# 9th

# ICHO

International Chemistry Olympiad

8 theoretical problems
3 practical problems

# THE NINTH
# INTERNATIONAL CHEMISTRY OLYMPIAD

## BRATISLAVA 1977
## CZECHOSLOVAKIA

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# THEORETICAL PROBLEMS

## PROBLEM 1

Compare three salts of a composition $M_2S_2O_x$ where x are three different small integers and M is an alkali metal. To each of the three salts apply some of the following assertions:

a) The O–O bond is characteristic for the anion.

b) The S–S bond is characteristic for the anion.

c) The S–O–S bond is characteristic for the anion.

d) It is formed by thermal decomposition of hydrogen sulphate.

e) It is formed by anodic oxidation of hydrogen sulphate.

f) It is formed by the reaction of an aqueous solution of sulphite with sulphur.

g) Its aqueous solution dissolves silver bromide.

h) Neutralisation of its aqueous solution with hydroxide MOH yields sulphate $M_2SO_4$.

i) In aqueous solution, it is able to oxidise Mn(II) salt to permanganate.

Problems:

1. Fill in the correct x values in the formulas given in the Table and indicate in the corresponding square by appropriate letters those assertions that may be applied to each of the given salts:

| | | | | | |
|---|---|---|---|---|---|
| $M_2S_2O$☐ | | | | | |
| $M_2S_2O$☐ | | | | | |
| $M_2S_2O$☐ | | | | | |

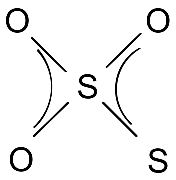
2. Write structural formulas of the anions of the above three salts and assign σ-bonds and π-bonds in them.
3. Write the chemical equations expressing the processes involved in the assertions under the letters d, e, f, g, h, i.

## SOLUTION

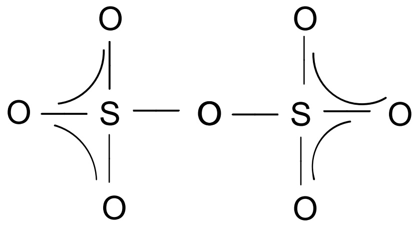
1.

| | | | | | |
|---|---|---|---|---|---|
| $M_2S_2O_3$ | b | f | g | | |
| $M_2S_2O_7$ | c | d | h | | |
| $M_2S_2O_8$ | a | e | i | | |

2.



$S_2O_3^{2-}$



$S_2O_7^{2-}$

3. d) $2\,HSO_4^- \rightarrow H_2O + S_2O_7^{2-}$

$2\,MHSO_4 \rightarrow H_2O + M_2S_2O_7$

e) $2\,HSO_4^- - 2e \rightarrow 2\,H^+ + S_2O_8^{2-}$

$2\,MHSO_4 - 2e \rightarrow 2\,H^+ + M_2S_2O_8$

f) $SO_3^{2-} + S \rightarrow S_2O_3^{2-}$

$M_2SO_3 + S \rightarrow M_2S_2O_3$

g) $AgBr + 2\,S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$

$AgBr + 2\,M_2S_2O_3 \rightarrow M_3[Ag(S_2O_3)_2] + MBr$

h) $S_2O_7^{2-} + 2\ OH^- \rightarrow 2\ SO_4^{2-} + H_2O$

$M_2S_2O_7 + 2\ MOH \rightarrow 2\ M_2SO_4 + H_2O$

i) $2\ Mn^{2+} + 5\ S_2O_8^{2-} + 8\ H_2O \rightarrow 2\ MnO_4^- + 10\ SO_4^{2-} + 16\ H^+$

$2\ MnSO_4 + 5\ M_2S_2O_8 + 8\ H_2O \rightarrow 2\ MMnO_4 + 4\ M_2SO_4 + 8\ H_2SO_4$

## PROBLEM 2 a

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

Attention

Make sure to open only the correct envelopes.

You lose points for an incorrectly opened envelope.

Return unopened envelopes together with your solution.

__________

Halogen X reacts with an aqueous solution of another halogen compound $KYO_3$ according to the equation:

$$X_2 + 2\,KYO_3 \rightarrow 2\,KXO_3 + Y_2$$

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

Choose the correct answer 1 or 2, open the correct envelope and continue in the solution according to the text in the opened envelope.

