13th

ICHO

International Chemistry Olympiad

6 theoretical problems
3 practical problems
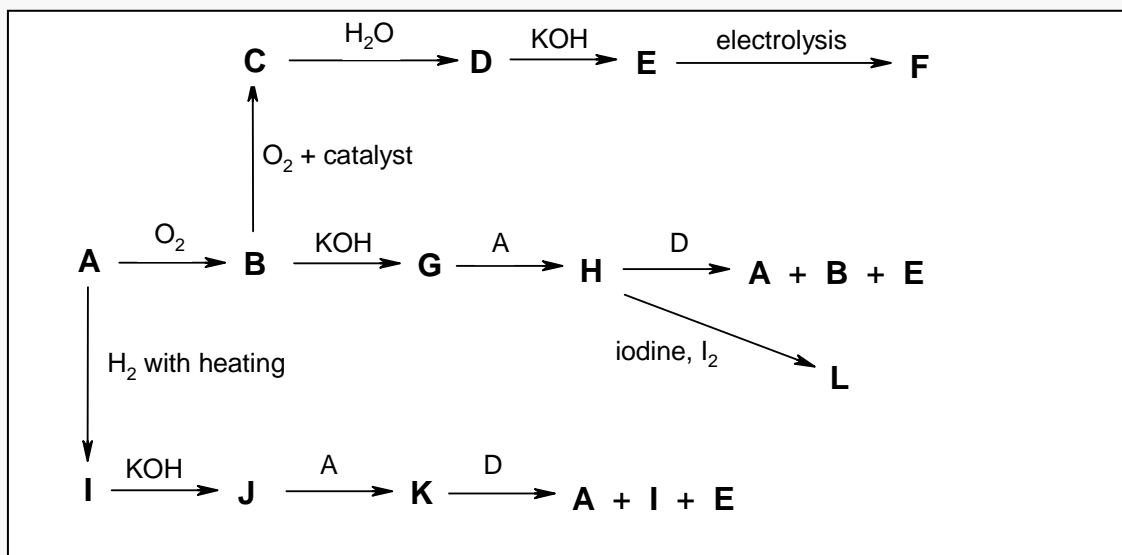
THE THIRTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD

BURGAS 1981
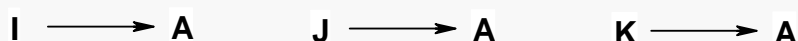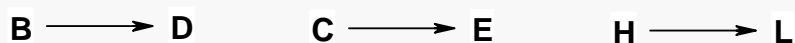### BULGARIA

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THEORETICAL PROBLEMS

PROBLEM 1

The sample **A** participates in the transformations in scheme 1. Only the products containing **A** are shown in the scheme 1.

Scheme 1

1. Substance **A** is a solid and is insoluble in water.

2. Substances **B** and **I** are gases soluble in water.

3. Substances **E**, **F**, **J** and **K** are solid and soluble in water.

4. Aqueous solutions of **B**, **G**, **H**, **I**, **J** and **K** react with **F**, the products in all cases being **E** and **D**.

5. The following transformations occur during the interaction with an aqueous solution of iodine:

B ⟶ D	C ⟶ E	H ⟶ L
I ⟶ A	J ⟶ A	K ⟶ A

Write the chemical equations for the above interactions and balance them.

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SOLUTION

(1) $S + O_2 \rightarrow SO_2$

(2) $2\ SO_2 + O_2 \rightarrow 2\ SO_3$

(3) $SO_3 + H_2O \rightarrow H_2SO_4$

(4) $2\ KOH + H_2SO_4 \rightarrow K_2SO_4 + 2\ H_2O$

(5) $2\ SO_4^{2-} - 2\ e- \rightarrow S_2O_8^{2-}$

(6) $SO_2 + 2\ KOH \rightarrow K_2SO_3 + H_2O$

(7) $K_2SO_3 + S \rightarrow K_2S_2O_3$

(8) $K_2S_2O_3 + H_2SO_4 \rightarrow K_2SO_4 + S + SO_2 + H_2O$

(9) $H_2 + S \rightarrow H_2S$

(10) $H_2S + 2\ KOH \rightarrow K_2S + 2\ H_2O$

(11) $K_2S + x\ S \rightarrow K_2S_{(x+1)}$

(12) $K_2S_{(x+1)} + H_2SO_4 \rightarrow K_2SO_4 + x\ S + H_2S$

(13) $SO_2 + 2\ H_2O + K_2S_2O_8 \rightarrow K_2SO_4 + 2\ H_2SO_4$

(14) $K_2SO_3 + H_2O + K_2S_2O_8 \rightarrow 2\ K_2SO_4 + H_2SO_4$

(15) $K_2S_2O_3 + 5\ H_2O + 4\ K_2S_2O_8 \rightarrow 5\ H_2SO_4 + 5\ K_2SO_4$

(16) $H_2S + 4\ H_2O + 4\ K_2S_2O_8 \rightarrow 5\ H_2SO_4 + 4\ K_2SO_4$

(17) $K_2S + 4\ H_2O + 4\ K_2S_2O_8 \rightarrow 4\ H_2SO_4 + 5\ K_2SO_4$

(18) $K_2S_{(x+1)} + (4x + 1)\ H_2O + 4\ x\ K_2S_2O_8 \rightarrow 5\ x\ H_2SO_4 + (4x + 1)\ K_2SO_4$ (+S)

