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.

GRADE 9

Problem 9-1.

Isotopomers are chemically identical compounds that differ in the atomic mass of one or more of their elements. For example, protium fluoride ($^{1}H^{19}H$) and deuterium fluoride ($^{2}H^{19}F$) are isotopomers of hydrogen fluoride.

a) *In nature, chlorine and bromine both occur in the form of two stable isotopes: ^{35}Cl and ^{37}Cl, ^{81}Br, and ^{79}Br. Calculate the natural abundance of each of these isotopes.*

b) *What isotopomers are possible for the Cl_2, Br_2, and BrCl molecules? Write their chemical formulas.*

c) *Calculate the mass percent of each isotopomer in a BrCl mixture prepared from naturally occurring chlorine and bromine.*

d) *How would you test experimentally the results of your calculations in part c)? Explain your reasoning.*

Problem 9-2.

Mixing concentrated and dilute solutions to achieve the desired concentration of solute is a routine procedure in the chemical laboratory.

Three different solutions of sodium bicarbonate, **A**, **B**, and **C**, were used to prepare three mixtures (No. 1, 2, 3). Each of these mixtures was teated with an excess of hydrochloric acid. The resulting carbon dioxide was collected and its volume measured (see the Table below).

Mixture No	Mass of solution A, g	Mass of solution B, g	Mass of solution C, g	Volume of gas evolved, dm^3 (S.T.P.)
1	150	100	50	8.92
2	150	100	150	12.09
3	100	100	100	8.85

a) *Calculate the mass percent of sodium bicarbonate in the initial solutions A, B, and C.*

b) *What is the mass percent of the salt in mixtures 1, 2, and 3?*

c) *What will be the percent composition of the solution prepared by combining mixture 3 with an equimolar amount of 10% (wt.) hydrochloric acid?*

d) *What will be the percent composition of the solution prepared by combining mixture 3 with an equimolar amount of 10% (wt.) sodium hydroxide?*

e) *Calculate the mass of the precipitate that will be produced if the solution prepared in part d) is cooled to 0 °C. The solubility of the precipitate at this temperature is 17.5 g per 100 g of water.*

NOTE: In this problem, assume that the solubility of CO_2 in water is negligible.

Problem 9-3.

When a certain metal **X** is heated at 600-700 °C, a reddish-yellow crystalline compound **A** is formed, which is 43.98% oxygen by weight. Reaction of **A** with oxalic acid, $H_2C_2O_4$, yields three oxides, one of which is an oxide **B**, containing 38.58% oxygen (by weight). Oxide **B** is amphoteric and readily soluble in alkalis and acids. When **B** is dissolved in aqueous alkali, a salt **C** is formed. The mass percent of sodium in compound **C** is 3.132 times smaller than that of oxygen. When the solution of **C** is cooled, a precipitate of compound **D** results. **D** is 49.24% oxygen by weight. When **B** is dissolved in sulfuric acid, a blue solution of salt **E** is obtained. Salt **E** is 49.08% oxygen by weight.

a) *Write the chemical formulas of compounds **A** through **E**.*

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

c) *When melted, compound **A** is an excellent conductor of electricity. Explain why.*

d) *Oxide **B** is readily soluble in water. What would a lithmus test of aqueous **B** show?*

Problem 9-4.

A gaseous mixture of a certain alkene **X** and oxygen has a density of 1.697 g/dm^3. The mole fraction of **X** in this mixture is 25%.

a) *Determine the molecular formula of alkene **X**.*
b) *Compound **X** exists as a pair of stereoisomers. Draw the structural formulas of these stereoisomers and provide their IUPAC names.*
c) *What products are formed when each of the stereoisomers of **X** reacts with bromine in CCl_4? Draw the stereochemical formulas of these compounds and give their IUPAC names.*
d) *The principal product of the reaction of **X** with aqueous bromine is 52.22% bromine by weight. Write the chemical equation for this reaction. Indicate the principal product and byproduct(s).*

Problem 9-5.

When the travelers in Jules Verne's novel "Les Enfants du capitaine Grant" (The Children of Captain Grant) were about to feast on a guanaco (South American llama) they had shot, they discovered that the meat had an unpleasant sour taste.

"The meat was too long kept, was it?" asked one of the travelers.

"No, but the meat had walked too much!" replied geographer Paganel and explained, "The guanaco is only good for eating when it is killed in a state of rest. If it has been long hunted, and gone over much ground before it is captured, it is no longer eatable."

a) The presence of what compound spoiled the travelers' meal? Give its common name and write the molecular formula.
b) Under certain conditions, this compound is formed in the human body. What are these conditions? Give your reasoning. Write the chemical equation representing the formation of this compound in the human body.
c) This compound exists as a pair of stereoisomers. What type of stereoisomerism do they represent? Draw a Fischer projection formula and give the IUPAC name (R,S-nomenclature) for each of these stereoisomers.
d) Which of the two stereoisomers is formed in the human body?
e) *This compound is found in most households. Give two examples of its occurrence. What role does this compound play?*

GRADE 10

Problem 10-1.