<u>Text in envelope 1</u>:

Your answer is correct. Continue.

Compound $KXO_3$ is oxidised in alkaline solution by halogen Y forming a compound $KX^{VII}O_4$ whereas halogen Y is reduced to halide KY:

$$KXO_3 + 2\,KOH + Y_2 \rightarrow KXO_4 + 2\,KY + H_2O$$

An aqueous solution of potassium halide KY yields with $AgNO_3$ solution a white precipitate AgY insoluble in water but readily soluble in aqueous ammonia solution.

3. Halogen Y is fluorine (envelope 3).
4. Halogen Y is chlorine (envelope 4).
5. Halogen Y is bromine (envelope 5).

Choose the correct answer 3, 4 or 5, open the corresponding envelope and carry on according to the instructions inside.

Text in envelope 2:

Your answer is incorrect. Choose envelope 1.

Text in envelope 3:

Your answer is incorrect. Choose answers 4 or 5.

Text in envelope 4:

Your answer is correct. Choose the final correct answer by indicating the correct alternative 6 or 7:

6. X = Br; $KXO_4 = KBrO_4$
7. X = I; $KXO_4 = KIO_4$

Text in envelope 5:

Your answer is incorrect. Choose answers 3 or 4.

## SOLUTION

The correct answers are as follows: 1, 4, 7.

## PROBLEM 2 b

The reaction of permanganate ions with hydrogen peroxide in an acidic solution gives Mn(II) salt and at the same time oxygen is released:

$$2\,MnO_4^- + 1\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 3\,O_2 + 4\,H_2O$$

$$2\,MnO_4^- + 3\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 4\,O_2 + 6\,H_2O$$

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O$$

$$2\,MnO_4^- + 7\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 6\,O_2 + 10\,H_2O$$

Problems:

1. The possible ratios of the reactants in the above equations express:
   a) all equations ☐
   b) only some of the equations ☐
   c) only one equation ☐
   d) none ☐

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

2. Which of the reactants is an oxidising agent and which is a reducing one?
3. How much potassium permanganate is needed to release 112 cm$^3$ of oxygen at STP conditions from an excess of hydrogen peroxide in acidic solution?

## SOLUTION

1. Correct is **c**.

   Explanation on the basis of electron balance:

   $Mn^{VII} + 5\,e \rightarrow Mn^{II}$

   $(O_2)^{-II} - 2\,e \rightarrow O_2^0$

   ----------------------------

   $2\,Mn^{VII} + 5\,(O_2)^{-II} \rightarrow 2\,Mn^{II} + 5\,O_2^0$

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

   Reducing agent: $H_2O_2$ or $(O_2)^{-II}$

3. $V(O_2)$ = 112 cm$^3$

$$n(O_2) = \frac{0.112\ \text{dm}^{-3}}{22.4\ \text{dm}^3\ \text{mol}^{-1}} = 0.005\ \text{mol}$$

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

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

## PROBLEM 3

The letters **A**, **B**, **C**, **D**, and **E** represent isomeric cyclobutane dicarboxylic acid, one of them being a racemic form.

It was shown that:

a) only compound **C** forms a cyclic anhydride easily,

b) **B** yields an cyclic anhydride only at higher temperatures,

c) of all the acids under investigation, only **A** releases carbon dioxide when heated,

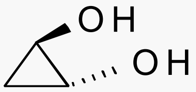
d) **D** and **E** do not change at higher temperatures,

e) 2 moles of diethyl ester of malonic acid when reacted with sodium ethoxide (EtONa), are transformed to sodium salt which by reaction with methylene iodide ($CH_2I_2$) yields a tetraester $C_{15}H_{24}O_8$. This new ester gives a tetraester $C_{16}H_{24}O_8$ in the reaction with 2 moles of sodium ethoxide and 1 mole of methylene iodide. The last mentioned tetraester is transformed by alkaline hydrolysis and subsequent acidification to a tetracarboxylic acid which when heated, gives a mixture of **B** and **E**.

