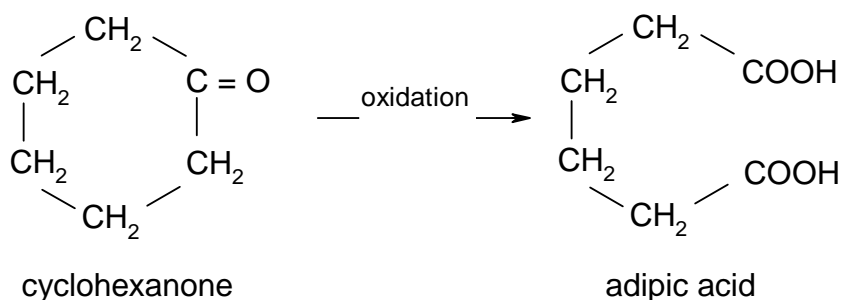
7.1 In general: ketone  $\xrightarrow{\text{oxidation}}$  carboxylic acid

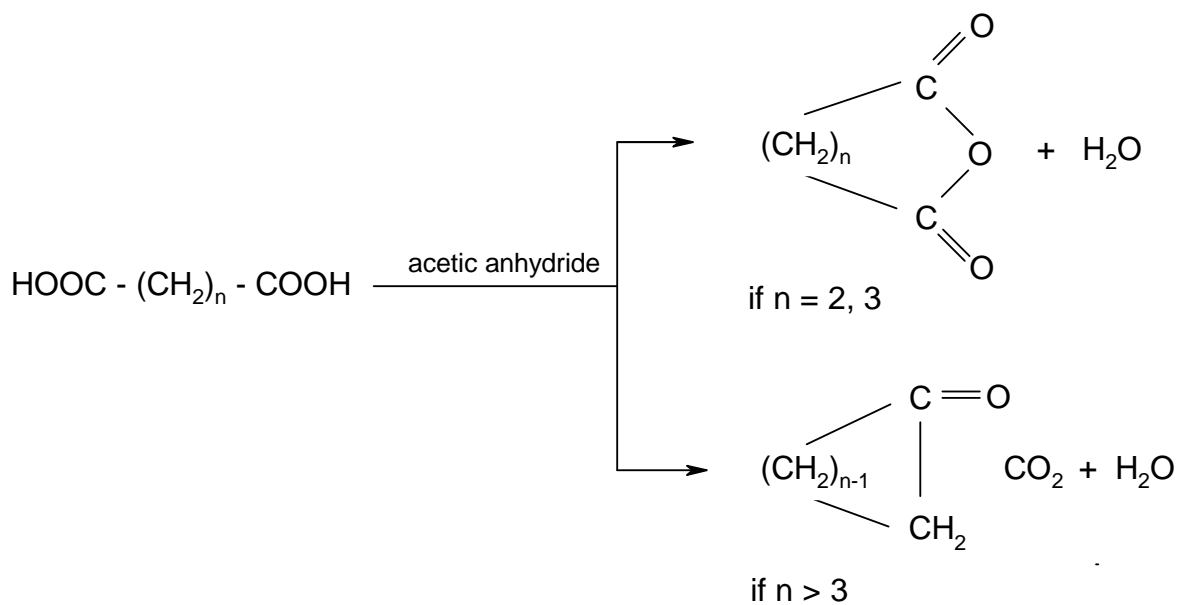
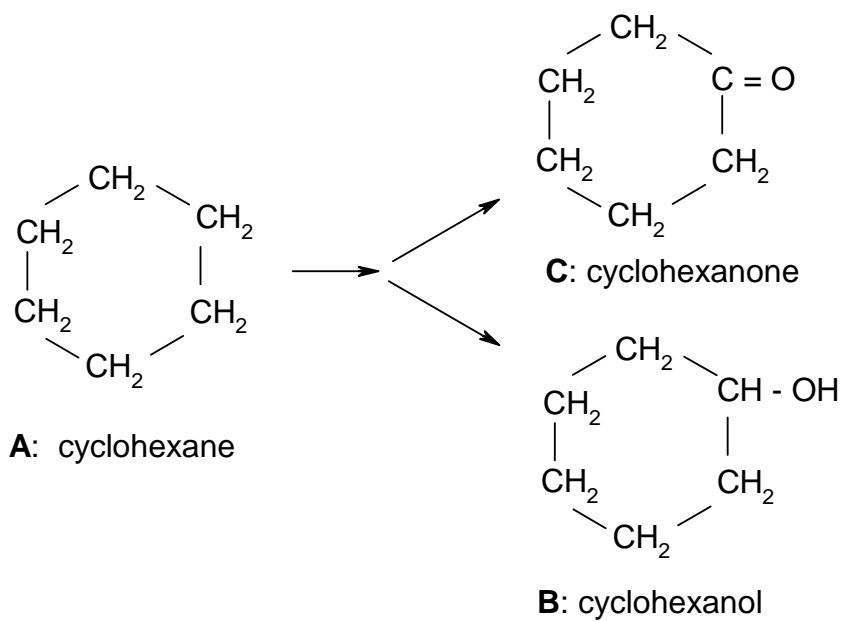


Product **D** is adipic acid which is a basic material in the production of nylon.



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 <sub>2</sub> H <sub>4</sub>	N <sub>2</sub> H <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> F <sub>2</sub>
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 <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO <sub>3</sub> <sup>2-</sup>	.....	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	.....
NH <sub>4</sub> <sup>+</sup>	N <sub>2</sub> H <sub>6</sub> <sup>2+</sup>	.....	NO <sub>2</sub> <sup>+</sup>	.....	N <sub>2</sub>

**SOLUTION**

a)

Assertion	Molecule			
	C <sub>2</sub> H <sub>4</sub>	N <sub>2</sub> H <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> F <sub>2</sub>
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 <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO <sub>3</sub> <sup>2-</sup>	CO <sub>2</sub>	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	C <sub>2</sub> <sup>2-</sup>
NH <sub>4</sub> <sup>+</sup>	N <sub>2</sub> H <sub>6</sub> <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>+</sup>	N <sub>2</sub> O <sub>4</sub>	N <sub>2</sub>



## PRACTICAL PROBLEMS

### PROBLEM 1 (practical)

Aqueous solutions of the following compounds:  $\text{AgNO}_3$ ,  $\text{HCl}$ ,  $\text{Ag}_2\text{SO}_4$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{NH}_3$  and  $\text{NaOH}$  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  $\text{cm}^3$  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 :     ↓

coloured precipitate: ↓↓

formation of a complex soluble in water: [ ]

evolution of a gas:     ↑

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

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

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

**PROBLEM 2 (practical)**

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

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  $\text{Na}_2\text{CO}_3$  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  $100 \text{ cm}^3$  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  $10.00 \text{ cm}^3$  of the solution into a  $100 \text{ cm}^3$  Erlenmeyer flask and dilute it to about  $30 \text{ cm}^3$  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.

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

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