Ascorbic acid (vitamin C, $C_6H_8O_6$) is an essential ingredient of a healthy diet. Deficiency of vitamin C results in scurvy, a serious gum disease. Vitamin C is a weak diprotic acid (H_2A) whose first and second dissociation constants are $10^{-4.17}$ and $10^{-11.57}$, respectively.

a) *Calculate the pH value of a 0.100 M solution of ascorbic acid.*
b) *Large doses of ascorbic acid do not lower the blood pH value significantly and hence are not life-threatening. Explain why.*
c) *Ascorbic acid enters the blood stream from the digestive system in the anionic form, HA-. Derive the equation relating the mole fraction of HA- anions to the pH value of the solution. At what pH will the concentration of HA- in the blood reach the maximum? Show and explain your calculations.*
d) *Consider a simplified model of the human body as a single chamber. Suppose that the initial concentration of vitamin C in the body is 3 times the threshold*

(i.e., the lowest concentration at which the vitamin shows a curing effect), and assume that the rate of loss of vitamin C is proportional to its concentration. For how long will the vitamin be active in the body if the half loss time is 4 hours? Show details of your calculation.

Problem 10-2.

Amino acids are amphoteric, i.e., they can act both as an acid and as a base. Amphoteric properties of amino acids have important ramifications in biology.

a) *What causes amino acids to have amphoteric properties?*
b) *Write the chemical equations to represent the reversible reactions at equilibrium in aqueous aminoacetic acid (glycine).*
c) *At a certain pH value, called the isoelectric point, the average charge of an amino acid molecule is zero. Calculate the pH value at the isoelectric point of glycine. For glycine, pK_a=2.34, pK_b=4.40; the ionic product for water $K_w=10^{-14}$. Show your calculations.*
d) *Calculate the average charge of a glycine molecule at pH=6.50.*
e) *Which is a stronger base: glycine or its ethyl ester? Explain.*

Problem 10-3.

A certain naturally occurring, optically inactive, carboxylic acid **X** was first isolated by Carl Scheele from plant matter. A complete combustion of a 257.4 mg sample of **X** in oxygen produces 354 mL of CO_2 and 96.5 mg of water. Titration of another sample of **X** of the same size requires 13.60 mL of 0.0987 M NaOH in the presence of methyl orange, but 40.80 mL in the presence of phenolphthaleine. Compound **X** plays an important role in cell metabolism, particularly the respiratory process.

a) *Determine the empirical formula of compound **X**.*
b) *Draw the structural formula of compound **X**. Motivate your answer.*
c) *What plant did Scheele use as a source of **X**?*
d) *In the human body, compound **X** undergoes enzymatic dehydration followed by hydration. This reaction produces an optically active isomer of **X**. Write the chemical reactions for these transformations. Label all stereocenters in the product with an asterisk.*

Problem 10-4.

A sample of ethyl ester of propanoic acid was placed in a flask containing 15.0 g of 12.0% (wt.) aqueous NaOH. The mixture was refluxed (to prevent the loss of the ester) for a sufficiently long period of time. When the reaction mixture was evaporated in air, a dry solid residue was obtained. The mass of this residue did not change upon storing in open air. One half of the residue was treated with an excess of hydrochloric acid to give 151 mL (S.T.P) of carbon dioxide. The second half was combined with 13.0 g of a 6.57% (wt.) sulfuric acid and the mixture was evaporated in an oil bath at 200 °C.

a) Draw the structural formula of the initial ester.
b) Give the IUPAC name of this compound.
c) Draw the structural formulas of all isomers of the ester.
d) Write chemical equations for the reactions occurring in this experiment.
e) Calculate the mass of the ester in the initial sample.
f) What is the mass of the solid residue obtained by evaporating the solution at 200 °C?

Problem 10-5.

A 1.824 g sample of calcium metal was dissolved in 150 g of hydrochloric acid containing 0.840% HCl by weight. When the reaction mixture was cooled to 5 ^oC, 1.824 g of a solid precipitate and a clear filtrate were formed. The entire experiment was carried out in the absence of CO_2.

a) *Write chemical equations for the reactions occurring in this experiment.*
b) *What is the quantitative composition of the filtrate?*
c) *What will you observe when the filtrate is heated? Explain.*
d) *If 60.5 dm^3 (S.T.P.) of CO_2 is bubbled through one half of the filtrate, what will be the mass of the resulting precipitate?*
e) *How many grams of calcium hydroxide are required to prepare 40 g of a $Ca(OH)_2$ solution saturated at 5 ^oC?*

GRADE 11

Problem 11-1.

[see Problem 10-5.]

Problem 11-2.