Problems:

1. Give formulas corresponding to the letters **A**, **B**, **C**, **D**, and **E**. Mark the group which is above the plane of the cycle ◀ , that under the plane with ⋯

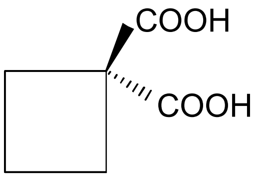
For example:



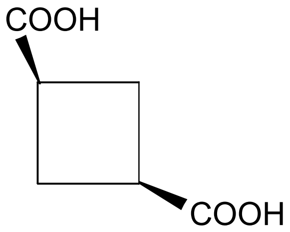
2. Express processes a), b), and c) by chemical equations.

## SOLUTION

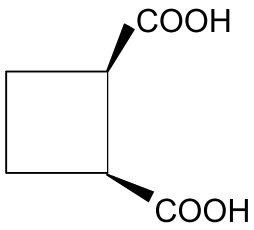
1.



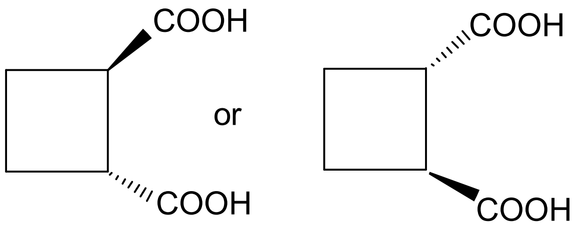
**A**



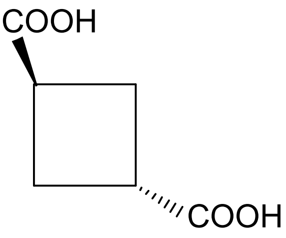
**B**



**C**

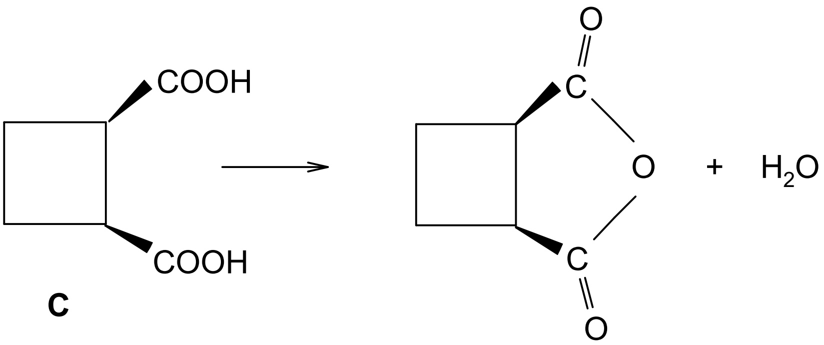


**D**



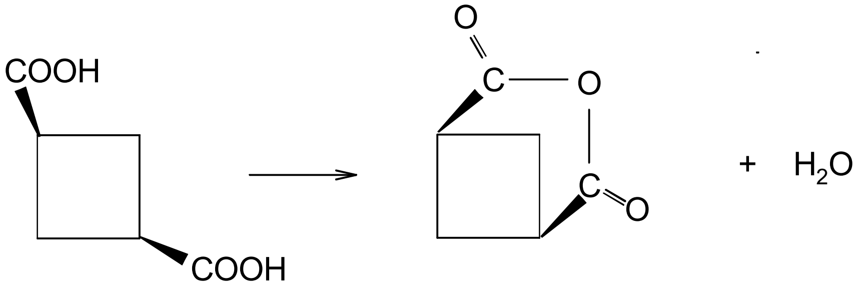
**E**

2. a)



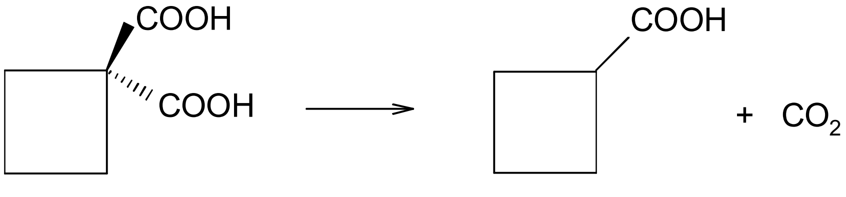
**C**

b)



**B**

c)



**A**

## PROBLEM 4 a

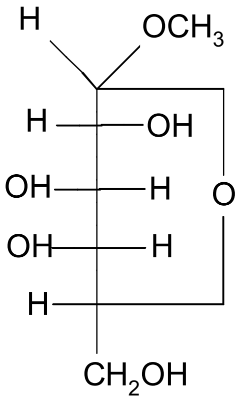
Note: The International Jury did not choose Task 4a for the competition but the alternative PROBLEM 4b.