(19) $SO_2 + 2\ H_2O + I_2 \rightarrow H_2SO_4 + 2\ HI$

(20) $K_2SO_3 + H_2O + I_2 \rightarrow K_2SO_4 + 2\ HI$

(21) $2\ K_2S_2O_3 + I_2 \rightarrow 2\ KI + K_2S_4O_6$

(22) $H_2S + I_2 \rightarrow 2\ HI + S$

(23) $K_2S + I_2 \rightarrow 2\ KI + S$

(24) $K_2S_x + I_2 \rightarrow 2\ KI + x\ S$

A: S **B**: SO_2 **C**: SO_3 **D**: H_2SO_4

E: K_2SO **F**: $K_2S_2O_8$ **G**: K_2SO_3 **H**: $K_2S_2O_3$

I: H_2S **J**: K_2S **K**: K_2S_x **L**: $K_2S_4O_6$

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PROBLEM 2

Maleic acid (H_2A) is a weak dibasic acid. The correlation between the relative quantities of H_2A, HA^-, A^{2-}:

$$\alpha_0 = \frac{c(H_2A)}{c} \qquad \alpha_1 = \frac{c(HA^-)}{c} \qquad \alpha_2 = \frac{c(A^{2-})}{c}$$

and pH values of the solution show that:

a) $\alpha_0 = \alpha_1$ for pH = 1.92

b) $\alpha_1 = \alpha_2$ for pH = 6.22

Find:

1. The values of the dissociation constants of maleic acid for the first (K_1) and the second (K_2) degree of dissociation.

2. The values of α_0, α_1, and α_2 for pH = 1.92 and pH = 6.22.

3. What is the value of pH when α_1 attains a maximum value? Find the maximum value of α.

4. Which of the acid-base indicators in the table are suitable for titration of a 0.1 M solution of maleic acid (as a monobasic and as a dibasic acid) with 0.1 M NaOH?

Fill in the table with the correct answers.

All the activity coefficients should be considered equal to 1.

Indicator	pH interval
Methyl green	0.1 – 2.0
Tropeolin 00	1.4 – 3.2
β-Dinitrophenol	2.4 – 4.0
Bromphenol blue	3.0 – 4.6
Congo red	3.0 – 5.2
Methyl red	4.4 – 6.2
Bromphenol red	5.0 – 6.8
Bromthymol blue	6.0 – 7.6
Phenol red	6.8 – 8.0
Cresol red	7.2 – 8.8

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Thymol blue	8.0 – 9.6
Phenolphthalein	8.2 – 10.0
Alizarine yellow	10.1 – 12.1
Tropeolin 0	11.0 – 13.0
1,3,5-Trinitrobenzene	12.2 – 14.0

Table

1		$K_1 =$
		$K_2 =$
2	pH = 1.92	$\alpha_0 =$
		$\alpha_1 =$
		$\alpha_2 =$
	pH = 6.22	$\alpha_0 =$
		$\alpha_1 =$
		$\alpha_2 =$
3		pH =
		$\alpha_1 =$
4		pH =
	First indicator equivalence point	1.
		2.
		3.
		4.
		pH =
	Second indicator equivalence point	1.
		2.
		3.
		4.

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SOLUTION

1. $\alpha_0 = \alpha_1$

    $K_1 = c_{H^+} = 10^{-pH} = 10^{-1.92} = 1.20 \times 10^{-2}$

    $\alpha_1 = \alpha_2$

    $K_2 = c_{H^+} = 10^{-pH} = 10^{-6.22} = 6.02 \times 10^{-7}$

2. $F = c_{H^+}^2 + K_1\, c_{H^+} + K_1\, K_2$

    $pH = 1.92; \quad c_{H^+} = 10^{-1.92} = 1.20 \times 10^{-2}; \quad F = 2.88 \times 10^{-4}$

    $\alpha_0 = \alpha_1 = \dfrac{c_{H^+}^2}{F} = \dfrac{(1.20 . 10^{-2})^2}{2.88 . 10^{-4}} = 0.500$

    $\alpha_2 = \dfrac{K_1\, K_2}{F} = \dfrac{1.20 . 10^{-2} \times 6.02 . 10^{-7}}{2.88 . 10^{-4}} = 2.51 \times 10^{-5}$

    $pH = 6.22; \quad c_{H^+} = 10^{-6.22} = 6.02 \times 10^{-7}; \quad F = 1.445 \times 10^{-8}$

    $\alpha_0 = \dfrac{c_{H^+}^2}{F} = \dfrac{(6.02 \times 10^{-7})^2}{1.445 \times 10^{-8}} = 2.51 \times 10^{-5}$

    $\alpha_{1 = }\alpha_2 = \dfrac{K_1\, K_2}{F} = \dfrac{1.20 \times 10^{-2} \times 6.02 \times 10^{-7}}{1.445 \times 10^{-8}} = 0.500$