A 40.12 mg sample of mercury was dissolved in an equivalent amount of 0.10 M nitric acid. Addition of aqueous potassium iodide to this solution produced a solid precipitate. The precipitate was dissolved in aqueous KI and then combined with aqueous AgNO3 to give 184.8 mg of a yellow precipitate which is 54.94% iodine by weight. The yellow precipitate was separated from the filtrate and heated at 45 ^oC to give a red compound which is 23.35% silver by weight.

a) *Write the chemical equations for all reactions occurring in this experiment. Explain your reasoning.*

Problem 11-3.

Viruses are assembled from proteins and nucleic acids. Tobacco mosaic virus (TMV) is 94% protein by mass, and the rest is RNA. The protein coat of TMV (capsid) is made up of a large number of individual polypeptide chains with a relatively low molecular mass (about 18000 g/mol). These chains are called protein subunits. When 100 g of TMV protein is completely hydrolyzed, the resulting mixture contains the following amounts of amino acids:

Amino acid	Ala	Arg	Asp	Val	Gly	Ile	Leu	Lys	Pro	Ser	Tyr	Thr	Glu	Trp	Phe	Cys
M, g/mol	89	174	133	117	75	131	131	146	115	105	181	119	147	205	165	121
Mass, g	7.2	11	14	9.4	3.0	7.5	8.3	1.7	5.3	9.7	4.2	11	13	3.5	7.6	0.70

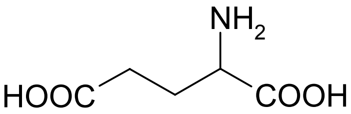
When TMV protein is treated with carboxypeptidase (an enzyme which hydrolyzes the carboxyl-terminal peptide bond), the resulting mixture contains about 2900 threonine (Thr) residues per TMV particle.

a) *How many residues of each amino acid form the protein coat of TMV?*
b) *Calculate the molar mass of a TMV protein subunit. Explain your reasoning.*
c) *How many protein subunits form the TMV capsid? Show and explain your calculations.*
d) *Calculate the molar mass of TMV and TMV RNA.*
e) *Assuming that the average molar mass of a ribonucleotide is 320 g/mol, estimate how many individual ribonucleotides form TMV RNA.*
f) *A polypeptide of what length is encoded by TMV RNA?*

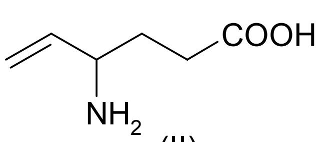
Problem 11-4.

One of the common approaches in rational drug design is based on the concept of bioisosterism, i.e., the ability of structurally different compounds to exhibit similar biological activity. The effect of bioisosterism is usually rationalized in terms of drug-receptor interactions. From this point of view, in order for two compounds to be bioisosteres, they must have: (1) similar functional groups separated by equal distances; (2) comparable acidity/basicity; (3) similar molecular shapes. γ-Aminobutyric acid (GABA) acts as a neurotransmitter (a molecule that carries signals between nerve cells) in the central nervous system. Disruption of GABA metabolism results in serious nervous disorders.

a) *Write the structural formula of GABA and give its IUPAC name.*
b) *Some of the eight compounds shown below are actually used as GABA substitutes. Analyze each of these structures and indicate whether it can be a bioisostere of GABA.*



(I)



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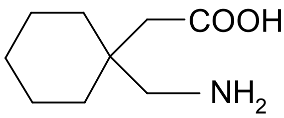

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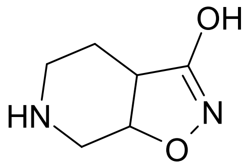

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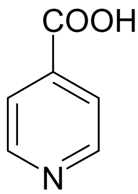

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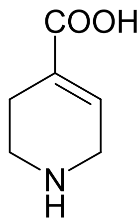

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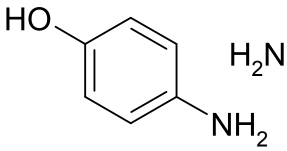

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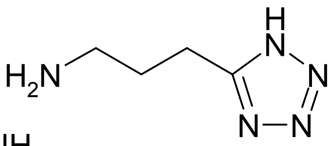


(VIII)

c) *In the human body, GABA is formed by the decarboxylation of a certain compound X. Write a chemical equation representing this transformation. Draw the structural formula of X and give its common and IUPAC names.*
d) *GABA can be synthesized from gases A and B by the following reaction sequence:*

$$A + B \xrightarrow{\text{base}} C \xrightarrow{H_2/Ni} D \xrightarrow{O_2/Cu,t} E \xrightarrow{NH_3} \text{GABA}$$

e) *Isomeric compounds **C** and **E** are 55.81% carbon and 37.17% oxygen by weight. The density of **C** and **E** relative to helium gas is 21.512. Draw the structural formulas of compounds **C** and **E***

Problem 11-5.