Compounds **A** and **B**, having the same summary formula $C_7H_{14}O_6$ but different physical properties (for example melting point and specific optical rotation), belong to the group of saccharides containing six-member heterocycles. When 1 % solution of sulphuric acid is added to compound A and B respectively, the same compound C containing 40.0 % C and 6.71 % H is obtained at boiling. After reducing compound C (for example catalytically with hydrogen or with hydride $Na[BH_4]$ ) a crystalline product D was isolated which did not reduce Fehling's reagent and showed no optical activity. Compound C was oxidised with a mild oxidising agent (e. g. with a cold sodium hypobromite solution) yielding a salt of polyhydroxy monocarboxylic acid of D-configuration.

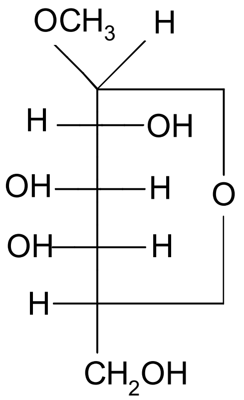
Problems:

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

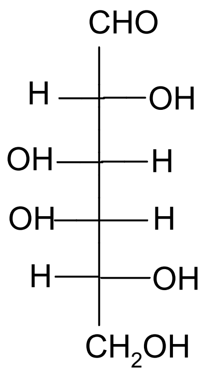
## SOLUTION



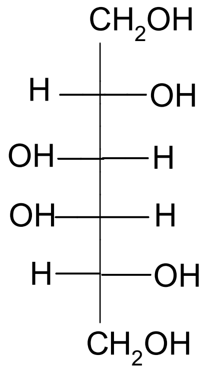
**A** (or **B**)



**B** (or **A**)



**C**



**D**

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

## PROBLEM 4 b

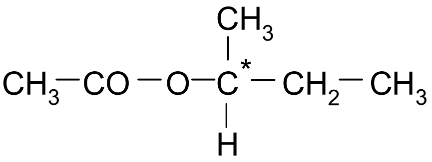
An optically active ester (11.6 g) having the summary formula $C_6H_{12}O_2$, was hydrolysed by heating with an excess of aqueous sodium hydroxide solution. After terminating the hydrolysis the alkaline reaction mixture was several times extracted with ether. The aqueous solution was not optically active. The united ether extracts were dried with anhydrous magnesium sulphate. The ether solution was filtrated, ether was distilled off from it and the residue was redistilled. 7.4 g (100 %) of a liquid boiling at 100 °C was obtained.

Problems:

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

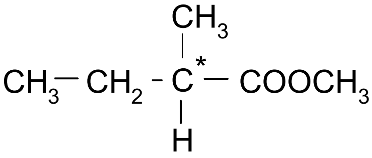
## SOLUTION

1.



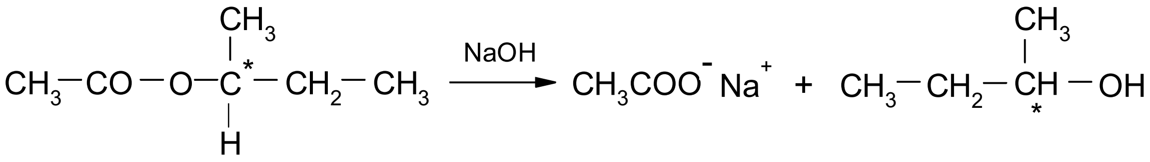
$$CH_3-CO-O-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C^*}}-CH_2-CH_3$$

2.

