BELARUS

Ministry of Education

Chemistry Olympiad

National Final

Theoretical Examination

Brest, March 27-31, 2006

BELARUSIAN CHEMISTRY OLYMPIAD

The Belarusian Chemistry Olympiad is an annual multilevel competition with more than three decades of tradition. The olympiads are organized and coordinated by faculty members of chemistry departments of major Belarusian universities with financial support from the Ministry of Education. Most participants are high school students of grades 9 through 11. It is not unusual, however, that exceptionally gifted students of the eighth grade compete in the National Final. To ensure that younger students are not discouraged by advanced topics while senior students are challenged to test the limits of their abilities, three different versions of the exam are administered at each level.

Within each grade, selection of nominees for the National Final is conducted in two rounds. In December-January, competitions within local school districts determine qualified participants for regional olympiads. The regional olympiads are held in February in each of the six administrative regions associated with the country's principal cities. The capital city of Minsk holds a separate competition elevated in status to regional. Approximately 30 students from each grade are nominated to sit for the National Exam.

The National Final consists of a theoretical exam and a laboratory practical. Each five-hour theoretical exam includes a 10-item multiple choice test and a set of 5 problems. The laboratory practical involves 1-2 experimental problems and lasts 4 to 5 hours. The winners of the National Final attend a study camp at the Belarusian State University (Minsk) in preparation for the International Olympiad.

PROBLEMS

GRADE 9

Problem 9-1

Interaction of metals with nitric acid results in a complex mixture of nitrogen reduction products whose precise composition is determined by many factors. The most important of these factors are the chemical nature of the metal, the size of metal particles, the concentration of nitric acid, and the reaction conditions (temperature, stirring, etc.)

a) *Apart from the metal nitrate, what nitrogen-containing products can be formed when a metal is dissolved in nitric acid? Write the chemical equations showing the formation of each product.*

b) *A 1.00 g sample of a certain metal was dissolved in an excess of aqueous nitric acid containing 15.0% HNO_3 by mass. The reaction produced 446 mL (S.T.P.) of a mixture of gases. An analysis showed that this mixture contains 117 mg of N_2 and 269 mg of NO and that the mass percent of elemental nitrogen in it is 60.7%. Calculate the density of this mixture of gases at 40.0 °C and 770 mm Hg.*

c) *What metal was reacted with nitric acid in this experiment? Write the chemical equation for this reaction.*

Problem 9-2

When a certain element **A** is heated in air, an oxide **B** is formed. Reaction of **B** with aqueous potassium bromate in the presence of nitric acid yields compounds **C**, **D**, and a salt **E**, which is an ingredient of black powder. At standard temperature and pressure, **D** is a red-colored liquid. A mixture of **C** with hydrochloric acid is one of the few chemical reagents capable of dissolving a certain metal **F**. When the latter reaction occurs, compounds **B** and **G** are formed and the solution turns light-yellow.

a) *Identify substances **A** through **G**, given that **G** is 41.77% chlorine by mass and that 1.00 g of **B** yields 1.306 g of **C**. Give your reasoning.*

b) *Write chemical equations for the reactions that occur in this experiment.*

c) *When compound **A** is boiled with aqueous Na_2SO_3, a new compound **H** is formed, which is 15.6% sulfur by mass. Determine the chemical composition and the structural formula of **H**.*

d) *Suggest two more ways in which metal **F** can be brought into solution. Write chemical equations for the corresponding reactions.*

Problem 9-3

A 0.50% solution of a certain monoprotic acid has a density of 1.00 g/cm^3. An experiment showed that 1.00 L of this solution contains 6.75×10^{21} ions and that the degree of dissociation of the acid is 10.6%.

a) *Identify the monoprotic acid used in this experiment. Show your calculations.*

b) *Calculate the dissociation constant of this acid and the pH of the solution.*

c) *How will the number of ions change if 1.00 L of the above solution is diluted to 3.00 L with distilled water? Support your answer with calculations.*

d) *Propose a synthesis of the acid from readily available reagents.*

Problem 9-4

A 6.70 g sample of a mixture of hexane and an unknown hydrocarbon was burned in oxygen in a sealed vessel. After the products were cooled, the vessel was found to contain

9.54 g of water and 5.00 L (at 300 K and 234.4 kPa) of a mixture of gases which is 20% CO and 80% by volume.

a) Determine the empirical formula of the unknown hydrocarbon, given that its mass percent in the initial sample was 10.15%.
b) Draw the structural formulas of all possible non-cyclic isomers of the unknown hydrocarbon given that its density relative to air is less than 4.
c) What volume of oxygen gas was used in this experiment?

Problem 9-5
The standard enthalpies of combustion of graphite and hydrogen gas are –393.5 and –285.8 kJ/mol, respectively.

a) Calculate the standard enthalpies of formation of carbon dioxide and water. Remember that the standard enthalpies of formation of elements in their most stable form are zero.
b) Combustion of a 1.00 g sample of sugar (sucrose) in an excess of oxygen releases 16.52 kJ of heat. Calculate the standard enthalpy of formation of sucrose.
c) When heated in the absence of oxygen, sucrose decomposes into two compounds. Calculate the enthalpy change for this process.
d) Estimate the minimum amount of sugar needed to replenish the energy lost by a mountaineer ascending Mount Everest (8848 m). Assume that the body mass is 70 kg, the equipment weighs 20 kg, and that the energy conversion efficiency of the human body is 10%.

GRADE 10

Problem 10-1
Compound **A** occurs in nature in the form of several minerals. When **A** is heated with element **X**, a valuable product **B** is obtained. **B** reacts with another element **Y** to produce compound **C**. Hydrolysis of **B** and **C** yields compounds **D** and **E**, respectively. Gas **D** is a valuable reagent for many synthetic organic reactions. Compound **E** is an antidipsotropic agent (a drug that induces an unpleasant reaction when taken with alcohol), but is mainly used as in the manufacture of a fertilizer **F** by hydrolysis. Elements **X** and **Y** are neighbors in the periodic table.

a) Identify elements **X, Y,** and compounds **A** through **F**.
b) Write the chemical equations to represent all of the above transformations.
c) Give the names of at least three minerals that contain compound **A**.
d) Write the chemical equations for the industrially important reactions that involve compound **D** and indicate conditions under which these reactions occur.

Problem 10-2
The following table contains thermodynamic data for several substances at 298 K and 1 bar.

Substance	$C(s)$	$H_2(g)$	$H_2O(l)$	$CH_3OH(l)$	$CH_3COOH(l)$	$CH_3COOCH_3(l)$
Enthalpy of formation, kJ/mol	–393.5	–285.8	0	–715.0	–864.8	–1589.5
Entropy, J/mol·K	5.68	130.5	70.0	126.7	159.8	225.2

a) Calculate the enthalpies of formation of the compounds appearing in the table.

b) *Calculate the amount of heat released when methanol reacts with acetic acid to form methyl acetate.*

c) *Calculate the equilibrium constant for the reaction of methanol with acetic acid.*

d) *What is the mass percent of methyl acetate in the equilibrium mixture obtained by combining 100 mL of 80% acetic acid (density 1.07 g/mL) and 100 mL of 80% methanol (0.87 g/mL). Assume all solutions to be ideal.*

e) *When methanol labeled with ^{18}O reacts with acetic acid, the ^{18}O atoms turn up in methyl acetate molecules. Based on this experimental fact, propose a mechanism for the acid-catalyzed esterification of methanol.*

Problem 10-3

A 12.25 g sample of an equimolar mixture of two unknown salts (both of which are stable at room temperature and pressure) was sealed in a 10.00 L vessel. The vessel was evacuated and heated to 100 °C. The pressure inside the vessel measured at this temperature was found to be 93.00 kPa. After the vessel was cooled to 20 °C, the pressure dropped to 24.35 kPa. The vessel was opened and a 0.945 g sample of the condensate was completely dissolved in 200 mL of distilled water. A litmus test of the resulting clear solution showed a neutral reaction. Addition of an excess of aqueous lead(II) nitrate to this solution produced 13.9 g of a precipitate which is 74.48% lead by mass.

a) *Identify the salts present in the initial mixture.*

b) *Calculate the mass percent of both salts in the initial mixture.*

c) *Write the chemical equations for the reactions occurring in this experiment.*

d) *What is the practical application of this mixture of salts?*

Problem 10-4

A certain acid **A** is a large-scale chemical used by food industry in the manufacture of wines, fruit beverages, and confectionery. Acid **A** can be obtained by the reduction of acid **B**. Complete combustion of a 10.0 g sample of **B** yields 3.60 g of a colorless liquid. When the gaseous products of this reaction are bubbled through aqueous alkali, they are completely absorbed and the mass of the solution increases by 11.73 g.