In 1883, E. Duclaux introduced the convention of designating an enzyme by the name of the substrate and the description of the enzyme's action, followed by the suffix "-ase". For example, choline acetyltransferase is an enzyme that transfers an acyl group (the action) to a choline molecule (the substrate) to yield acetylcholine.

Shown below is a reaction sequence representing biosynthesis of adrenaline (**F**), one of the most important hormones, from phenylalanine (3-phenyl-2-aminopropanoic acid, **A**):

A $\xrightarrow{\text{phenylalanine hydroxylase}}$ tyrosine (**B**) $\xrightarrow{\text{tyrosine hydroxylase}}$ 3,4-dihydroxy-phenylalanine (**C**) $\xrightarrow{\text{3,4-dihydroxyphenylalanine (DOPA) decarboxylase}}$

dopamine(**D**) $\xrightarrow{\text{dopamine } \beta\text{-decarboxylase}}$ noradrenaline (**E**) $\xrightarrow{\text{phenylethanolamine N-methyltransferase}}$ adrenaline (**F**)

a) *Draw the structural formula of compound A and the stereochemical formulas of its isomers. Show the absolute configuration of the stereocenters (R,S-nomenclature).*

b) *Draw the structural formulas of compounds* ***B*** *through* ***F****.*
Hints: (1) the first two reactions in the above sequence occur at the least sterically hindered site of the aromatic ring of the substrate; (2) the β-position in the dopamine molecule is at the second carbon atom of the chain starting at the amino group.

c) *Dopamine deficiency has been implicated as one of the causes of Parkinson's disease, even though dopamine molecules cannot cross the hematoencephalic barrier. What compound and in which enantiomeric form can be used to treat Parkinson's disease? Draw its structural formula. Motivate your choice.*

KEY SOLUTIONS

GRADE 9.

Problem 9-1.

a) $x(^{35}Cl) = 0.7735$;
$x(^{37}Cl) = 0.2265$;
$x(^{81}Cl) = 0.4520$;
$x(^{79}Br) = 0.5480$;

b) There are three isotopomers of Cl_2 and as many isotopomers of Br_2: $^{35}Cl^{35}Cl$, $^{37}Cl^{35}Cl$, $^{37}Cl^{37}Cl$, $^{79}Br^{79}Br$, $^{79}Br^{81}Br$, $^{81}Br^{81}Br$.
There are four isotopomers of BrCl: $^{35}Cl^{79}Br$, $^{35}Cl^{81}Br$, $^{37}Cl^{79}Br$, $^{37}Cl^{81}Br$.

c) The probability of finding each isotope of Cl and Br in the BrCl molecule is equal to the mole fraction of that isotope in the naturally occurring mixture. The mole fraction of each isotopomer of BrCl is therefore equal to the product of the natural abundances of the Cl and Br isotopes from which the molecule is built:

j	Isotopomers	M, g/mol	Mole fraction	Mass fraction
1	$^{35}Cl^{79}Br$	114	0.42388	0.419
2	$^{37}Cl^{79}Br$	116	0.1241	0.125
3	$^{35}Cl^{81}Br$	116	0.3496	0.352
4	$^{37}Cl^{81}Br$	118	0.1024	0.105

d) Using mass spectrometry. The mass spectrum of BrCl will contain a triplet with relative peak intensities:
I(114) : I(116) : I(118) = 0.424 : (0.124+0.350) : 0.102 = 89.5 : 100 : 21.5.

Problem 9-2.

a) $w_A = 0.1241$;
$w_B = 0.089$;
$w_C = 0.1189$.

b) $w_1 = 0.1115$;
$w_2 = 0.1134$;
$w_3 = 0.1107$.

c) w(NaCl) = 5.41 %.

d) 158 g of 10%(wt.) NaOH is required.

e) The amount of Na_2CO_3 produced is 41.87 g. $w(Na_2CO_3)$ = 9.14%.

Problem 9-3.

a) **A** – V_2O_5
B – VO_2
C – $Na_2V_4O_9$
D – $Na_2V_4O_9 * 7H_2O$
E – $VOSO_4$.

b) $4V + 5O_2 \longrightarrow 2V_2O_5$;
$V_2O_5 + H_2C_2O_4 \longrightarrow 2VO_2 + 2CO_2 + H_2O$;
$4VO_2 + 2NaOH \longrightarrow Na_2V_4O_9 + H_2O$;
$VO_2 + H_2SO_4 \longrightarrow VOSO_4 + H_2O$.

c) The reason is the ionic dissociation of V_2O_5:
$V_2O_5 = VO_2^+ + VO_3^-$.