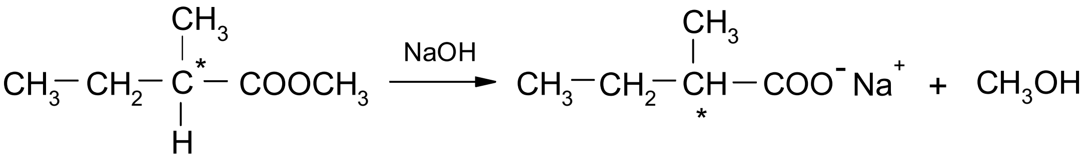


$$CH_3-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C^*}}-COOCH_3$$

**3.**



$$CH_3-CO-O-\underset{H}{\overset{CH_3}{C^*}}-CH_2-CH_3 \xrightarrow{NaOH} CH_3COO^- Na^+ + CH_3-CH_2-\underset{*}{\overset{CH_3}{CH}}-OH$$



$$CH_3-CH_2-\underset{H}{\overset{CH_3}{C^*}}-COOCH_3 \xrightarrow{NaOH} CH_3-CH_2-\underset{*}{\overset{CH_3}{CH}}-COO^- Na^+ + CH_3OH$$

## PROBLEM 5

Two copper(I) salts of the organic acids HA and HB, slightly soluble in water, form a saturated solution in buffer of a given pH.

Problems:

1. What will be the concentration of $Cu^+$ cations in the solution if the solubility products of the two salts are $K_s(CuA)$ and $K_s(CuB)$ and the ionisation constants of the acids are $K_a(HA)$ and $K_a(HB)$?

## SOLUTION

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

$$a = n(A^-) + n(HA) + n(CuA)$$

$$b = n(B^-) + n(HB) + n(CuB)$$

$$m = n(Cu^+) + n(CuA) + n(CuB)$$

The amounts of precipitates are eliminated from the equations:

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

because, when forming a system of both solid salts, the total number of particles A and B ($a + b$) must be equal to the total number of cations $Cu^+$, i. e. to the value of $m$. When the amounts of substances are divided by the volume of the solution, we get concentrations, and thus:

$$[A^-] + [HA] + [B^-] + [HB] = [Cu^+] \qquad (1)$$

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

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

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

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

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

$$[\mathrm{Cu}^+] = [\mathrm{A}^-]\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HA})}\right) + [\mathrm{B}^-]\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HB})}\right) \qquad (6)$$

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

$$[\mathrm{Cu}^+] = \frac{K_\mathrm{s}(\mathrm{CuA})}{[\mathrm{Cu}^+]}\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HA})}\right) + \frac{K_\mathrm{s}(\mathrm{CuB})}{[\mathrm{Cu}^+]}\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HB})}\right) \qquad (7)$$

$$[\mathrm{Cu}^+] = \sqrt{K_\mathrm{s}(\mathrm{CuA})\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HA})}\right) + K_\mathrm{s}(\mathrm{CuB})\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HB})}\right)}$$

## PROBLEM 6

Amino acids can be determined by measuring the volume of nitrogen released in their reaction with nitrous acid (Van Slyke's method), for example:

$$CH_3CH(NH_2)COOH + HNO_2 \rightarrow CH_3CH(OH)COOH + N_2 + H_2O$$

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

$$CH_3CH(NH_2)COOH + HClO_4 \rightarrow CH_3CH(N^+H_3)COOH + ClO_4^-$$

The excess of the perchloric acid is determined then by titration with a volumetric solution of sodium acetate (carried out in a non-aqueous solution).

50.0 $cm^3$ of a 0.100-normal solution of perchloric acid were added to a sample of glycine in glacial acetic acid. The excess of the perchloric acid was determined after the reaction by titration with 0.150-normal volumetric solution of sodium acetate. The consumption was 16.0 $cm^3$.

Problem:

1. What would be the volume of the nitrogen released at a pressure of 102 658 Pa and a temperature of 20 °C when assumed that the same quantity of sample were analysed by the Van Slyke's method?

## SOLUTION

$n(HClO_4) = V c = 0.0500\ dm^3 \times 0.100\ mol\ dm^{-3} = 0.00500\ mol$

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

Consumed in the reaction:

$n(HClO_4) = (0.00500 - 0.00240)\ mol = 0.00260\ mol$

$V(HClO_4) = 0.0260\ dm^3$

Since:

$n(HClO_4) = n(\text{glycine}) = n(N_2) = 0.0260\ mol$

then:

$$V(N_2) = \frac{nRT}{p} = \frac{0.0260\ mol \times 8.314\ J mol^{-1} K^{-1} \times 293.1\ K}{102.658\ kPa} = 0.617\ dm^3$$

## PROBLEM 7

Photosynthesis by be summarised by the overall equation:

$$CO_2\,(g) + H_2O\,(l) \xrightarrow[\text{chlorophyll}]{\text{light}} C_6H_{12}\,(s) + 6\,O_2\,(g)$$

for which values of $\Delta H$ and $\Delta S$ at 25 ℃ are as follows:

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

$\Delta H = 2.816 \times 10^6$ J mol$^{-1}$, $\Delta S = -182$ J K$^{-1}$ mol$^{-1}$ if $\Delta H$ and $\Delta S$ values are related to one mole of reaction changes.