a) *Draw Fischer projection formulas for the three stereoisomers of acid **B** and designate their absolute configuration using the R,S-nomenclature.*

b) *Draw a plausible structural formula of the acid **A** and name this compound, given that **A** exists in the form of two stereoisomers.*

c) *The dissociation constants of acid **A** are $10^{-3.46}$ an $10^{-5.10}$. Calculate the pH of a 0.100 M solution of **A**.*

d) *At 140 °C, acid **A** loses one water molecule and turns into acid **C**. The neutralization of 1.00 g of **C** requires 172 mL of 0.100 M KOH. Rapid heating of **A** to 180 °C produces a cyclic anhydride (compound **D**) of another acid which is isomeric with **C**. When **A** is heated with caution to 100 °C, it forms compound **E**, which is 41.39% carbon and 55.14% oxygen by mass and does not react with aqueous bromine. Draw the structural formulas of compounds **C**, **D**, and **E**.*

Problem 10-5

Neuropeptides, compounds regulating physiological processes in the human body, attract considerable attention of biochemists. In particular, opioid neuropeptides are involved in pain perception and a number of mental disorders. The brains of many mammals contain enkephalins, pentapeptides that act on opiate receptors. Structurally,

enkephalins are pentapeptides differing only by the C-terminal amino acid. The name of this amino acid is reflected in the name of the enkephalin.

a) *A complete hydrolysis of [leucine]enkephalin produces the following amino acids: glycine (aminoacetic acid, Gly), leucine (2-amino-4-methylpentanoic acid, Leu), tyrosine (2-amino-3(4'-hydroxyphenyl)-propanoic acid, Tyr), and phenylalanine (2-amino-3-phenylpropanoic acid, Phe). Draw the structural formulas of these amino acids.*

b) *The N-terminal amino acid of a certain enkephalin is tyrosine. The product of partial hydrolysis of this peptide contains fragments with a relative molecular mass of 132 and 238. Determine the primary structure of this enkephalin.*

c) *Estimate the pH of the isolelectric point of [leucine]enkephalin.*

GRADE 11

Problem 11-1

A 1.000 g sample of impure calcium carbide was dissolved in 100.0 g of water. The resulting gas was collected and its volume was found to be 312.7 cm^3 at 24.50 °C and 1.125 atm. The volume of the remaining solution was 98.47 cm^3. The solution was transferred to a graduated flask and diluted with distilled water to 250.0 mL. A 10.00 mL sample of the dilute solution was titrated with 11.98 cm^3 of 0.01480 M aqueous HNO_3.

a) *What is the mass percent of impurities in the initial sample of calcium carbide?*

b) *Calculate the density and pH of the solution obtained in the reaction of calcium carbide with water.*

c) *What would be the pH of the solution if the sample were dissolved not in water but in 100 g of hydrochloric acid that is 0.440% HCl by mass? Show your calculations. Assume that the density of the resulting solution is the same as in the case of pure water.*

Problem 11-2

Reaction of organic compounds **A**, **B**, and **C** with a certain element **X** produces a liquid compound **Y** and a gas **Z** (at S.T.P). The following incomplete table shows quantitative results of the synthesis of **Y** and **Z** from these reactants.

Compound	Mass, g	Mass of **X**, g	Mass of **Y**, g	Mass of **Z**, g
A	1.24	0.684	1.795	0.129
B	1.24	0.708		0.0891
C	1.24	0.735	1.929	

It is also known that if the starting compound is **C**, then compounds **X** and **Y** are formed in equimolar amounts.

a) *Identify compounds **A**, **B**, **C**, **X**, and **Y**. Give your reasoning.*

b) *Write the chemical equations for the reactions involved in this experiment.*

Problem 11-3

The blood-sugar level can be quantitatively determined by the Hagedorn-Jensen method. This technique is based on the ability of iron(III) compounds to oxidize glucose to gluconic acid. A simplified outline of the procedure is as follows. A prepared 0.100 mL sample of blood is transferred to a flask, combined with 2.00 mL of 5.015 mM solution of sodium hexacyanoferrate(III) and heated on a water bath. The resulting solution is treated

with an excess of aqueous zinc chloride and then with an excess of aqueous potassium iodide in the presence of acetic acid. The free iodine produced in the latter reaction is titrated with 5.00 mmol/L sodium thiosulfate.

a) *Write the chemical equations for the reactions that occur in this analysis.*
b) *Why cannot a solution of an iron(III) salt (for instance, chloride or nitrate) be used in this method? Explain.*
c) *What is the purpose of zinc chloride? Support your answer with chemical equations.*
d) *Calculate the concentration (in mg/L) of glucose in the initial blood sample given that the titration required 1.31 mL of sodium thiosulfate.*

Problem 11-4

In 1855, the German chemist Adolph Kolbe deduced chemical formulas of three organic acids **A**, **B**, and **C** based on the formula of carbonic acid which he represented as $2HO.[C_2O_2],O_2$.

Acid	Kolbe's formula
A	$HO.(C_2H_3)[C_2O_2],O$
B	$HO.H[C_2O_2],O$
C	$2HO.\begin{bmatrix} C_2O_2 \\ C_2O_2 \end{bmatrix},O_2$

a) *Draw the structural formulas and give the common names of acids **A**, **B**, and **C**. Explain your reasoning.*
b) *Using the data from the table deduce the relative atomic masses of carbon, hydrogen, and oxygen used by Kolbe. Give your reasoning.*
c) *Draw the structural formula of benzyl aldehyde in Kolbe's notation.*
d) *A well-known organic reaction discovered by Kolbe in 1849 involves salts of carboxylic acids. Name this reaction, describe it briefly and give an example.*

Problem 11-5

Methanol is synthesized on a commercial scale by the reaction

$$CO(g) + 2H_2(g) \rightleftarrows CH_3OH(g)$$
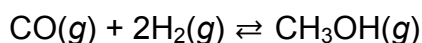
The equilibrium constant of this process at 500 K is $K_p=6.10 \times 10^{-3}$ bar^{-2}. The equilibrium of this reaction can be shifted by varying the temperature, pressure, or the composition of the mixture.

a) *A certain volume of syngas (a mixture of carbon monoxide and hydrogen gas used for the synthesis of methanol by the above reaction) was obtained by gasification of coal with superheated steam. Write the chemical equation for this reaction. Calculate the mole fractions of all components in the equilibrium mixture in the synthesis of methanol at 500 K and a total pressure of 100 bar, assuming that the syngas contained no water.*
b) *Syngas can be also produced from methane and water. Write the chemical equation for this reaction. Calculate the mole fractions of all components in the equilibrium mixture for the synthesis of methanol at 500 K and a total pressure of 100 bar assuming that the syngas was prepared from methane.*
c) *A 1.00 mol sample of methanol is placed into an evacuated 1.00 L vessel and heated to 500 K. What is the dissociation degree of methanol at this temperature? Assume that only methanol molecules undergo decomposition.*

SOLUTIONS

GRADE 9

Problem 9-1

a) NO_2, NO, N_2O, N_2, NH_4NO_3. Reaction of metals with nitric acid is usually accompanied by the reduction of nitrogen atoms, not the protons. As a rule, the lower the concentration of nitric acid and the more active the metal, the lower is the oxidation number of nitrogen in the reduction product. The following reactions illustrate this trend:

$Cu + 4HNO_3(conc.) = Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$;

$3Pb + 8HNO_3(dil.) = 3Pb(NO_3)_2 + 2NO\uparrow + 4H_2O$;

$4Mg + 10HNO_3(conc.) = 4Mg(NO_3)_2 + N_2O\uparrow + 5H_2O$;

$5Mn + 12HNO_3(dil.) = 5Mn(NO_3)_2 + N_2\uparrow + 6H_2O$;

$4Mg + 10HNO_3(dil.) = 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$.
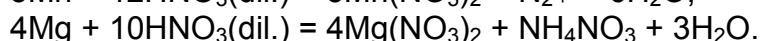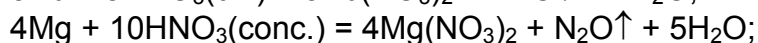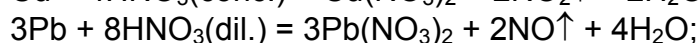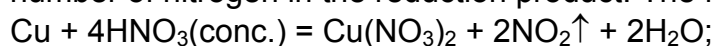
b) The amount of gases produced by the reaction of the unknown metal with nitric acid is

$\dfrac{446}{22,4}$ = 19.9 mmol, of which $\dfrac{117}{28,0}$ = 4.18 mmol is N_2 and $\dfrac{269}{30,0}$ = 8.97 mmol is NO.

Hence, the mixture contains at least one more component in the amount of

(19.9 – 4.18 – 8.97) = 6.75 mmol.