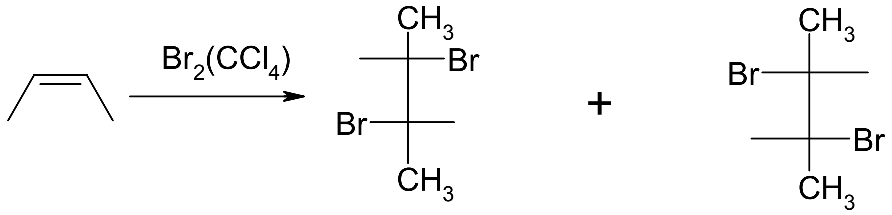
d) VO_2 is amphoteric, so its aqueous solution will have a pH value close to 7.

Problem 9-4.

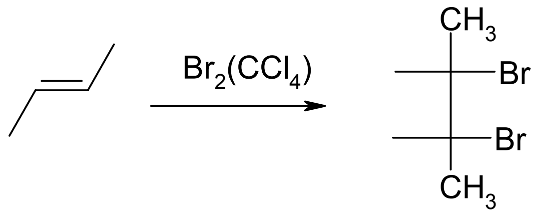
a) Butene, C_4H_8.

b) 2-butene, cis-2-butene, and trans-2-butene (or Z-2-butene and E-2-butene).

c) The following reactions take place:

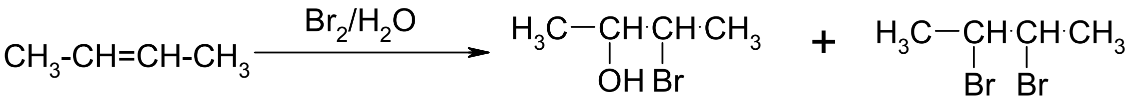


(R,R)-2,3-dibromobutane (S,S)-2,3-dibromobutane



(R,S)-2,3-dibromobutane (meso-form)

d)



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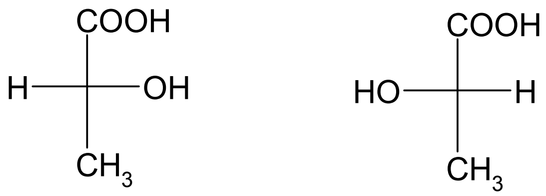
Problem 9-5.

a) Lactic (2-hydroxypropanoic) acid, $CH_3CH(OH)COOH$.

b) Sustained physical activity increases oxygen consumption. In the absence of oxygen, muscle tissues switch to anaerobic respiration in which glucose breaks down into lactic acid molecules:
$C_6H_{12}O_6$ ---> $2CH_3CH(OH)COOH$.

c) Enantiomers.



(R)- (S)-

d) S-lactic acid (L-isomer) only.

e) Sour milk, sauerkraut, pickles, etc.

GRADE 10

Problem 10-1.

a) Because there is a large difference between the first and second dissociation constants, it is sufficient to take into account only the first dissociation step. $[H^+]$ = $2.57*10^{-3}$ and pH = 2.59

b) Blood contains appreciable amounts of weak acid anions (carbonate, bicarbonate, citrate, etc.) and so can act as a buffer.

c) The mole fraction of HA^- (i.e., $\frac{[HA^-]}{C}$) has the following dependence on the pH value:

$$\alpha(HA^-) = \frac{K_1 \cdot [H^+]}{[H^+]^2 + K_1 \cdot [H^+] + K_1 \cdot K_2}.$$

To find the optimal pH value, we take the derivative of alpha with respect to $[H^+]$

and solve the equation: $\frac{d\alpha[H^+]}{d[H^+]} = \frac{\frac{1}{K_1} - \frac{K_2}{[H^+]^2}}{\left(\frac{[H+]}{K_1} - \frac{K_2}{[H^+]}\right)^2} = 0.$

This gives $[H^+]^2 = K_1{*}K_2$ and pH = $\frac{pK_1 + pK_2}{2}$ = 7.87.

d) This reaction is first order in the reactant.

Therefore, t = $t_{½}{*}\frac{\ln 3}{\ln 2}$ = 6.34 h = 380 min.

Problem 10-2.

a) Amino acids contain carboxy groups which behave like acids and amino groups which behave like bases:
$-COOH + H_2O$ Ω $-COO^- + H_3O^+$;
$-NH_2 + H_2O$ Ω $-NH_3^+ + OH^-$.

b) $H_2NCH_2COOH + H_2O$ Ω $H_2NCH_2COO^- + H_3O^+$;
$H_2NCH_2COOH + H_2O$ Ω $^+H_3NCH_2COOH + OH^-$;
H_2NCH_2COOH Ω $^+H_3NCH_2COO^-$;
$H_3O^+ + OH^-$ Ω $2H_2O$.

c) At the isoelectric point, $[A^+] = [A^-]$. Therefore, $[H^+]^2 = K_w \cdot \frac{K_a}{K_b}$.

pH = $\frac{14 + pK_a - pK_b}{2}$ = 5.97.

d) It can be shown that the average charge <Z> of a glycine molecule is given by

$$\frac{\frac{K_b}{K_aK_w}[H^+]^2 - 1}{\frac{K_b}{K_aK_w}[H^+]^2 + \frac{1}{K_a}[H^+] + 1}.$$

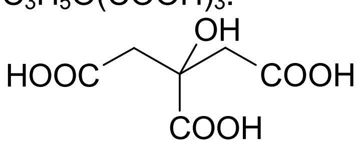
At pH = 6.50, $[H^+] = 10^{-6.50}$. Substitution of this value into the above equation gives <Z> = 0.84.

e) Glycine (pK_b = 4.40) is a stronger base than its ethyl ester (pK_b = 6.30) because of the "field effect".