Imagine that there have been devised electrodes that would allow selective reduction of oxygen to water and oxidation of glucose to carbon dioxide in a galvanic cell, i. e a reverse process when compared with that of the photosynthetic reaction.

Problems:

1. What will be the electromotive force of the cell in which light energy would be transformed to electric energy by means of the photosynthetic reaction?
   Note: In the envelope you can find the relation between the electromotive force and the change of free enthalpy of the reaction. (Attention: If you open the envelope you lose some points.)
2. In case we would want to quantify the symbol "light" in the equation of photosynthesis, we would ask: how many moles of photons with wavelength for example 500 nm take part in the above reaction? Calculate.
3. Calculate, what would be the electric power of a square swimming pool with a side of 10 m containing green algae capable of the photosynthetic reaction if under average illumination a current of 1 mA can be expected from the area of 1 cm$^2$.

## SOLUTION

1. Two alternative solutions:

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

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

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

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

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

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

Relation between the electromotive force and the change of free enthalpy of the reaction taking place in a cell:

$$-\Delta G = n\, F\, E$$

where n is so-called charge number

where n is the number of moles of charges which passed through the electrode during the reaction.

In our case, n has the value equal to 24 since one molecule of oxygen is reduced according to the equation:

$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$

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

Since one voltcoulomb is one joule, then:

$$E = \frac{-(-2.87\times10^6)\ \text{V C mol}^{-1}}{24 \times 96\,487\ \text{C mol}^{-1}} = 1.24\ \text{V}$$

$$E = \frac{-(-2.87\times10^6)\ \text{V C}}{24\ \text{mol} \times 96\,487\ \text{C mol}^{-1}} = 1.24\ \text{V}$$

2. Energy of absorbed photons is the only source of energy which enables the course of photosynthesis, and therefore, the number of absorbed photons x multiplied by their energy must be equal to the increase of energy in the system, i. e. to the value of $2.87 \times 10^6$ J. Thus:

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

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

$$= \frac{2.87 \times 10^6\ \text{J} \times 500.10^{-9}\ \text{m}}{6.6256.10^{-34}\ \text{J s} \times 2.9979.10^{8}\ \text{m s}^{-1} \times 6.022.10^{23}\ \text{mol}^{-1}} =$$

= 11.99 ≈ 12 mol of photons

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

The total electric power :

$1.24\ V \times 10\ A\ m^{-2} \times 100\ m^2 = 1.24\ kW$

## PROBLEM 8 a

Note: The International Jury did not choose Task 8a for the 9th IChO but the alternative Task 8b.

Due to the lack of other methods in the middle of the 19th century a chemist determining the molar mass of a new element **X** chose the following procedure:

He succeeded in preparing four compounds **A**, **B**, **C**, and **D** containing the element **X** and determined its content (in mass %) in each of the compounds. At 250 °C all four compounds were in gaseous state. They were individually transferred into previously evacuated flasks until the pressure reached the value of $1.013 \cdot 10^5$ Pa and then the flasks were weighed. After subtracting the weight of the empty flask, the mass of the gas inside was determined. This procedure was repeated with nitrogen. Thus the following Table of data was obtained:

| Gas | Total mass of gas | Content of element X in gas (mass %) |
|---|---|---|
| $N_2$ | 0.652 g | 0 |
| **A** | 0.849 g | 97.3 |
| **B** | 2.398 g | 68.9 |
| **C** | 4.851 g | 85.1 |
| **D** | 3.583 g | 92.2 |

Problem:

1. Determine the probable molar mass of element **X**.

### SOLUTION

$$n(N_2) = \frac{m(N_2)}{M(N_2)} = \frac{0.652 \text{ g}}{28 \text{ g mol}^{-1}} = 0.0233 \text{ mol}$$

At a temperature of 250 °C all the substances **A**, **B**, **C**, and **D** are considered to behave as ideal gases and according to Avogadro's law:

$$n(N_2) = n(\mathbf{A}) = n(\mathbf{B}) = n(\mathbf{C}) = n(\mathbf{D})$$

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

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

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

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

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

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

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

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

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

Because in one molecule of a compound there must be at least one atom **X** or its integer multiple, we must calculate the highest common measure of the molar masses obtained. It is in our case equal to 35.45 g mol$^{-1}$ in average which can be considered as the probable molar mass of element **X**. It is only the most probable value because its integer fraction cannot be excluded.