Suppose there is only one unknown component in the mixture with a molecular mass M and the mass percent of nitrogen w. Then

$0.607 = \dfrac{117 + 8,97 \cdot 14,0 + 6,75 \cdot M \cdot w}{117 + 269 + 6,75 \cdot M}$, which yields $M = \dfrac{8,3}{4,1 - 6,75 \cdot w}$.

None of the possible nitrogen reduction products satisfies this equation. Let us recall, however, that the reaction of metals with nitric acid can also form small amounts of hydrogen gas. This assumption does not contradict the problem statement.

In order to calculate the density of the product mixture relative to air, we first compute its average molecular mass:

$M = \dfrac{2,0 \cdot 6,75 + 117 + 269}{19,9}$ = 20.1 g/mol.

The density can now be found from the ideal gas law:

$p \cdot V = n \cdot R \cdot T = \dfrac{m}{M} \cdot R \cdot T$

$\rho = \dfrac{m}{V} = \dfrac{M \cdot p}{R \cdot T}$ = 0,792 g/L.

c) All gaseous products of the reaction are formed by the reduction of nitric acid. The only electron donor in this reaction is the metal.

$2N^{+5} + 10e^- = N_2$;

$N^{+5} + 3e^- = N^{+2}$;

$2H^{+1} + 2e^- = H_2$.
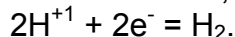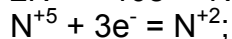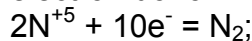
Formation of the specified amount of gases requires

(4.18 × 10 + 8.97 × 3 + 6.75 × 2) = 82.2 mmol of electrons.

Thus, the molar mass of the metal is

$M = 10^3 \dfrac{1,00}{82,2}$ = 12.16x g/mol.

The only possibility is $x = 2$ and $M = 24.32$, meaning that the unknown metal is Mg (magnesium).

The amount of magnesium metal is $\dfrac{1000}{24,3}$ = 41.15 mmol.

The balanced equation for the reaction can be written as
$41.15Mg + xHNO_3 = 41.15Mg(NO_3)_2 + 4.18N_2 + 8.97NO + 6.75H_2 + yH_2O$.
Filling in the missing coefficients and switching to integers, we obtain:
$1329Mg + 3218HNO_3 = 1329Mg(NO_3)_2 + 135N_2\uparrow + 290NO\uparrow + 218H_2\uparrow + 1391H_2O$.
Stoichiometry per one magnesium atom:
$Mg + 2,42HNO_3 = Mg(NO_3)_2 + 0,102N_2\uparrow + 0,218NO\uparrow + 0,164H_2\uparrow + 1,05H_2O$.

Problem 9-2
a) The red-colored liquid **D** is bromine (Br_2), **E** is potassium nitrate (KNO_3).
   The reaction of **B** with potassium bromate is:
   $B + HNO_3 + KBrO_3 \rightarrow C + Br_2 + KNO_3$.
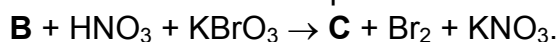
   This suggests that **C** is a hydroxide. Then $\dfrac{1,306}{1,00} = \dfrac{m(B)}{m(Б)} = \dfrac{M(H_xAO_y)}{\frac{1}{2}M(A_2O_z)} = \dfrac{1 \cdot x + 16 \cdot y + A}{\frac{1}{2}(2 \cdot A + 16 \cdot z)}$,

   which gives $M(A) = (3.3x + 52.3y - 34.1z)$ g/mol.
   The only admissible solution is x = 2, y = 4, z = 4, which corresponds to **A** = Se,
   B = SeO_2, and **C** = H_2SeO_4.
   According to the description, **F** appears to be a noble metal, in which case **G** is its Cl-
   complex. Assuming that the number of chlorine atoms in this complex is n, the

   molecular mass is $M(Ж) = \dfrac{35,45}{0,4177} \cdot n = 84,9 \cdot n$ g/mol.

   The only possible value of n is 4, that is, **F** = Au, **G** = $H[AuCl_4]$.
b) The following reactions take place:
   $4H_2O + 2KBrO_3 = 5H_2SeO_4 + Br_2 + 2KNO_3$;
   $3H_2SeO_4 + 8HCl + 2Au = 3SeO_2 + 2H[AuCl_4] + 6H_2O$.
c) Chemical properties of selenium are similar to those of sulfur. Thus, we can assume
   that when Se is boiled with aqueous Na_2SO_3, the following reaction occurs:
   $Se + Na_2SO_3 = Na_2SSeO_3$.
   (this is similar to the formation of sodium thiosulfate: $S + Na_2SO_3 = Na_2S_2O_3$).
   Our conjecture can be tested by computing the molecular mass of this compound from
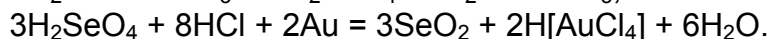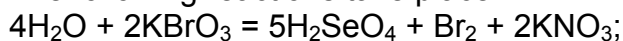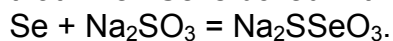
   the known the mass percent of sulfur: $M = \dfrac{32}{0,156} \cdot n = 205 \cdot n$ g/mol, where n is the

   number of S atoms. **H** is indeed Na_2SSeO_3. The anion of **H** is a tetrahedron:
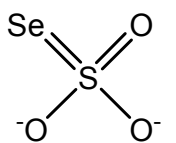
d) Gold metal can be brought into solution with a mixture of a strong oxidizing agent and a
   complexing agent at elevated temperatures:
   $Au + HNO_3 + 4HCl = H[AuCl_4] + NO\uparrow + 2H_2O$.
   Another techniques is the cyanide method:
   $4Au + 8KCN + O_2 + 2H_2O = 4K[Au(CN)_2] + 4KOH$.

Problem 9-3
a) A weak monoprotic acid dissociates by the equation: $HA \rightleftarrows H^+ + A^-$.
   The sample contains $1000 \times 1.00 \times 0.0050 = 5.00$ g of the acid.

   The total number of ions in the solution is $\dfrac{6,75 \cdot 10^{21}}{6,02 \cdot 10^{23}} = 0.01122$ mol, formed by the

   dissociation of $\dfrac{0,01122}{2} = 0.00561$ mol of the acid.

1 L of the solution contains $\dfrac{0,00561}{0,106} = 0.0529$ of the undissociated acid.

The molar mass of the acid is $M = \dfrac{5,00}{0,0529} = 94.5$ g/mol.

The fact that the molar mass is half-integer suggests that the molecule of the acid contains an odd number of Cl atoms. A suitable solution is chloroacetic acid: $ClCH_2COOH$.

b) At equilibrium:
$[H^+] = 0.00561$ M;
$[A^-] = 0.00561$ M;
$[HA] = (0.0529 - 0.00561) = 0.0473$ M.
The equilibrium constant is:

$$K_a = \frac{(0,00561)^2}{0,0473} = 6,65 \cdot 10^{-4}$$

pH = –log(0.00561) = 2.25.

c) Accodring to the Le Chatelier principle, when a solution of a weak electrolyte is diluted, the degree of dissociation increseas. The concentration of the acid in the dilute solution is $\dfrac{0,0529}{3} = 0.0176$ mol/L.

Let the degree of dissociation of the acid in this solution be a.
Then

$$6,65 \cdot 10^{-4} = \frac{(0,0176 \cdot a)^2}{0,0176 \cdot (1-a)}, \text{ which gives } a = 0.177.$$

The total number of ions in the dilute solution is therefore:
$3 \times 0.0176 \times 2 \times 0.177 \times 6.02 \times 10^{23} = 1.13 \times 10^{22}$.
In general, when the concentration of a weak electrolyte decreases by a factor of n, the degree of dissociation increases by a factor of $\sqrt{n}$ while the number of ions per unit volume of the solution decreases by $\sqrt{n}$.

d) $Cl_2 + CH_3CO_2H \rightarrow ClCH_2CO_2H + HCl$.

Problem 9-4
a) Let the formula of the unknown hydrocarbon be C_xH_{2y}. Then we have:

$$C_xH_{2y} + \frac{2x+y}{2}O_2 \rightarrow xCO_2 + yH_2O;$$

$$C_6H_{14} + \frac{19}{2}O_2 \rightarrow 6CO_2 + 7H_2O.$$
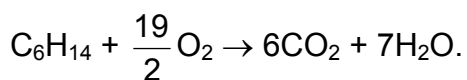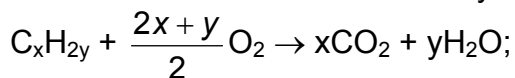
(Possible presence of CO in the products does not affect the following argument).
$M(C_6H_{14}) = 86.0$ g/mol.
$M(H_2O) = 18.0$ g/mol.
The initial mixture contained

$6.70 \times 0.1015 = 0.68$ g or $\dfrac{0,68}{12 \cdot x + 2 \cdot y}$ mol of the unknown hydrocarbon and

$(6.70 - 0.68) = 6.02$ g or $\dfrac{6,02}{86,0} = 0.0700$ mol of hexane.