3. $(\alpha)'_{c_{H^+}} = \dfrac{\left[K_1 F - K_1\, c_{H^+} (2 c_{H^+} + K_1) \right]}{F^2} = 0$

    $c_{H^+}^2 = K_1\, K_2$

    $c_{H^+} = \sqrt{(1.20 \times 10^{-2} \times 6.02 \times 10^{-7}} = 8.50 \times 10^{-5}\ mol\ dm^{-3}$

    $F = 1.034 \times 10^{-6} \qquad pH = 4.07$

    $\alpha_1 = \dfrac{K_1\, c_{H^+}}{F} = \dfrac{1.20 \times 10^{-2} \times 8.50 \times 10^{-5}}{1.034 \times 10^{-6}} = 0.986$

    The pH and the maximum value of α_1 can be estimated either by calculating α_1 for a set of values of c_{H^+} in the interval $1 \times 10^{-5} - 1 \times 10^{-3}\ mol\ dm^{-3}$ or from the condition that α_1 can reach a maximum value only when $\alpha_0 = \alpha_2$

4. The first equivalence point is found in the region of the α_1 maximum at pH = 4.07 where $\quad c_{HA^-} = c_{NaHA} = \dfrac{0.1}{2} = 0.05\ mol\ dm^{-3}$.

    The second equivalence point is found in the alkaline region, where:

    $c_{OH^-} = c_{HA^-} \qquad c_{A^{2-}} = \dfrac{0.1}{3} - c_{OH^-} = 0.0333$

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$$c_{H+}^2 = \frac{K_2\, c_{HA^-}}{c_{A^{2-}}} = \frac{K_2\, c_{OH^-}}{c_{A^{2-}}} = \frac{K_2\, K_w}{c_{H^+}\, c_{A^{2-}}}$$

$$c_{H^+} = \sqrt{\frac{K_2\, K_w}{c_{A^{2-}}}} = \sqrt{\frac{6.02\times10^{-7} \times 1\times10^{-14}}{0.0333}} = 4.25\times10^{-10}\ mol dm^{-3}$$

pH = 9.37

Indicators:
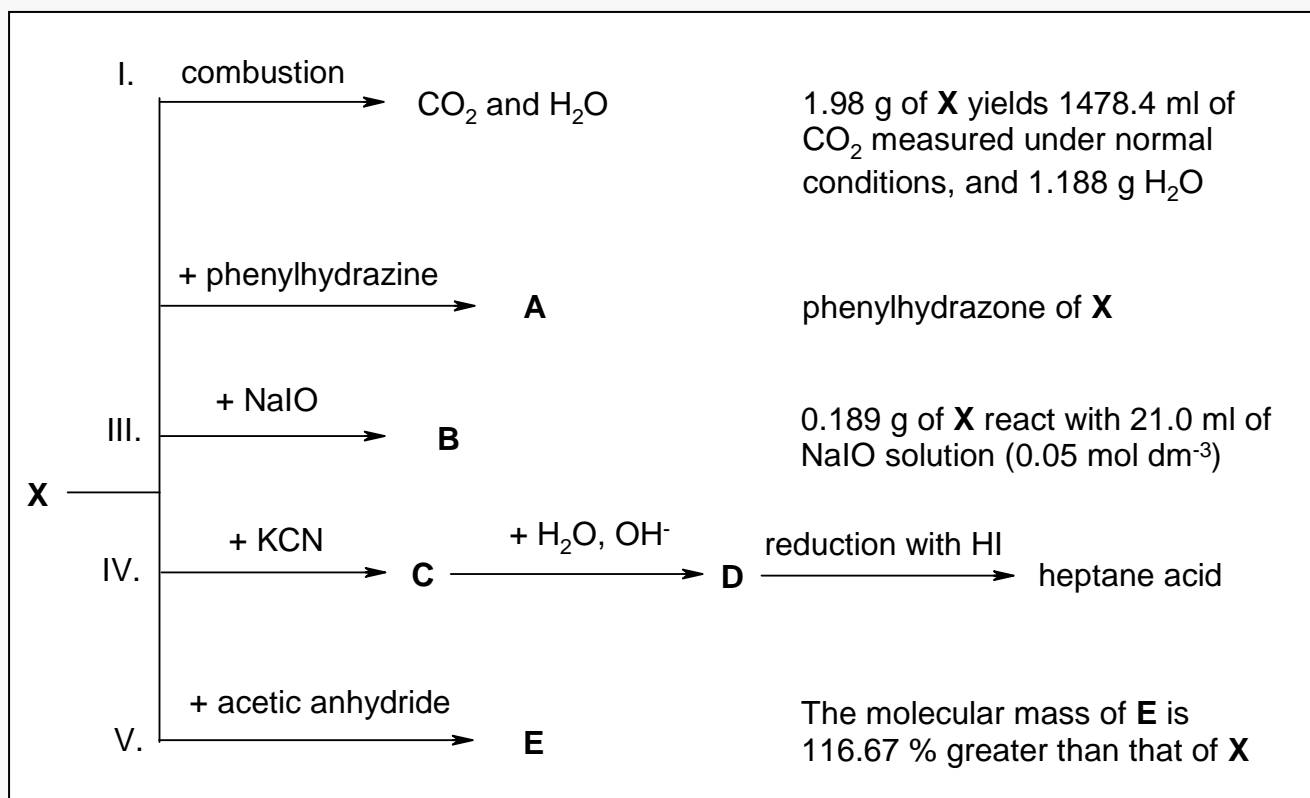
Bromphenol blue, Congo red, thymol blue, phenolphthalein.