Problem 10-3.

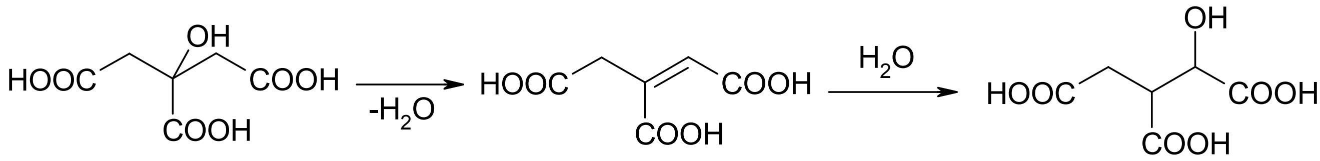
a) **X** – $C_6H_8O_7$.

b) Titration of **X** in the presence of phenylphthaleine requires three times as much alkali as titration in the presence of methyl orange. Therefore, the molecule of **X** contains at least three carboxy groups.
In the presence of methyl orange, titration of 1 mol of **X** requires 1 mol of alkali. Hence the molar mass of **X** is M = 192 g/mol. The molecular and empirical formulas of **X** are identical.
Assuming that one molecule of **X** contains 3 carboxy group, we obtain the formula $C_3H_5O(COOH)_3$.



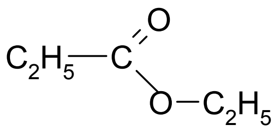
c) Citric acid was originally isolated by Scheele from lemons.

d)



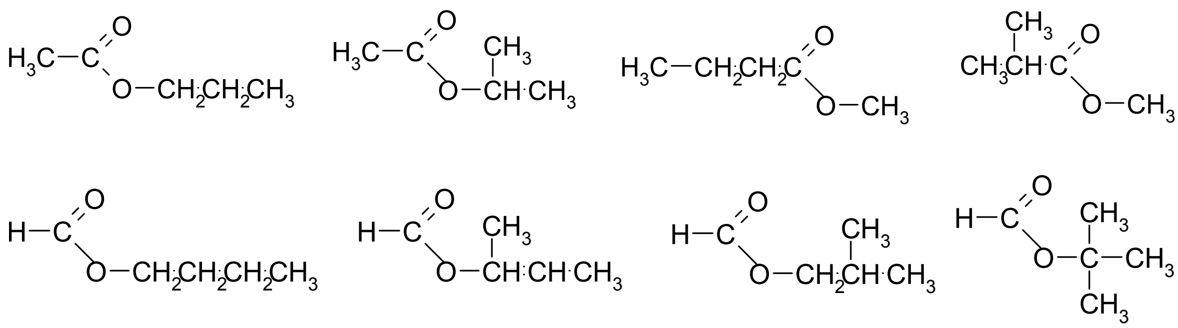
Problem 10-4.

a)



b) Ethyl propanoate.

c)



d) $C_2H_5COOC_2H_5 + NaOH \text{ ---> } C_2H_5COONa + C_2H_5OH$.
Volatile ethanol is lost during the evaporation of the solution in open air, while NaOH reacts with CO_2 to form sodium carbonate:
$2NaOH + CO_2 \text{ ---> } Na_2CO_3 + H_2O$.
When the residue is treated with sulfuric acid, the following reactions take place:
$Na_2CO_3 + H_2SO_4 \text{ ---> } Na_2SO_4 + CO_2 + H_2O$:
$2C_2H_5COONa + H_2SO_4 \text{ ---> } Na_2SO_4 + 2C_2H_5COOH$.

e) One half of the residue produced $\frac{0{,}151}{22{,}4}$ = 6.741 mmol of CO_2. The entire residue would have produced 13.48 mmol of CO_2. Therefore, the amount of Na_2CO_3 in the residue is 13.48 mmol, and the amount of NaOH used is 26.96 mmol.
The initial mixture contained 45.0 mmol of NaOH, of which
(45.0 – 26.96) = 18.0 mmol was used up during the saponification of the ester.
Hence, the initial sample contained 18.0 mmol of the ester.
The mass of the initial ester sample is 18.0*102 = 1.84 g.

f) The amount of sulfuric acid used was $\frac{13{,}0 \cdot 0{,}0657}{98}$ = 8.715 mmol.
One half of the solid residue obtained by the evaporation of the reaction mixture contained 9.0 mmol of C_2H_5COONa and 6.74 mmol of Na_2CO_3.
Upon the reaction with sulfuric acid, the mixture contained 6.74 mmol of Na_2SO_4 and (9.0 – 2*(8.715 – 6.74) = 5.07 mmol of C_2H_5COONa.
The mass of the solid residue is 6.74*142 + 5.07*96 = 1.44 g.