The reaction produced $\dfrac{9,54}{18,0} = 0.530$ mol of water and

$$\frac{p \cdot V}{R \cdot T} = \frac{234,4 \cdot 5,00}{8,314 \cdot 300} = 0.470 \text{ mol of gases.}$$

The following stoichiometric relations:

$$x \cdot \frac{0,68}{12 \cdot x + 2 \cdot y} + 6 \times 0.0700 = 0.470,$$

$$y \cdot \frac{0,68}{12 \cdot x + 2 \cdot y} + 7 \times 0.0700 = 0.530,$$

give $\dfrac{x}{y} = \dfrac{5}{4}$.

Therefore, the empirical molecular formula of the unknown hydrocarbon is C_5H_8.

b) According to the problem statement, the molecular mass of the hydrocarbon does not exceed $29 \times 4 = 116$ g/mol. The molecular mass of the C_5H_8 fragment is 68 g/mol. Hence the true molecular formula of the unknown hydrocarbon is also C_5H_8. Non-cyclic hydrocarbon of this composition must contain one triple or two double bonds:
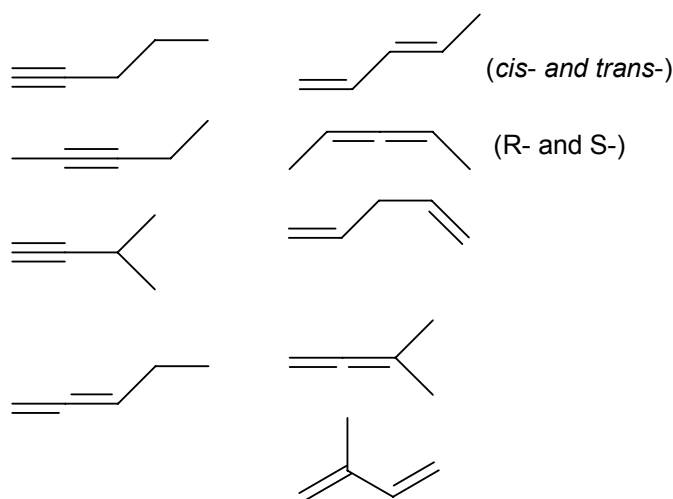
c) The combustion produced 0.530 mol of water, $0.470 \times 0.20 = 0.094$ mol of CO, and $0.470 \times 0.80 = 0.376$ mol of CO_2.

The reaction products contain $(0.530 + 0.094 + 0.376 \cdot 2) = 1.376$ mol of oxygen atoms or $\dfrac{1,376}{2} = 0.688$ mol of O_2. The volume of this amount of oxygen gas at S.T.P. is $0.688 \times 22.4 = 15.4$ L.

Problem 9-5

a) The standard enthalpies of combustion are the enthalpies of the following reactions:

$C + O_2 = CO_2 + 393.5$ kJ;

$H_2 + \dfrac{1}{2} O_2 = H_2O + 285.8$ kJ.
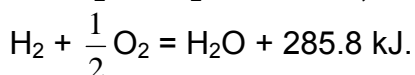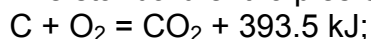
Thus, $\Delta_f H^0(CO_2) = -393.5$ kJ/mol.
$\Delta_f H^0(H_2O) = -285.8$ kJ/mol.

b) Oxidation of sucrose is described by the equation.

$C_{12}H_{22}O_{11} + 12O_2 = 12CO_2 + 11H_2O + Q.$
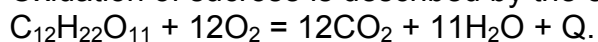
1.00 g or $\dfrac{1,00}{342} = 2.924 \times 10^{-3}$ mol of sucrose yields 16.52 kJ of heat.

Hence $Q = \dfrac{16,52}{2,924 \cdot 10^{-3}} = 5650$ kJ.

$\Delta_cH^0(C_{12}H_{22}O_{11})$ = –5650 kJ/mol.

$\Delta_cH^0(C_{12}H_{22}O_{11})$ = $12\Delta_fH^0(CO_2)$ + $11\Delta_fH^0(H_2O)$ – $\Delta_fH^0(C_{12}H_{22}O_{11})$.

This gives $\Delta_fH^0(C_{12}H_{22}O_{11})$ = 12 × (–393.5) + 11 × (–285.8) – (–5650) = –2216 kJ/mol.

c) $C_{12}H_{22}O_{11}$ = 12C + $11H_2O\uparrow$.

Δ_rH^0 = $11\cdot\Delta_fH^0(H_2O)$ – $\Delta_fH^0(C_{12}H_{22}O_{11})$ = 11 × (–285,8) – (–2216) = –928 kJ/mol.

d) $\Delta E = mgh$ = (70 + 20) × 9.8 × 8848 = 7.80 × 10^6 J = 7.8 MJ.

Assuming a 10% energy conversion efficiency, the ascent requires 78 MJ. The mass of sucrose furnishing this amount of energy is:

$$m(\text{sucrose}) = \frac{78\cdot10^3}{16,52} = 4.7 \times 10^3 \text{ g} = 4.7 \text{ kg}.$$

GRADE 10

Problem 10-1

a) As neighbors in the periodic table, elements **X** and **Y** belong either to the same group or to the same row. Because **D** is a reagent for many organic reactions, it probably contains carbon. In that case, at least one of compounds **A** and **X** also contains carbon. This allows us to deduce that:

A = $CaCO_3$;

B = CaC_2;

C = $CaCN_2$;

D = C_2H_2;

E = NH_2CN;

F = NH_2CONH_2;

X = C;

Y = N.

b) The following reactions occur:

$CaCO_3 + 4C = CaC_2 + 3CO\uparrow$;

$CaC_2 + N_2 = CaCN_2 + C$;

$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2\uparrow$;

$CaCN_2 + 2H_2O = Ca(OH)_2 + NH_2CN$;

$NH_2CN + H_2O = NH_2CONH_2$.
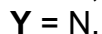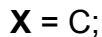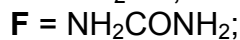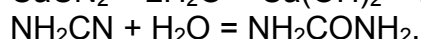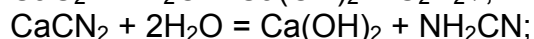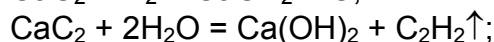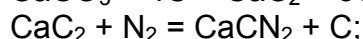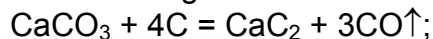
c) Calcium carbonate occurs in the form of such minerals as lime, chaulk, and marble.
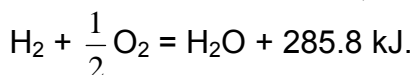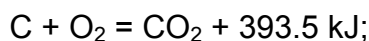
d) Examples of industrial applications of acetylene:
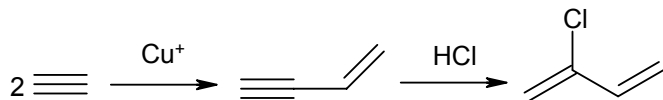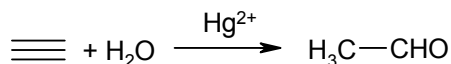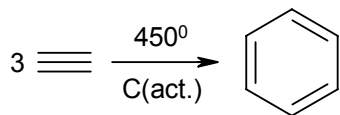
Problem 10-2

a) By definition, standard enthalpies of formation of elements are zero:

$\Delta_fH^0(C)$ = 0.

$\Delta_fH^0(H_2)$ = 0.

The standard enthalpy of combustion is the enthalpy of the following reaction:

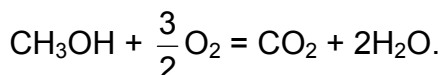C + O$_2$ = CO$_2$ + 393.5 kJ;

H$_2$ + $\frac{1}{2}$O$_2$ = H$_2$O + 285.8 kJ.

Hence

Δ_fH^0(CO$_2$) = –393.5 kJ/mol.

Δ_fH^0(H$_2$O) = –285.8 kJ/mol.

Consider now the oxidation reactions for the organic compounds:

CH$_3$OH + $\frac{3}{2}$O$_2$ = CO$_2$ + 2H$_2$O.

Δ_cH^0(CH$_3$OH) = Δ_fH^0(CO$_2$) + 2Δ_fH^0(H$_2$O) – Δ_fH^0(CH$_3$OH),
from which Δ_fH^0(CH$_3$OH) = (–393.5) + 2 × (–285.8) – (–715.0) = –250.1 kJ/mol.