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PROBLEM 3

Compound **X** has been isolated from a neutral product. Different reagents have been used to establish the structure of X. The following results were obtained:

I.   combustion

→ CO_2 and H_2O 1.98 g of **X** yields 1478.4 ml of CO_2 measured under normal conditions, and 1.188 g H_2O

+ phenylhydrazine

→ **A**   phenylhydrazone of **X**

III.   + NaIO

→ **B**   0.189 g of **X** react with 21.0 ml of NaIO solution (0.05 mol dm^{-3})

X

IV.   + KCN   + H_2O, OH$^-$ reduction with HI

→ **C** ────→ **D** ────────→ heptane acid

V.   + acetic anhydride

→ **E**   The molecular mass of **E** is 116.67 % greater than that of **X**

1. What conclusions can be drawn on the composition and the structure of **X** on the basis of the data obtained from each of the above interactions. The conclusions should be formulated in the most concise and clear way. Fill in the table without describing how you reached your conclusions.

I.   …………………………………..

II.   …………………………………..

III.   …………………………………..

IV.   …………………………………..

V.   …………………………………..

2. Write the formula of substance **X** on the basis of the data about the composition and structure obtained in point 1.

3. Write the formulae of substances **A**, **B**, **C**, **D**, and **E** and the formula for heptane acid.

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4. To what natural substances could this structure correspond? Write the name of the substance and draw the structural formula which best describes its structure properties.

5. Give three properties of this compound that do not correspond to the structure found in point 2.
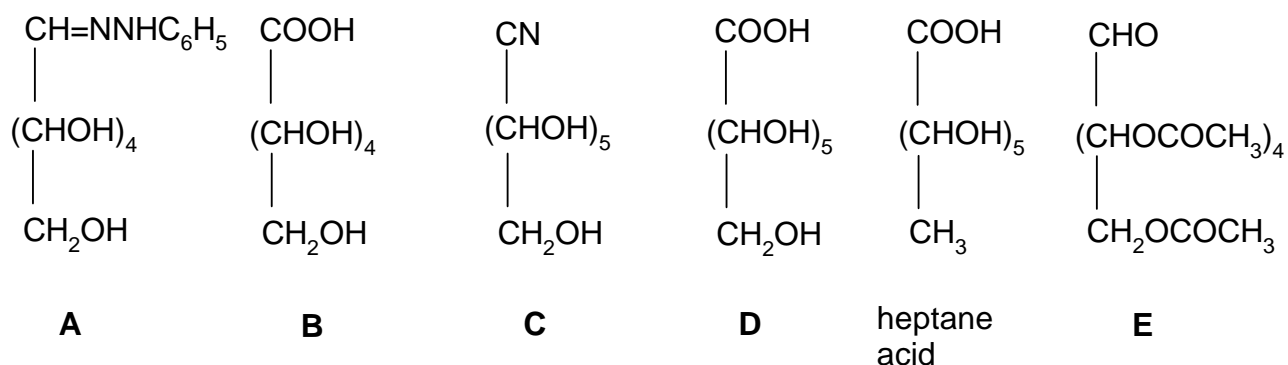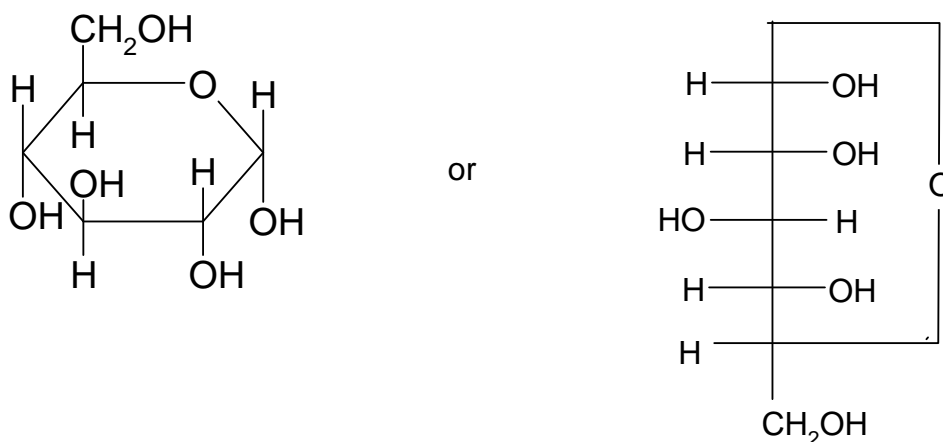
SOLUTION

1.

Reaction	Yielding
I	The simplest empirical formula, CH_2O
II	Presence of a C=O group
III	Presence of a –CHO group
	M, calculated for a single CHO- 180/n
	(n – number of CHO groups)
IV	Continuous chain of 6 C atoms
	1 CHO, $C_6H_{12}O_6$ (M = 180)
V	5 OH groups

2. $HOCH_2(CHOH)_4CHO$

3.