Problem 10-5.

See the solution of Problem 11-1.

GRADE 11

Problem 11-1.

a) $Ca + 2HCl = CaCl_2 + H_2\uparrow$;
$Ca + 2H_2O = Ca(OH)_2 + H_2\uparrow$.

b) The amount of calcium metal in the sample was $\frac{1824}{40,0}$ = 45.6 mmol.

The hydrochloric acid solution contained $\frac{150 \cdot 0,84}{100 \cdot 36,5}$ = 34.52 mmol of HCl, which reacted with $\frac{34,52}{2}$ = 17.26 mmol of Ca metal to give 17.26*111 = 1916 mg of $CaCl_2$.

The rest of Ca metal (45.6 – 17.26) = 28.34 mmol reacted with water to give 28.34*74 = 2097 mg of $Ca(OH)_2$.

$CaCl_2$ is readily soluble in water, while $Ca(OH)_2$ is only slightly soluble. Therefore, a fraction of the $Ca(OH)_2$ precipitated.

The final solution contained (2097 – 1824) = 273 mg of $Ca(OH)_2$ and 1916 mg of $CaCl_2$. The mass of water is (150 – 150*0,0084 – $\frac{28,34 \cdot 2 \cdot 18}{1000}$) = 147.72 g.

c) The solution will become cloudy because of additional precipitation of $Ca(OH)_2$. The solubility of $Ca(OH)_2$ decreases with temperature.

d) One half of the filtrate contains $\frac{273}{2}$ = 136.5 mg or $\frac{136,5}{74}$ = 1.84 mmol of $Ca(OH)_2$.

When CO_2 is bubbled through the solution, the following reactions can occur:
$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$;
$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$.

The amount of CO2 bubbled trough the filtrate is 60.5/22.4=2.70 mmol. Therefore, the precipitate contains (1.84 – (2.70 – 1.84)) = 0.98 mmol or 0.98*100 = 98 mg of $CaCO_3$.

e) We will assume that the presence of Ca^{2+} ions does not affect the solubility of $Ca(OH)_2$. [This is only an approximation. Strictly speaking, the calculation should be based on the solubility product of $Ca(OH)_2$, which can be estimated from the data of part a).]

In this approximation, 147.72 g of water dissolves at most 273 mg of $Ca(OH)_2$. In order to prepare 40 mL of saturated aqueous $Ca(OH)_2$, one needs

273*$\frac{40}{147,72 + 0,273}$ = 73.9 mg of $Ca(OH)_2$.

Problem 11-2.

a) Dilute nitric acid is reduced to NO:
$3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 2NO\uparrow + 4H_2O$;
$Hg(NO_3)_2 + 2KI = HgI_2\downarrow + 2KNO_3$;
$2KI + HgI_2 = K_2[HgI_4]$;

The amount of mercury in the sample is $\frac{40,12}{200,6}$ = 0.200 mmol.

Assuming that the yellow precipitate contains 1 Hg atom per formula unit, the molecular mass of this precipitate is $\frac{184.8}{0.2}$ = 924 g/mol.

Given that the mass percent of iodine is 54.95%, the formula unit of the precipitate contains $\frac{924 \cdot 0.5494}{126.9}$ = 4 iodine atoms and $\frac{924 - 200.6 - 4 \cdot 126.9}{107.9}$ = 2 Ag atoms.

Thus, the chemical formula of the precipitate is Ag_2HgI_4.
$K_2[HgI_4] + 2AgNO_3 = Ag_2[HgI_4]\downarrow + 2KNO_3$;
The mass percent of silver in Ag_2HgI_4 is 23.35%. Since the sample was heated at a low temperature, its composition must have remained the same.
The change in color can be explained by following the rearrangement:
$Ag_2[HgI_4] = HgAg[AgI_4]$
(yellow) (red)

Problem 11-3.

a) The least abundant amino acid in TMV protein is cysteine (Cys).
Let us assume that each protein subunit contains just one Cys residue. Then the number of other amino acid residues is given by the formula:

$$N_i = \frac{121}{0.70}\cdot\frac{m_i}{M_i}.$$

Using the data from the table we obtain:

Amino-acid	Ala	Arg	Asp	Val	Gly	Glu	Ile	Leu
N_i	14	11	18	14	7	15	10	11
АК	Lys	Pro	Ser	Tyr	Thr	Tir	Phe	Cys
N_i	2	8	16	4	16	3	8	1

The total number of amino acid residues in a TMV protein subunit is 158.
The molecular mass of this protein chain does not exceed $18*10^3$.
Therefore, the molecular formula of TMV protein coincides with the empirical formula.

b) Formation of each peptide bond is accompanied by the release of one water molecule. Thus, the molecular mass of the protein subunit is
$\sum N_i*(M_i - 18) = 17387$ g/mol.

c) Carboxypeptidase splits out one amino acid at the C-terminus of each protein subunit. Thus, the number of subunits in the capsid is 2900.