## PROBLEM 8 b

Among other factors, deterioration of the environment is manifested also by air pollution with carbon monoxide. Its most powerful source are combustion engines. The toxicity of carbon monoxide is caused by the fact that it forms with the blood dye - haemoglobin (Hb), the compound carbonyl haemoglobin (HbCO):

$$\text{Hb} + \text{CO} \rightarrow \text{HbCO}$$

The chemical bond in carbonyl haemoglobin is about 200 times stronger than that in oxyhaemoglobin ($HbO_2$) originating under common conditions. Consequently, haemoglobin cannot be used in oxygen transfer. The lack of oxygen starts to be felt from 50 ppm carbon monoxide in the air, i. e. 10 % carbonyl haemoglobin in blood.

Air oxygen dissolves in blood in the lungs and its concentration under common conditions is kept at $1.6 \times 10^{-6}$ mol dm$^{-3}$ by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to $8 \times 10^{-6}$ mol dm$^{-3}$

Problems:

1. Calculate the rate of oxyhaemoglobin formation if the rate constant is $k = 2.1 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ (at 37 °C – normal body temperature).
2. In some cases (carbon monoxide poisoning) an increase of the rate of oxyhaemoglobin formation up to $1.1 \times 10^{-4}$ mol dm$^{-3}$ s$^{-1}$ is needed.
   a) Calculate the required concentration of oxygen assuming that the concentration of haemoglobin in blood is constant.
   b) Suggest of practical solution on the assumption that the concentration of oxygen in blood is proportional to the pressure of oxygen entering the lungs.

## SOLUTION

1. $v = k\,[\text{Hb}][\text{O}_2]$

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

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

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

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

Because 1 mole of oxygen ($O_2$) is needed to form 1 mole of oxyhaemoglobin, the rate of oxygen consumption is the same as the of oxyhaemoglobin formation.

2. $[O_2] = \dfrac{v}{k\,[\text{Hb}]}$

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

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

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

$\underline{[O_2] = 6.5 \times 10^{-6} \text{ mol dm}^{-3}}$

The oxygen concentration must increase up to 6.5 × $10^{-6}$ mol $\text{dm}^{-3}$. Oxygen concentration can be affected by elevation of air pressure only partially. The fourfold increase of oxygen concentration would demand an increase of the air pressure four times in comparison with the normal value. This pressure would be harmful for living organisms and therefore, air enriched with oxygen is breathed.

# PRACTICAL PROBLEMS

## PROBLEM 1 (practical)

You will follow the concentration change of one of the reactants by the method of comparative visual colorimetry. From data obtained experimentally plot graphically the change of the reactant concentration in dependence on time.

Procedure:

1. *Making of the comparative colorimetric scale of bromine solution*

Measure with a syringe into 10 identical test-tubes the following quantities of bromine water (0.01-molar): into the first one – 10.0 cm$^3$; 2nd – 9.0 cm$^3$; 3rd – 8.0 cm$^3$, ....... 9th – 2.0 cm$^3$; into the tenth one – 1.0 cm$^3$. Then add to all the test-tubes (except the first one) distilled water to reach a total volume of 10.0 cm$^3$ in each. Seal the test-tubes with stoppers and mix the solutions. Put the test-tubes in a stand with a white background. Finally calculate the concentration (in mol dm$^{-3}$) of bromine in the solutions in all test-tubes.

2. *Reaction of bromine solution with formic acid*

Carry out the reaction by mixing 100.0 cm$^3$ of bromine solution with 1.0 cm$^3$ of 1.00-molar solution of formic acid. Immediately after mixing transfer 10.0 cm$^3$ of the resulting solution to the test-tube identical with that used for colorimetric scale. By comparing the colour shade of the reaction mixture (in one-minute intervals) with that of the solutions in the scale, investigate changes of bromine concentration in dependence on time.