$CH=NNHC_6H_5$	COOH	CN	COOH	COOH	CHO
$(CHOH)_4$	$(CHOH)_4$	$(CHOH)_5$	$(CHOH)_5$	$(CHOH)_5$	$(CHOCOCH_3)_4$
CH_2OH	CH_2OH	CH_2OH	CH_2OH	CH_3	CH_2OCOCH_3
A	**B**	**C**	**D**	heptane acid	**E**

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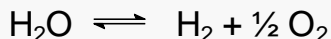
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4.   D – (+) – glucose
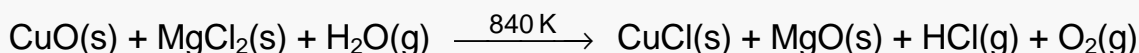

5.   –   does not participate in some reactions typical for aldehydes (e. g. with $NaHSO_3$ or Schiff's reagent),

      –   the mutarotation phenomenon,

      –   a stronger reactivity of one of the five OH groups (displayed for example in the interaction with CH_3OH and HCl leading to the methylation of only one OH group).
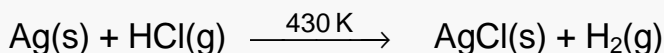
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PROBLEM 4

The thermal decomposition of water

$$H_2O \rightleftharpoons H_2 + \frac{1}{2} O_2$$

can be traced ($\alpha = 10^{-3}$) at temperature above 1700 K. This process can be realized at temperatures 800 – 900 K as well as through subsequent stages carried out in a cycle. Suggest such a process on the basis of the reactions:

$$CuO(s) + MgCl_2(s) + H_2O(g) \xrightarrow{840\,K} CuCl(s) + MgO(s) + HCl(g) + O_2(g)$$

and

$$Ag(s) + HCl(g) \xrightarrow{430\,K} AgCl(s) + H_2(g)$$

satisfying the following requirements:

1. Only water should be consumed during the process.
2. Oxygen and hydrogen alone should be the end products of the process.
3. In addition to the above substances, a 25 % ammonia solution is needed for the cycle.
4. The temperature for each step in the cycle should not exceed 840 K.

SOLUTION

1. $2\ CuO + 2\ MgCl_2 + H_2O \xrightarrow{840\,K} 2\ CuCl + 2\ MgO + 2\ HCl + 0.5\ O_2$

2. $Ag + 2\ HCl \xrightarrow{430\,K} 2\ AgCl + H_2$

3. $2\ CuCl + 4\ NH_3 \longrightarrow 2\ [Cu(NH_3)_2]^+ + 2\ Cl^-$

4. $2\ AgCl + 4\ NH_3 \longrightarrow 2\ [Ag(NH_3)_2]^+ + 2\ Cl^-$

5. $2\ [Cu(NH_3)_2]^+ + 2\ [Ag(NH_3)_2]^+ \longrightarrow 2\ Ag \downarrow + 2\ [Cu(NH_3)_4]^{2+}$

6. $2\ [Cu(NH_3)_4]^{2+} + 2\ MgO \xrightarrow{boiling} 2\ CuO \downarrow + 2\ Mg^{2+} + 8\ NH_3 \uparrow$

7. $2\ Mg^{2+} + 4\ Cl^- \xrightarrow{evaporation} 2\ MgCl_2$

8. $H_2O \longrightarrow H_2 + 0.5\ O_2$

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PROBLEM 5

Compounds **B** and **C** are structural isomers. They can be obtained when hydrocarbon **A** interacts with chlorine. Hydrocarbon **A** is a basic product of an industrial organic synthesis. It can react with ozone, yielding an ozonide.

Isomer **B** can be used for the technical production of compounds **D** and **E** that are the initial compounds in the production of the fibre nylon:

$6,6$-H–[NH(CH$_2$)$_6$NHCO(CH$_2$)$_4$CO]$_n$– OH.

Compound **D** is soluble in bases, **E** in acids.

The reaction between isomer **C** and an alcohol solution of an alkaline base yields monomer **F** which is used for the production of chloroprene (neoprene) rubber

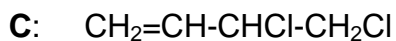–[–CH$_2$CCl = CHCH$_2$–]$_n$.
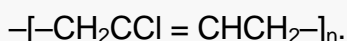
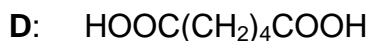This method has a technical application.

1. Write down the structural formulae of **A**, **B**, **C**, **D**, **E**, **F** and their names in the IUPAC nomenclature.

2. Write down the mechanism of the reaction between hydrocarbon **A** and chlorine. What type of reaction is it in terms of its mechanism? Which of the two isomers is obtained in larger quantities under ordinary conditions?

3. Write down the equations for:
   – the production of **D** and **E** from isomer **B**,
   – the production of monomer **F** from isomer **C**,
   – the ozonolysis of hydrocarbon **A** and hydrolysis of the ozonide.

4. Write down the chemical scheme for an industrial production of hydrocarbon **A** from the hydrocarbon which is main component of natural gas.