CH$_3$COOH + 2O$_2$ = 2CO$_2$ + 2H$_2$O.
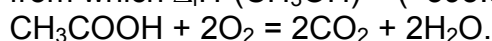
Δ_cH^0(CH$_3$COOH) = 2·Δ_fH^0(CO$_2$) + 2·Δ_fH^0(H$_2$O) – Δ_fH^0(CH$_3$COOH), from which

Δ_fH^0(CH$_3$COOH) = 2 × (–393.5) + 2 × (–285.8) – (–864.8) = –493.8 kJ/mol.

CH$_3$COOCH$_3$ + $\frac{7}{2}$O$_2$ = 3CO$_2$ + 3H$_2$O.
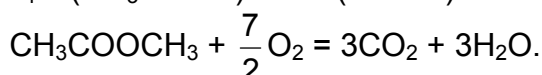
Δ_cH^0(CH$_3$COOCH$_3$) = 3·Δ_fH^0(CO$_2$) + 3·Δ_fH^0(H$_2$O) – Δ_fH^0(CH$_3$COOCH$_3$),
so that Δ_fH^0(CH$_3$COOCH$_3$) = 3 × (–393.5) + 3 × (–285.8) – (–1589.5) = –448.4 кJ/mol.

b) The equation for the esterification of methanol is:

CH$_3$OH + CH$_3$COOH ⇄ CH$_3$COOCH$_3$ + H$_2$O.
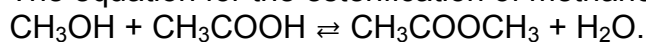
For this reaction:

Δ_rH^0 = Δ_fH^0(CH$_3$COOCH$_3$) + Δ_fH^0(H$_2$O) – Δ_fH^0(CH$_3$OH) – Δ_fH^0(CH$_3$COOH) =
= (–448.4) + (–285.8) – (–250.1) – (–493.8) = 9.7 kJ/mol.

c) To determine the equilibrium constant, we need the standard entropy and the Gibbs free energy for the reaction:

Δ_rS^0 = S^0(CH$_3$COOCH$_3$) + S^0(H$_2$O) – S^0(CH$_3$OH) – S^0(CH$_3$COOH) =
= 225.2 + 70.0 – 126.7 – 159.8 = 8.7 J·mol^{-1}·K^{-1}.

Δ_rG^0 = Δ_rH^0 – T·Δ_rS^0 = 9.7 – 298·($\frac{8,7}{1000}$) = 7.11 kJ/mol.

On the other hand,

Δ_rG^0 = –R·T·lnK, which gives K = exp($\frac{-\Delta G}{R \cdot T}$) = 0.0568.

d) The reaction mixture initially was composed of:

100 × 1.07 = 107 g of the solution of CH$_3$COOH which contained

107 × 0.80 = 85.6 g or $\frac{85,6}{60,1}$ = 1.42 mol of CH$_3$COOH and

100 × 0.87 = 87 g of the solution of CH$_3$OH which contained

87 × 0.80 = 69.6 g or $\frac{69,6}{32,0}$ = 2.18 mol of CH$_3$OH.

The mass of H$_2$O is (107 + 87 – 69.6 – 85.6) = 38.8 g or $\frac{38,8}{18,0}$ = 2.16 mol.

Suppose the reaction produces x mol of the ester. Then

$$0,0568 = \frac{[CH_3COOCH_3] \cdot [H_2O]}{[CH_3OH] \cdot [CH_3COOH]} = \frac{x \cdot (2,16 + x)}{(1,42 - x) \cdot (2,18 - x)}.$$
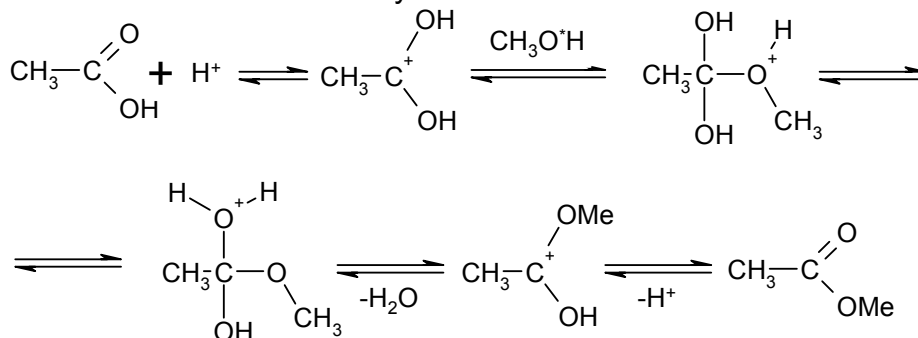
(Note that the concentration of water is comparable with concentrations of the other reactants and therefore must be included in the expression for the equilibrium constant).

Solution of the last equation gives x = 0.0723 mol.

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$M(CH_3COOCH_3)$ = 74.1 g/mol.

$w(CH_3COOCH_3)$ = $\dfrac{74,1 \cdot 0,0723}{(107 + 87)}$ = 0.0276 or 2.76%.

e) Mechanism of the acid-catalyzed esterification:

Problem 10-3

a) The pressure build-up inside the vessel means that one or both salts undergo decomposition or that they react with each other. The amount of gases in the mixture of products is before cooling:

$$\frac{p \cdot V}{R \cdot T} = \frac{93,00 \cdot 10,00}{8,314 \cdot (273 + 100)} = 0.300 \text{ mol};$$

and after cooling:

$$\frac{p \cdot V}{R \cdot T} = \frac{24,35 \cdot 10,00}{8,314 \cdot (273 + 20)} = 0.100 \text{ mol}.$$

The difference (0.300 – 0.100) = 0.200 mol represents the amount of condensed water vapors. The mass of water is therefore 0.200 × 18.0 = 3.60 g.

The litmus test indicates that the products do not hydrolyze in water.

Let us assume that the chemical formula of the precipitate is Pb_xA_2, where A is the anion, and x is its charge.

$$0,7448 = \frac{207,2 \cdot x}{207,2 \cdot x + 2 \cdot A}, \text{ which gives } M(A) = 35.5x \text{ g/mol.}$$

Therefore, the precipitate is $PbCl_2$, and the solution contains an alkali or alkaline earth metal.

The number of moles of the product is $\dfrac{13,9}{278,2}$ = 0.0500 mol, which corresponds to 0.100 mol of Cl^- ions or 35.5 × 0.100 = 3.55 g.

The mass of metal cations in the condensate is (9.45 – 3.55 – 3.60) = 2.30 g, hence M=23. The metal is sodium. Thus, the reaction involved a salt of sodium metal and an unknown chloride. Since the reaction products include water and a gas, we assume that the mixture contained ammonium chloride and sodium nitrite. The gas produced by the reaction of NH_4Cl and $NaNO_2$ is nitrogen.

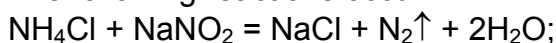The initial mixture of salts contained 0.1 mol of NH_4Cl and 0.1 mol of $NaNO_2$.

This conjecture is borne out by calculations: 0.1 × (53.5 + 69) = 12.25 g.
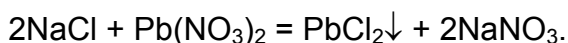
b) The mass fractions of the salts are:

$$w(NH_4Cl) = \frac{53,5}{53,5 + 69,0} = 0.437;$$

$$w(NaNO_2) = \frac{69,0}{53,5 + 69,0} = 0.563.$$

c) The following reactions occur:

$NH_4Cl + NaNO_2 = NaCl + N_2\uparrow + 2H_2O$;

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$2NaCl + Pb(NO_3)_2 = PbCl_2\downarrow + 2NaNO_3$.

d) An equimolar mixture of NH_4Cl и $NaNO_2$ is used in the laboratory for the preparation of small quantities of nitrogen gas.

Problem 10-4

a) Combustion of **B** produces only water (the colorless liquid) and carbon dioxide (the gas absorbed by aqueous alkali). Therefore, **B** is composed of carbon, hydrogen, and oxygen (is an acid).

$M(H_2O) = 18.0$ g/mol.

$M(CO_2) = 44.0$ g/mol.

The amount of H_2O is $\dfrac{3,60}{18,0} = 0,200$ mol

and the amount of CO_2 is $\dfrac{11,73}{44,0} = 0,267$ mol.

The sample contains

$(10.0 – 0.200 \times 2 \times 1.0 – 0.267 \times 12.0) = 6.40$ g or 0.400 mol of oxygen atoms.

Hence $n(C) : n(H) : n(O) = 2 : 3 : 3$.

Because the number of hydrogen atoms in an organic acid molecule must be even, the molecular formula of **B** should be $C_4H_6O_6$. Thus, **B** is tartaric acid.