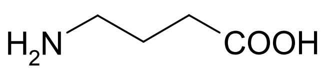
d) The molar mass of TMV is $\frac{2900\cdot 17387}{0.94} = 5.364*10^7$ g/mol.
The molar mass of TMV RNA is $0.06*5.364*10^7 = 3.218*10^6$ g/mol.

e) The number of nucleotides is $\frac{3.218\cdot 10^6}{320} = 10000$.

f) Each amino acid is encripted by a codon consisting of three nucleotides.
The RNA molecule encodes the information about a polypeptide containing about $\frac{10000}{3} = 3333$ amino acids.

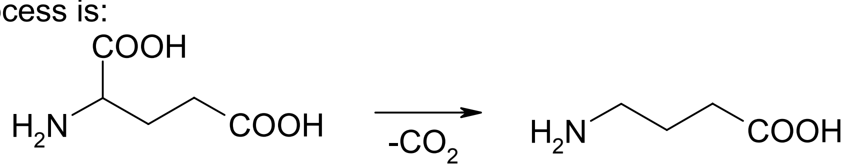
Problem 11-4.

a) The formula of γ-aminobutyric acid (GABA) is:



b) II, III, and V.

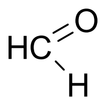
c) The process is:



2-amino-pentanedioic (glutamic) acid.

d) The ratio of C, H, and O atoms present in compounds **C** and **E** is:
C : H : O = 4.65 : 6.96 : 2.32 = 2 : 3 : 1.
The molar mass is 21.512*4 = 86 g/mol.
The molecular formula is $C_4H_6O_2$.

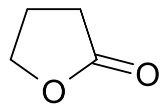
$HC\equiv CH$ **A**



B

$HOCH_2C\equiv CCH_2OH$ **C**

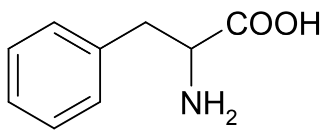
$HOCH_2CH_2CH_2CH_2OH$ **D**



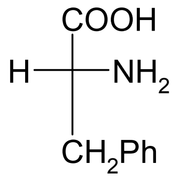
E

Problem 11-5.

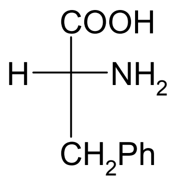
a) The structural formulas of compound A and its enantiomers are:



A

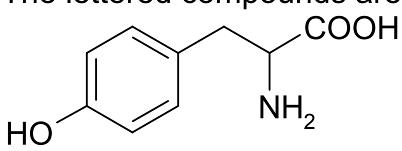


(R-)

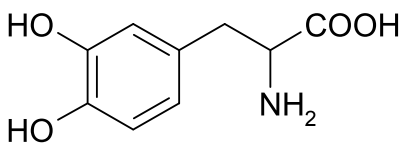


(S-)

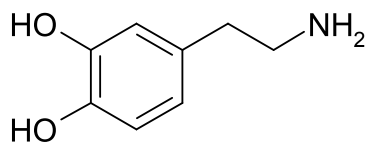
b) The lettered compounds are as follows:



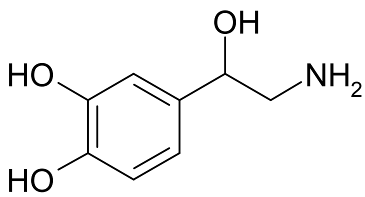
B



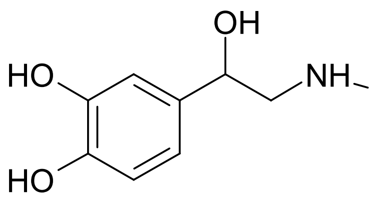
C



D

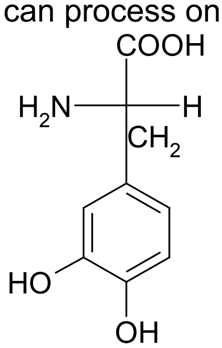


E



F

c) 3,4-Dihydroxyphenylalanine (DOPA), the bioprecursor of dopamine. Since all naturally occurring amino acids are of the L-type, enzymes in the human body can process only its L-form.



(S)-DOPA

Translated by **V.Staroverov**