5. For chloroprene rubber, write down the formulae of the possible steric forms of the elementary unit.
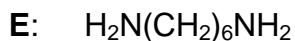
SOLUTION

1. **A**: CH$_2$=CH-CH=CH$_2$

     1,3-butadiene

   B: ClCH$_2$-CH=CH-CH$_2$Cl

     1,4-dichloro-2-butene

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C: $CH_2=CH-CHCl-CH_2Cl$

3,4-dichloro-1-butene

D: $HOOC(CH_2)_4COOH$

hexanedioic acid

E: $H_2N(CH_2)_6NH_2$

1,6-hexandiamine

F: $CH_2=CCl-CH=CH_2$

2-chloro-1,3-butadiene

2.

1,4-dichloro-2-butene

3. $ClCH_2CH=CHCH_2Cl + 2\ KCN \longrightarrow NCCH_2CH=CHCH_2CN + 2\ KCl$

$NCCH_2CH=CHCH_2CN + H_2 \xrightarrow{\text{cat.}} NCCH_2CH_2CH_2CH_2CN$

$NC(CH_2)_4CN + 4\ H_2O \xrightarrow[\text{(HO}^-\text{ or H}^+)]{\text{cat.}} HOOC(CH_2)_4COOH + 2\ NH_3$

$NC(CH_2)_4CN + 4\ H_2 \longrightarrow H_2N(CH_2)_6NH_2$

$CH_2=CHCHClCH_2Cl + OH^- \longrightarrow CH_2=CH–CCl=CH_2 + Cl^- + H_2O$

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$$CH_2{=}CH{-}CH{=}CH_2 \ + \ 2 \, O_3 \ \longrightarrow$$

(structure: CH₂–O–CH—CH–O–CH₂ with O—O—O—O bridge)

(structure) $+ \ 2 \, H_2O \ \longrightarrow \ 2 \, HCHO \ + \ OHCCHO \ + \ 2 \, H_2O_2$

4.

$$CH_4 \xrightarrow[\triangle]{-\,H_2} CH{\equiv}CH \xrightarrow[Hg^{2+}]{+\,H_2O} CH_3CHO \xrightarrow[OH^-]{+\,CH_3CHO} CH_3CH(OH)CH_2CHO \longrightarrow$$

$$\xrightarrow[Ni]{+\,H_2} CH_3CH(OH)CH_2CH_2OH \xrightarrow{-\,H_2O} CH_2{=}CH{-}CH{=}CH_2$$

or

$$CH_4 \xrightarrow[\triangle]{-\,H_2} CH{\equiv}CH \xrightarrow[OH^-]{+\,HCHO} HOCH_2{-}C{\equiv}C{-}CH_2OH \longrightarrow$$

$$\xrightarrow[Ni]{+\,H_2} HO(CH_2)_4OH \xrightarrow{-\,H_2O} CH_2{=}CH{-}CH{=}CH_2$$

or

$$CH_4 \xrightarrow[\triangle]{-\,H_2} CH{\equiv}CH \xrightarrow[Cu_2Cl_2\,.\,2\,NH_4Cl]{+\,HC{\equiv}CH} CH_2{=}CH{\equiv}CH \longrightarrow$$

$$\xrightarrow[Zn + NaOH]{[H]} CH_2{=}CH{-}CH{=}CH_2$$

or

$$CH_4 \xrightarrow[\triangle]{-\,H_2} CH{\equiv}CH \xrightarrow[Hg^{2+}]{+\,H_2O} CH_3CHO \xrightarrow[Ni]{+\,H_2} CH_3CH_2OH \longrightarrow$$

$$\xrightarrow[cat.]{-\,H_2,+\,H_2O} CH_2{=}CH{-}CH{=}CH_2$$

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5.

$$-CH_2 \diagdown \atop Cl \diagup C = C \diagup ^{CH_2-} _{H}$$

$$-CH_2 \diagdown \atop Cl \diagup C = C \diagup ^{H} _{CH_2-}$$

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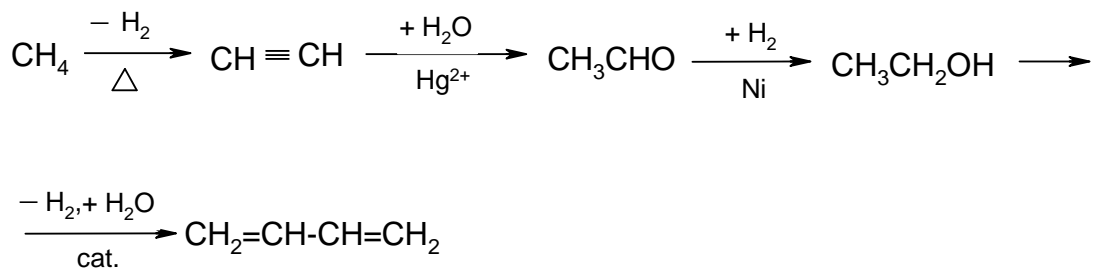edited by Anton Sirota,
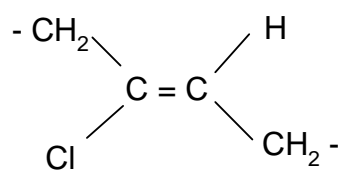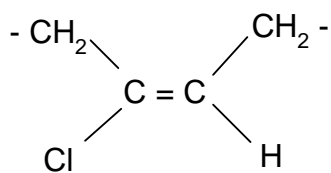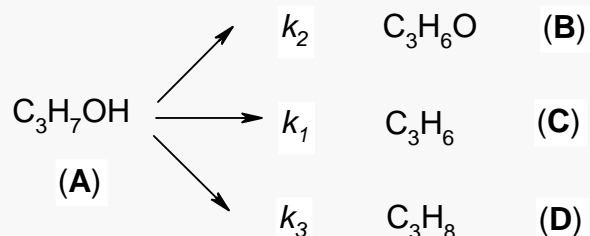ICHO International Information Centre, Bratislava, Slovakia