Tartaric acid exists in the form of three stereoisomers:
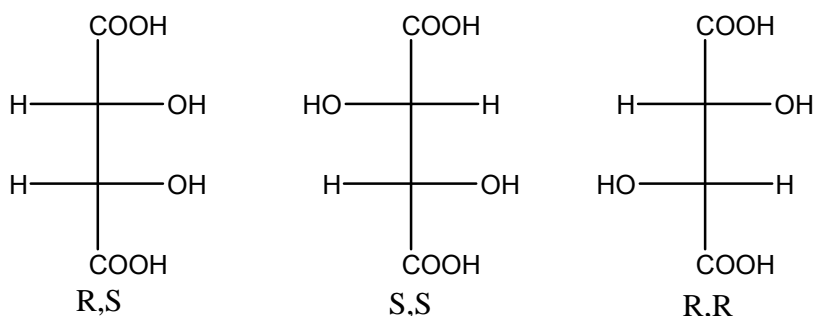
b) Compound **A** is also a diprotic carboxylic acid but it contains only one chiral center. This is malic acid:
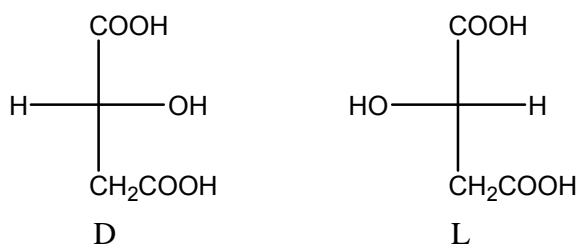
c) We have the following system of equations:

$$c = [H_2A] + [HA^-] + [A^{2-}] = 0,1$$

$$[H^+] = [HA^-] + 2[A^{2-}]$$

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]} = 3,47 \cdot 10^{-3}$$

$$K_2 = \frac{[H^+][A^{2-}]}{[A^{2-}]} = 7,94 \cdot 10^{-6}$$

After some manipulations:

$$[H^+] = \sqrt[3]{-K_1[H^+] + [H^+](0,1K_1 + K_1K_2) + 0,2K_1K_2}\ .$$

Solving this equation by the method of successive approximations we obtain:
$[H^+] = 5.73 \times 10^{-3}$.
pH = 2.24.

d) One equivalent amount of acid **C** in an acid-base reaction is $\dfrac{1,00}{0,100 \cdot 0,172} = 58,1$ g/mol.

Since **C** undergoes dehydration, it is most likely a diprotic acid. All these conditions are satisfied by the assumption that **C** is HOOC–CH=CH–COOH. Because only the *cis*-isomer of this acid can form a cyclic anhydride, we conclude that **C** is fumaric acid and **D** is maleic anhydride:
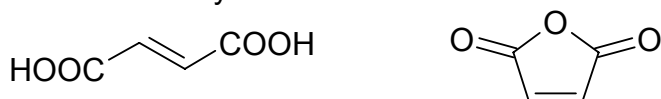
В - фумаровая кислота   Г - малеиновый ангидрид.
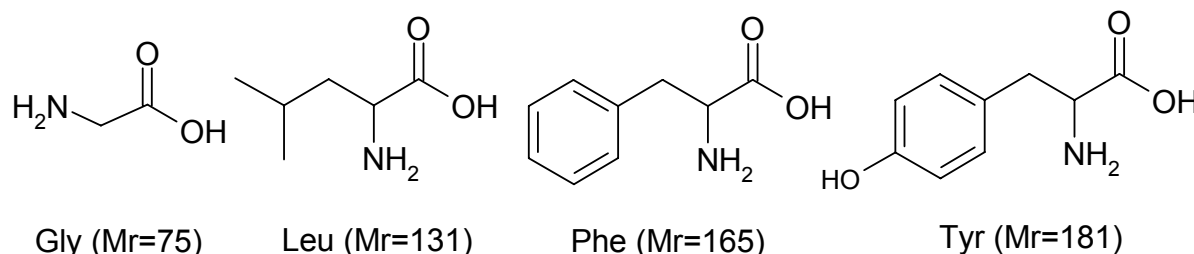
The empirical formula of **E** is:

$$n(\text{C}) : n(\text{H}) : n(\text{O}) = \frac{41,39}{12,01} : \frac{100 - 41,39 - 55,14}{1,008} : \frac{55,14}{16,00} = 1 : 1 : 1.$$

Because a molecule of **A** contains 4 carbon atoms, the number of carbon atoms in **E** must be a multiple of 4. This suggests that **E** is a lactide:
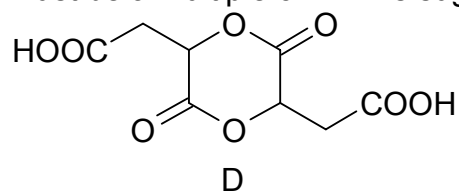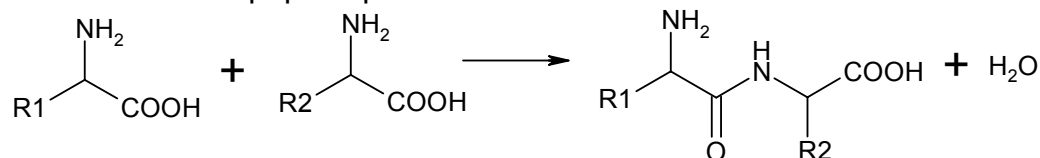

Problem 10-5

a) The structures of the amino acids are as follows:

Gly (Mr=75)   Leu (Mr=131)   Phe (Mr=165)   Tyr (Mr=181)

b) Formation of a dipeptide produces one water molecule:

Therefore, M(dipeptide) = M(amino acid 1) + M(amino acid 2) – 18.
Generalizing this result to longer peptide chains we obtain

$$M(\text{пептида}) = \sum_{i=1}^{n} M(\text{аминокислоты} - i) - 18 \cdot (n - 1).$$

Note that the molecular masses of individual amino acids in the initial peptide are all odd. Because the molecular masses of both products of partial hydrolysis are even, these fragments must be dipeptides (tetrapeptides can be ruled out because the molecular masses 132 and 238 are not large enough).
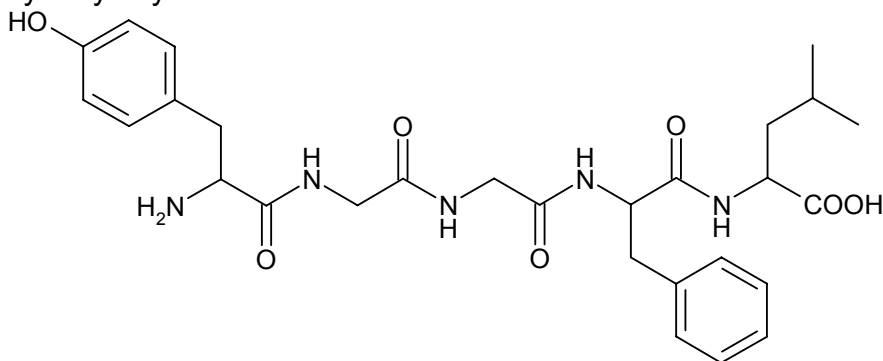Let us now examine each possible outcome in greater detail.

The molecular mass $M_r = 132$ can be assigned only to Gly-Gly ($132 = 2 \times 75 - 18$)
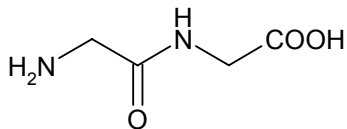
Similarly, the fragment with $M_r = 238$ can be only the dipeptide of glycine and tyrosine ($238 = 75 + 181 - 18$). Since the N-terminal amino acid is Tyr, the C-terminal acid is Leu. The complete primary structure of the enkephalin is Tyr-Gly-Gly-Phe-Leu:

c) The molecule of [leucine]enkephalin contains no acidic or basic fragments other than the terminal COOH and NH_2 groups. Therefore, the isoelectric point of this peptide should be close to the isoelectric point of an α-amino acid such as glycine, pI ~ 6.

GRADE 11

Problem 11-1

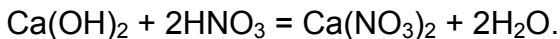a) The reaction of calcium carbide with water, $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow$,

produced $\dfrac{1{,}125 \cdot 101.3 \cdot 0{,}3127}{8{,}314 \cdot (273{,}15 + 24{,}50)} = 0.01440$ mol of C_2H_2.

$M(CaC_2) = 64.10$ g/mol.

The sample contained 0.01440 mol or $0.01440 \times 64.10 = 0.9230$ g of CaC_2.

The mass percent of impurities in the sample is $\dfrac{1{,}000 - 0{,}9230}{1{,}000} = 0.0770$ or 7.70 %.

b) The titration is based on the reaction:

$Ca(OH)_2 + 2HNO_3 = Ca(NO_3)_2 + 2H_2O$.

The 10.00 mL sample contained $\dfrac{11{,}98 \cdot 0{,}01480}{2} = 0.08865$ mmol of $Ca(OH)_2$.

The entire 250.0 mL solution contained $0.08865 \times 25 = 2.216$ mmol of $Ca(OH)_2$.