Put the data in a table containing time ($t$) and concentration of $Br_2$.

Task:

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

Questions:

1. Write the equation for the reaction of bromine with formic acid assuming that the reactants are in stoichiometric amounts.

2. In analytical chemistry a volumetric solution of bromine can be prepared by dissolving a mixture of bromate and bromide in acid medium. Explain this mode of preparation by means of a chemical equation in ionic form.

## SOLUTION

Questions:

1. $HCOOH (aq) + Br_2 (aq) \rightarrow CO_2 (g) + 2 H^+ (aq) + 2 Br^- (aq)$
2. $BrO_3^- + 5 Br^- + 6 H^+ \rightarrow 3 Br_2 + 3 H_2O$

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## PROBLEM 2

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

Procedure:

For the reaction of a hypochlorite solution with a propanone use solutions tempered at laboratory temperature (check). Put 100,0 cm$^3$ of a hypochlorite solution into a thermobeaker, insert a thermometer and keep adding a 4-molar solution of propanone in 1,0 cm$^3$ portions from burette, stirring the reaction mixture continuously by means of the thermometer (carefully, do not break!). Stir the reaction mixture thoroughly after each addition and read the highest temperature reached. Keep on adding the propanone solution as long as the temperature rises. Then add three more portions and finish the experiment. Keep the reaction mixture for possible later use.

Problems:

1. Draw a titration curve from the data of the temperature changes and consumption of propanone solution. Read the end point of the titration from the curve. Express the equivalent amounts of the reactants in moles.
2. Write equation for the chemical reaction and name the product that is formed.
3. Suggest a calculation for the approximate value of the reaction heat from the data obtained.
4. Consider the procedure of isolation of the product from the reaction mixture and give the method of its identification.
5. The exact concentration of a hypochlorite solution can also by determined by measuring the volume of oxygen released after catalytic decomposition of hypochlorite. Illustrate the principle of this method by means of a chemical equation and show schematically the procedure for the calculation.

## SOLUTION

2. $CH_3COCH_3 + 3\ ClO^- \rightarrow \underset{\text{chloroform}}{CHCl_3} + 2\ OH^- + CH_3COO^-$

3. Calculation of heat evolved in the course of the reaction:

   $Q = m\, c\, \Delta t$

   $Q$ – reaction heat,

   $m$ – mass of the solution,

   $c$ – specific heat capacity of the solutions taking part in the reaction,

   $\Delta t$ – temperature difference (elevation of temperature)

   On the basis of the data obtained in the task, it is possible to calculate $Q$ value per one mole of reactant.

4. The mixture contains:

   reactants – (excess of about 3 cm$^3$ of the 4-molar propanone solution),

   products – $CHCl_3$, $OH^-$, $CH_3COO^-$.

   Acetone and chloroform are separated from other substances in the aqueous solution by means of a separatory funnel and a subsequent distillation.

   Identification of chloroform: smell, density.

5. $2\ ClO^- \rightarrow O_2$

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

## PROBLEM 3

If a known excess of hydroxide solution with a known concentration is added to a weighed sample of ammonium salt and the liberated ammonia is removed by boiling, it is possible to determine the unreacted quantity of hydroxide by titration with a volumetric solution of an acid.

Procedure:

Three samples of an ammonium salt, weighed with accuracy of 0.001 g, are at your disposal. Introduce each of them into a 250 cm$^3$ Erlenmeyer flask. Add 50.0 cm$^3$ of a 0.2-normal sodium hydroxide solution to each sample. Put several boiling stones into each mixture and heat the flasks slowly on a small flame till there is no more ammonia in the liberating vapours. After expelling ammonia, cool the solution to the laboratory temperature, add 2 or 3 drops of indicator solution (Bromothymol blue) and titrate with a 0,2-normal volumetric solution of oxalic acid to the first lasting yellow colour of the solution.

Problems:

1. Calculate the molar mass of ammonium salt from the experimental data.
2. The sample is a salt of a monobasic inorganic acid. Consider which one.
3. Calculate the absolute and relative error of your determination.
4. Give reactions by means of which ions of the salt can be proved in the solution.