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PROBLEM 6

The catalytic decomposition of isopropanol on the surface of a V_2O_5 catalyst, leading to the products in the scheme, satisfies a first order kinetic equation.

$$C_3H_7OH \quad \overset{k_2}{\nearrow} \quad C_3H_6O \quad \textbf{(B)}$$
$$\textbf{(A)} \quad \overset{k_1}{\rightarrow} \quad C_3H_6 \quad \textbf{(C)}$$
$$\quad \overset{k_3}{\searrow} \quad C_3H_8 \quad \textbf{(D)}$$

Five seconds after initiation of the reaction at 590 K, the concentrations of the components in the reaction mixture are:
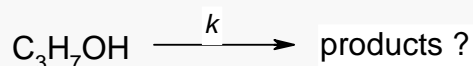
$c_A = 28.2$ mmol dm^{-3}

$c_B = 7.8$ mmol dm^{-3}

$c_C = 8.3$ mmol dm^{-3}

$c_D = 1.8$ mmol dm^{-3}

1. What is the initial concentration c_0 of C_3H_7OH in the system?

2. What is the value of the rate constant k for the process:

$$C_3H_7OH \quad \overset{k}{\longrightarrow} \quad \text{products ?}$$

3. What is the interval of time ($\tau_{1/2}$) in which the concentration of C_3H_7OH will reach the value $c = c_0/2$?

4. What are the values of rate constants k_1, k_2, and k_3?

5. What are the values of concentrations c_B, c_C, c_D at $t = \tau_{1/2}$?

   The equation describing the concentration changes of **A** with time t for the first order reaction has the form:

   $c_A = c_0 \exp(-k\,t)$

   or

   $\log (c_0 / c_A) = 0.4343\,k\,t$

or

   $\ln (c_0 / c_A) = k\,t$

Fill in the table with the answers obtained.

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1	$c_0 =$
2	$k =$
3	$\tau_{1/2}$
4	$k_1 =$
	$k_2 =$
	$k_3 =$
5	$c_B =$
	$c_C =$
	$c_D =$

SOLUTION

1. $c_0 = c_A + c_B + c_C + c_D = 28.2 + 7.8 + 8.3 + 1.8 = 46.1$ mmol dm^{-3}

2. $k = \dfrac{1}{0.4343\,t} \log\left(\dfrac{c_0}{c_A}\right) = \dfrac{1}{0.4343\times 5} \log\left(\dfrac{46.1}{28.2}\right) = 0.0983\ s^{-1}$

3. $t = \tau_{1/2} = \dfrac{1}{0.4343\,k} \log\dfrac{\frac{c_0}{2}}{c_0} = \dfrac{1}{0.4343\times 0.0983} \log 2 = 7.05$ s

4.

$v_1 = \dfrac{\Delta c_B}{\Delta t} = k_1\,c_A$

$v_2 = \dfrac{\Delta c_C}{\Delta t} = k_2\,c_A$

$v_3 = \dfrac{\Delta c_D}{\Delta t} = k_3\,c_A$

$v = v_1 + v_2 + v_3 = k\,c_A$

(1) $k_1 + k_2 + k_3 = k = 0.0983$ s^{-1}

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(2) $\quad \dfrac{\Delta c_B}{\Delta c_C} = \dfrac{c_B - 0}{c_C - 0} = \dfrac{c_B}{c_C} = \dfrac{k_1}{k_2} = \dfrac{7.8}{8.3} = 0.940$

(3) $\quad \dfrac{\Delta c_B}{\Delta c_D} = \dfrac{c_B - 0}{c_D - 0} = \dfrac{c_B}{c_D} = \dfrac{k_1}{k_3} = \dfrac{7.8}{1.8} = 4.33$

From equations (1) – (3):

$k_1 = 0.0428 \text{ s}^{-1}$

$k_2 = 0.0455 \text{ s}^{-1}$

$k_3 = 0.00988 \text{ s}^{-1}$

5.   At $t = \tau_{1/2} = 7.05$ s

     (4) $\quad c_A = \dfrac{c_0}{2} = c_B + c_C + c_D = 23.05 \text{ mmol dm}^{-3}$

From equations (2) – (4):

$c_B = 10.0 \text{ mmol dm}^{-3}$

$c_C = 10.7 \text{ mmol dm}^{-3}$

$c_D = 2.32 \text{ mmol dm}^{-3}$

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PRACTICAL PROBLEMS

PROBLEM 1

Fourteen numbered test tubes contain solutions of pure inorganic substances. Each test tube contains only one substance. The samples contain the following ions:

cations K^+, Na^+, Hg_2^{2+}, Ag^+, NH_4^+, Ba^{2+}, Sr^{2+}, Fe^{3+};

anions OH^-, NO_3^-, Cl^-, SCN^-, I^-, CO_3^{2-}, $Cr_2O_7^{2-}$, CrO_4^{2-}, $Fe(CN)_6^{4-}$, $Co(NO_2)_6^{3-}$.