The concentration of $Ca(OH)_2$ in the 98.47 cm^3 = 0.09847 dm^3 of the solution was

$\dfrac{2{,}216 \cdot 10^{-3}}{0{,}09847} = 22.51 \times 10^{-3}$ mol/dm^3.

$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$.

The concentration of OH^- ion in this solution is $2 \times 22.51 \times 10^{-3} = 0.04502$ mol/dm^3.

pOH = $-\log[OH^-]$ = $-\log(0.04502)$ = 1.35.

pH = $(14 - pOH)$ = $(14 - 1.35)$ = 12.65.

The solution contains $0.09847 \times 22.51 \times 10^{-3} = 2.216$ mmol of $Ca(OH)_2$.

The total amount of $Ca(OH)_2$ of 14.40 mmol.

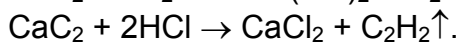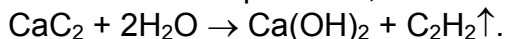The precipitate contains $(14.40 - 2.216) = 12.18$ mmol of $Ca(OH)_2$.

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$M(C_2H_2)$ = 26.04 g/mol.
$M[Ca(OH)_2]$ = 74.09 g/mol.
The mass of the solution is
$(100.0 + 0.9230 - 0.01440 \times 26.04 - 12.18 \times 74.09)$ = 99.64 g.

The density of the solution is $\dfrac{99{,}64}{98{,}47}$ = 1.012 g/cm^3.

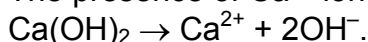c) In the second experiment, the following reactions occurred:
   $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow$.
   $CaC_2 + 2HCl \rightarrow CaCl_2 + C_2H_2\uparrow$.
   $M(HCl)$ = 36.46 g/mol.

   100.0 g of 0.440% hydrochloric acid contains $\dfrac{100{,}0 \cdot 0{,}00440}{36{,}46}$ = 12.06 mmol HCl.

   The amount of CaC_2 reacted with HCl is $\dfrac{12{,}06}{2}$ = 6.03 mmol. The reaction produced

   6.03 mmol of $CaCl_2$.
   The presence of Ca^{2+} ions from $CaCl_2$ in the solution reduces the solubility of $Ca(OH)_2$.
   $Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$.
   From part b), the concentration of $Ca(OH)_2$ in the saturated solution is 0.02251 M,
   which gives $K_s(Ca(OH)_2) = [Ca^{2+}][OH^-]^2 = 0.02251 \times (2 \times 0.02251)^2 = 4.56 \times 10^{-5}$.
   Thus, $(0.01440 - 0.00603)$ = 0.00837 mol of CaC_2 reacted with water to give 0.00837
   mol of $Ca(OH)_2$.
   Suppose the solution contains x mol of $Ca(OH)_2$.
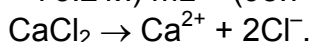   The precipitate contains $(0.00837 - x)$ mol of $Ca(OH)_2$.
   The mass of the resulting solution is
   $(100.0 + 0.9230 - 0.01440 \times 26 \times 04 - (0.00837 - x) \times 74.09) = (99.93 + 74.09x)$ g.

   Since the density is 1.012 g/mL, the volume of the solution is $\dfrac{99{,}93 + 74{,}09 \cdot x}{1{,}012}$ = (98.74

   + 73.21x) mL = (98.74 + 73.21x) × 10^{-3} L.
   $CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$.
   The reaction with HCl produced 6.03 mmol of $CaCl_2$, dissociation of which produced
   6.03 mmol of Ca^{2+} ions.
   The solution contains $(6.03 \times 10^{-3} + x)$ mmol of Ca^{2+} ions and 2x mmol of OH$^-$ ions.

   $[Ca^{2+}] = \dfrac{6{,}03 \cdot 10^{-3} + x}{(98{,}74 + 73{,}21 \cdot x) \cdot 10^{-3}}$ mol/L, $[OH^-] = \dfrac{2 \cdot x}{(98{,}74 + 73{,}21 \cdot x) \cdot 10^{-3}}$ mol/L.

   $K_s(Ca(OH)_2) = [Ca^{2+}] \cdot [OH^-]^2$.

   $\dfrac{6{,}03 \cdot 10^{-3} + x}{(98{,}74 + 73{,}21 \cdot x) \cdot 10^{-3}} \cdot (\dfrac{2 \cdot x}{(98{,}74 + 73{,}21 \cdot x) \cdot 10^{-3}})^2 = 4.56 \times 10^{-5}$.

   Solution of this equation gives x = 0.001231 mol.

   $[OH^-] = 2 \times \dfrac{0{,}001231}{(98{,}74 + 73{,}21 \cdot 0{,}001231) \cdot 10^{-3}}$ = 0.02491 mol/L.

   pOH = –log(0.02491) = 1.60.
   pH = (14 – 1.60) = 12.40.

Problem 11-2
a) First we use the principle of mass conservation to complete the table:

Compound	Mass, g	Mass of **X**, g	Mass of **Y**, g	Mass of **Z**, g
A	1.24	0.684	1.795	0.129
B	1.24	0.708	1.859	0.0891
C	1.24	0.735	1.929	0.046

The fact that immediately stands out is that the mass of gas **Z** is unusually low. Given the ratio $n(Y) : n(Z) = 1:1$, the ratio of molecular mases of **Y** and **Z** is

$$M(Y) : M(Z) = \frac{1,929}{0,046} = 41.9.$$

This is a very large number, so gas **Z** must by hydrogen**.**
Since the reaction of **C** produces **X** and **Y** in equimolar amounts, we can expect that
$n(C) = n(X) = n(Y) = n(Z)$.

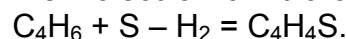Then $n(H_2) = \dfrac{0,046}{2} = 0.023$ mol and $M(X) = \dfrac{0,735}{0,023} = 32$ g/mol.

Element **X** is sulfur.

$$M(C) = \frac{1,24}{0,023} = 53.9 \text{ g/mol.}$$

Few organic compounds have this molecular mass, and only some of those can react with sulfur. This suggests that **C** is butyne, C_4H_6.
The molecular formula of **Y**:
$C_4H_6 + S - H_2 = C_4H_4S$.

$$M(Y) = \frac{1,929}{0,023} = 83.9 \text{ г/моль. Compound } \mathbf{Y} \text{ is thiophene.}$$

Now let us identify compounds **A** and **B**.
Since the products of all three reactions are the same, **A** and **B** must be hydrocarbons.

Assuming $n(S) = n(A)$, we obtain $n(S) = \dfrac{0,684}{32} = 0.0214$ mol.

$$M(A) = \frac{1,24}{0,0214} = 57.9 \text{ g/mol. } \mathbf{A} \text{ is butane, } C_4H_{10}.$$

Similarly we obtain $M(B) = 56$ g/mol. **B** is butene, C_4H_8.

A – *n*-butane, C_4H_{10};
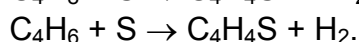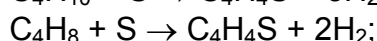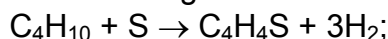**B** – isometic butenes, C_4H_8 (1-butene, *cis*-2-butene, *trans*-2-butene);
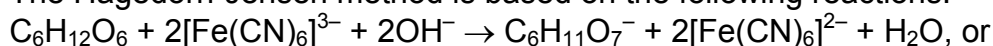**C** – 1-butyne, 2-butyne;
X – sulfur, S;
Y – thiophene, C_4H_4S;
Z – hydrogen gas, H_2.

b) The following reactions occur:
 $C_4H_{10} + S \rightarrow C_4H_4S + 3H_2$;
    $C_4H_8 + S \rightarrow C_4H_4S + 2H_2$;
    $C_4H_6 + S \rightarrow C_4H_4S + H_2$.

Problem 11-3
a) The Hagedorn-Jensen method is based on the following reactions:
    $C_6H_{12}O_6 + 2[Fe(CN)_6]^{3-} + 2OH^- \rightarrow C_6H_{11}O_7^- + 2[Fe(CN)_6]^{2-} + H_2O$, or

$2K_3[Fe(CN)_6] + 2KI + 8CH_3COOH = 2K_4[Fe(CN)_6] + I_2\downarrow + 8CH_3COOK$

$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$
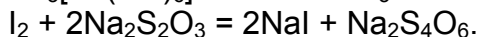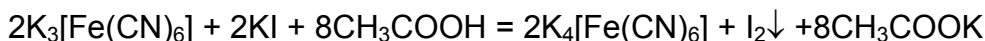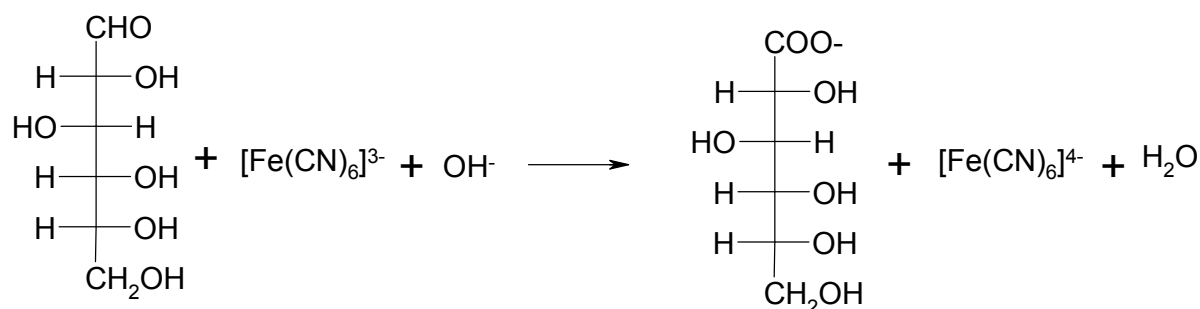
b) The pH of blood is about 7.4. Iron(III) ions would form insoluble $Fe(OH)_3$.

c) Zinc chloride binds hexacyanoferrate(II) ions thereby increasing the oxidizing capacity of $K_3[Fe(CN)_6]$:

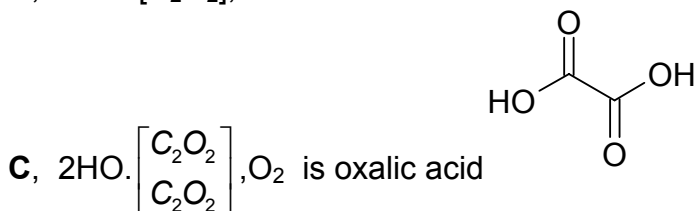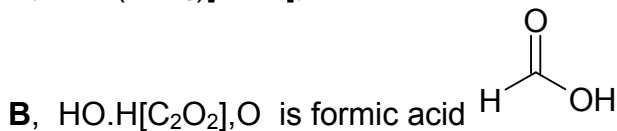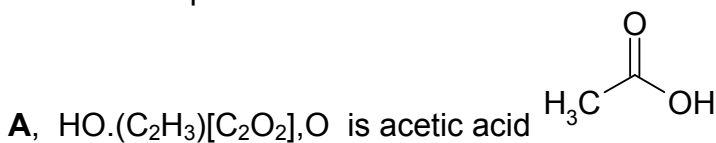$ZnCl_2 + K_4[Fe(CN)_6] = K_2Zn[Fe(CN)_6]\downarrow + 2KCl.$
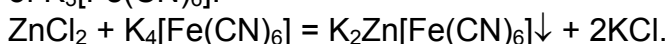
d) The blood sample contained

$$\frac{2,00 \cdot 5,015 \cdot 10^{-3} - 0,00655}{2} = 0.00174 \text{ mmol or } 0.00174 \times 180 = 0.3132 \text{ mg of glucose.}$$

The sugar-blood level was $\dfrac{0,3132}{0,000100} = 3132$ mg/L.

Problem 11-4

a) Each OH-unit in Kolbe's notation represents the OH fragment of the carboxyl group. The number of $[C_2O_2]$ fragments may refer to the number of carbonyl groups. Based on these assumptions we conclude that

A, $HO.(C_2H_3)[C_2O_2],O$ is acetic acid

B, $HO.H[C_2O_2],O$ is formic acid

C, $2HO.\begin{bmatrix} C_2O_2 \\ C_2O_2 \end{bmatrix},O_2$ is oxalic acid

b) Note that the number of carbon and oxygen atoms in Kolbe's formulas is double the actual number. This suggests that the relative atomic masses of these elements used in Kolbe's time are half their present-day values, i.e. 6 and 8, respectively. The same cannot be said about hydrogen whose atomic mass was 1 in Kolbe's time as it is now.

c) $H.(C_{12}H_5)[C_2O_2],O$

d) Kolbe reaction: electrolysis of salts of carboxylic acids yielding the corresponding alkane.

Problem 11-5

a) The coal gasification reaction is

$C + H_2O \rightarrow CO + H_2.$
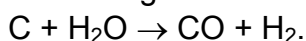
The equilibrium constant for the synthesis of methanol is

$$K_p = \frac{p(CH_3OH)}{p(CO) \cdot p^2(H_2)} = 6,10 \cdot 10^{-3}.$$

It will be convenient to describe the composition of the equilibrium mixture in terms of mole fractions (x_i). The partial (p_i) and total (p) pressures for a mixture of ideal gases are related by the formula: $p_i = p \cdot x_i$.

From $K_p = \frac{p(CH_3OH)}{p(CO) \cdot p^2(H_2)} = \frac{1}{p^2} \cdot \frac{x(CH_3OH)}{x(CO) \cdot x^2(H_2)} = 6,10 \cdot 10^{-3}$

we obtain $K_x = \frac{x(CH_3OH)}{x(CO) \cdot x^2(H_2)} = K_p \cdot p^2 = 61$.

Let us assume that the initial amounts of CO and H_2 are 1 mol each and that the amount of CH_3OH in the equilibrium mixture is x mol. The equilibrium mixture contains $(1 - x)$ mol of CO and $(1 - 2x)$ mol of H_2.

The total amount of gases ($CH_3OH+CO+H_2$) in the equilibrium mixture is then $x + (1 - x) + (1 - 2x) = (2 - 2x)$ mol. The equilibrium constant can be written as:
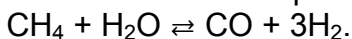
$$K_x = \frac{\dfrac{x}{2-2 \cdot x}}{(\dfrac{1-x}{2-2 \cdot x}) \cdot (\dfrac{1-2 \cdot x}{2-2 \cdot x})^2} = \frac{4 \cdot x \cdot (1-x)}{(1-2 \cdot x)^2} = 61.$$

Solution of this equation gives x = 0.436.

The composition of the equilibrium mixture is as follows:

Component	CH_3OH	CO	H_2
Mole fraction	0.387	0.500	0.113

b) The reaction for the production of syngas from methane and water is:
$CH_4 + H_2O \rightleftarrows CO + 3H_2$.

Since the conditions of the methanol synthesis have not changed, we will use some of the results from part a). Let the initial amount of CO in the reactor be 1 mol and the initial amount of H_2 3 mol. At equilibrium, we have x mol of CH_3OH, $(1 - x)$ mol of CO and $(3 - 2x)$ mol of H_2. The total amount of gases is $(4 - 2x)$ mol.
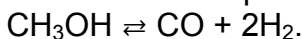
The equilibrium constant can be written as:

$$K_x = \frac{\dfrac{x}{4-2 \cdot x}}{(\dfrac{1-x}{4-2 \cdot x}) \cdot (\dfrac{3-2 \cdot x}{4-2 \cdot x})^2} = \frac{x \cdot (4-2 \cdot x)^2}{(1-x) \cdot (3-2 \cdot x)^2} = 61.$$

Solution of this equation gives x = 0.944.

The composition of the equilibrium mixture is as follows:

Component	CH_3OH	CO	H_2
Mole fraction	0.447	0.027	0.526

c) Methanol decomposes according to the equation:
$CH_3OH \rightleftarrows CO + 2H_2$.

This reaction is the reverse of the synthesis of methanol from syngas, so it is described by the same equilibrium constant as the synthesis. The only difference is that the total pressure is now determined by the degree of dissociation of methanol rather than by external factors. All components of the equilibrium mixture at 500 K are in the gas state.

$$K_x = \frac{x(CH_3OH)}{x(CO) \cdot x^2(H_2)} = K_p \cdot p^2.$$

Let the amount of dissociated methanol be x mol. Then the equilibrium mixture contains $(1 - x)$ mol of CH_3OH, x mol of CO, and $2x$ mol of H_2. The total number of moles of gases in the mixture is $(1 + 2x)$.

The equilibrium pressure can be found from the ideal gas law:

$$p = \frac{n \cdot R \cdot T}{V} = \frac{(1 + 2 \cdot x) \cdot RT}{V}.$$

Thus, $K_x = \dfrac{\dfrac{1-x}{1+2 \cdot x}}{(\dfrac{x}{1+2 \cdot x}) \cdot (\dfrac{2 \cdot x}{1+2 \cdot x})^2} = \dfrac{(1-x) \cdot (1+2 \cdot x)^2}{4 \cdot x^3} = K_p \cdot p^2 = K_p (\dfrac{(1+2x)RT}{V})^2.$

hence $\dfrac{(1-x)}{4 \cdot x^3} = K_p \cdot (\dfrac{R \cdot T}{V})^2.$

Solution of the latter equation gives $x = 0.260$ (i.e., 26.0%).

Translated by **V.Staroverov**