Determine the contents of the test tubes. In addition to reactions between samples, the only other possible reagent is a solution of hydrochloric acid with a concentration of 2 mol dm^{-3}.

Fill in the following information on the sheet provided:

1. The chemical formulae of the individual samples and the numbers of the corresponding test tubes.
2. The chemical formulae in ionic form on the basis of which you demonstrated the presence of individual cations present in the samples.

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PROBLEM 2

Determine the samples in the test tubes using the following reagents:

$FeCl_3$ (2.5 % aqueous solution), water, 2,4-dinitrophenylhydrazine, Lucas' reagent ($ZnCl_2$ – HCl), NaOH (5 % aqueous solution), $NaHCO_3$ (5 % aqueous solution), HCl (conc.), Fehling's solution (an alkaline aqueous solution containing Cu^{2+} ions; this is prepared immediately prior to use by mixing identical volumes of Fehling's solutions I and II), Tollen's reagent (prepared immediately prior to use by mixing identical volumes of 10 % solution of $AgNO_3$ and an NaOH solution with a concentration 2 mol dm^{-3}. Finally, ammonia is added dropwise to complete dissolution of silver dioxide.

Write the results of your observations during testing the unknown substances with the reagents into the table provided.

Write the (IUPAC) names and structural formulae for the substances in the test tubes.

Write the chemical equations for the reactions on the basis of which the individual substances were identified. Write only a reaction scheme where this not possible.

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PROBLEM 3

Volumetric determination of sodium carbonate and sodium hydrogen carbonate simultaneously.

A) *Procedure:*

1. Determination of the precise concentration of an HCl solution (0.1 mol dm^{-3}) using borax $Na_2B_4O_7 . 10 H_2O$ as a standard.

   Principle:

   An aqueous solution of sodium tetraborate reacts with hydrochloric acid to form trihydrogenboric acid.

   Procedure:

   25.00 cm^3 of a standard borax solution with a concentration of about 0.05 mol dm^{-3} (the exact borax concentration is written on the label on the volumetric flask; the solution needs not be diluted with water to a volume of 100 cm^{-3}) is transferred into a titration flask, 1 to 2 drops of methyl red are added and the solution is titrated to the first orange coloration of the yellow solution. The titration should be carried out at least twice. The consumption of hydrochloric acid should be designated by symbol V_1.

2. Volumetric determination of Na_2CO_3 and $NaHCO_3$ simultaneously.

   Procedure:

   The sample in a volumetric flask (250 cm^3) should be diluted to the mark with distilled water from which the carbon dioxide has been removed by boiling, and mix.

   a) Part of the solution (25 cm^3) is titrated with an HCl solution using methyl orange (2 drops) to the first red coloration of the originally yellow solution. The sample is boiled 2 to 3 minutes to release carbon dioxide. Then the solution is cooled and the titration is continued to a clear red coloration of the solution. The titration should be carried out at least twice. The consumption of hydrochloric acid should be designated as V_2 (average of titration values).

   b) A further part of the sample (25.00 cm^3) is transferred to an Erlenmeyer flask and mixed with 25.00 cm^3 of the NaOH solution with a concentration of 0.1 mol dm^{-3}. Add 10 cm^3 of a 10 % solution of $BaCl_2$ and 2 drops of phenolphthalein. Excess hydroxide should be titrated immediately in the presence of a white precipitate formed, using an HCl solution whose precise concentration has been determined

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   c) in part 1. The consumption of hydrochloric acid should be denoted as V_3 (average values of at least two titrations).

   d) Carry out the same titration as in part b) without the sample (blank). The consumption of HCl is designated as V_4 (average of two titrations).

Use the results of the above experiments to calculate the amounts of Na_2CO_3 and $NaHCO_3$ in the sample.

B)   <u>Results</u>

   The results should be written into the form provided in which you should note the following:

a) The ionic equation for the reaction according to which the concentration of the HCl solution was determined.

b) The ionic equation for the reaction used in the determination of Na_2CO_3 and $NaHCO_3$ simultaneously.

c) The volume of hydrochloric acid consumed in the titration of 25.00 cm^3 of borax solution.

d) Calculation of the HCl concentration (in mol dm^{-3}).

e) Consumption of the HCl solution – V_2, V_3, and V_4.

f) Mass amounts of Na_2CO_3 and $NaHCO_3$ in the sample in grams.

$M(Na_2CO_3)$ = 105.989 g mol^{-1}

$M(NaHCO_3)$ = 84.007 g mol^{-1}

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