

BELARUS
Ministry of Education

National Final. Theoretical round

Belarus, Vitebsk, March 26 - 31, 2001



Belarusian Chemistry Olympiads

Chemistry Olympiads have been administered in Belarus for more than 30 years. The competition is held every year in four rounds. All students of grades 9, 10, and 11 are eligible to participate in the first round. Approximately 100 students go to the National Final. The Final consists of two sessions: theoretical and practical, given separately for each grade. The theoretical part of 5 hours duration is a written exam which normally includes 6 problems. The practical examination contains 1-2 experimental problems and lasts 4-5 hours.

Translated by V.Staroverov ©, 2001

Grade 9.

Problem 9-1.

A sample of an alkali metal oxide was dissolved in an aqueous solution of a certain hydrohalic acid. The resulting solution contained only the corresponding metal halide. The mass fraction of solute in the final solution is the same as the mass fraction of the hydrogen halide in the initial acid solution.

- What is the quantitative relationship between the mass fraction of the salt in the neutralized solution and the molar mass of the alkali metal? Derive the general formula.
- On the basis on this formula, determine what metal and what acid were used in the experiment.

Problem 9-2.

Zirconium, a silvery white lustrous metal, is an indispensable component of alloys used in the nuclear power industry for the construction of nuclear reactors. One of the chief sources of zirconium is the mineral zircon (49.76% zirconium and 15.32% silicon). Zirconium metal is produced commercially by the Kroll process and by other methods. In the Kroll process, a blend of zircon and coke is treated with chlorine at 1000 °C, and the resultant zirconium tetrachloride is reduced with magnesium metal to give a zirconium metal sponge. The sponge is purified, arc-melted, and formed into ingots.

- Determine the chemical formula of zircon.
- Write the chemical equations for the preparation of zirconium by the Kroll process.
- How many metric tons of zirconium can be obtained from 32.5 metric tons of a zircon ore which contains 12.4% barren rock, if the actual yield of the metal is 95.5% (by mass)?
- The zirconium sponge is always contaminated with another metal that is very difficult to remove. What is this metal and why does it remain in the sponge?

Problem 9-3.

Metals in the solid state form crystal lattices. The unit cell of one such lattice type, the face-centered cubic (fcc), is a regular cube with metal ions at each corner and at the center of each face. One of the allotropic modifications of a certain metal X has an fcc structure in which the shortest distance between ions is 0.288 nm.

When a strip of zinc is placed in 500 mL of a 0.10 mol/L solution of the chloride of X, the mass of the strip increases by 4.94 g. If X is reacted with chlorine at high temperatures and the product is dissolved in hydrochloric acid, evaporation of the resulting solution gives yellows crystals containing 50.0% X (by mass).

- a) Identify the substance X.
- b) Calculate the density of X in the crystalline state.
- c) Write chemical equations for the reactions that occur in these experiments.
- d) Identify the compound that forms the yellow crystals.

Problem 9-4.

A certain gas A is a component of atmospheric air and plays an important role in the biochemistry of all life forms. A strip of magnesium burns in A to produce a grey mixture of a white substance B and a black substance C. Both B and C are virtually insoluble in dilute acids and bases. Combustion of C in oxygen yields A. When magnesium is burned in gas D, which is another component of atmospheric air, a white substance E is formed. The latter dissolves rapidly in acids and decomposes in water to produce gas F with a characteristic pungent odor.

- a) Identify compounds A through F.
- b) Write the chemical equations to represent the transformations of these compounds.
- c) The interaction of A with F is a commercial method of production of a certain valuable fertilizer. Name this fertilizer and write the chemical equation for its production.

Problem 9-5.

A 1.92 L sample (at STP) of a gaseous mixture of hydrocarbons that is 12.6% elemental hydrogen (by mass) was burned in an excess of oxygen. The volatile combustion products were dried and bubbled through 400 mL of a 4.82% (by mass) NaOH solution with a density of 1.05 g/cm³.

- a) Calculate the initial mass of the hydrocarbon mixture given that its specific gravity relative to nitrogen is 2.27.
- b) What volume is occupied by the resulting carbon dioxide at 40 C and 110 kPa?
- c) Determine the qualitative and quantitative composition of the solution obtained by bubbling the carbon dioxide gas through the NaOH solution.

Problem 9-6.

A chemical analysis of an organic compound (a colorless liquid at STP) gives 14.40% hydrogen (by mass). When a 0.870 g sample of this compound is burned completely in oxygen and the combustion products are bubbled through an excess of lime water, 6.20 g of a precipitate is formed. The specific gravity of vapors of this compound relative to dry air is approximately 2.5 times greater than that of ethane.

- a) Determine the empirical formula of the organic compound under investigation.
- b) Draw all of its plausible isomeric structures.

- c) Give the IUPAC names for any pair of the isomers that belong to different classes.
- d) What volume of air (at STP) containing 20.8% oxygen gas (by volume) is required for the combustion of 10.4 g of this organic compound?

Grade 10.

Problem 10-1.

A test tube sealed with a rubber stopper contains equal volumes of chlorine and hydrogen gases at 20 C and 101 kPa. When the test tube is exposed to bright sunlight, the stopper is shot out.

- a) Explain why the stopper shoots out of the test tube.
- b) Write the equation for the reaction that occurs in this experiment. What is the mechanism?
- c) Calculate the degree of conversion of the initial gases at the instant the stopper is shot out. Assume that the gases are ideal and have the same heat capacity of 20 J/mol K. The standard enthalpy of formation of hydrogen chloride is -92.3 kJ/mol. The stopper is shot out when the pressure inside the test tube exceeds the atmospheric pressure by 15%.

Problem 10-2.

A white solid substance X underwent a series of tests in which samples of X were calcined in a flow of various gases and the resultant solid residues were weighed. The experimental data are summarized in the following table:

Test No.	Gas on entry	Change in the mass of the sample, %
1	N ₂	-37.9
2	NH ₃	-51.7
3	O ₂	-31.0
4	HCl	+9.5
5	HCl+Cl ₂	-100

In all tests the mixture on exit contained, aside from the initial gases, the same unknown gas Y. In test No. 5, a reddish-brown substance Z condensed on the colder parts of the apparatus.

- a) Using the data provided identify the lettered compounds.
- b) Write the equations for the reactions that occur in these experiments.
- c) What is the structure of Z in the gas phase?

Problem 10-3.

Until the 19th century, black powder (gunpowder) was the only explosive known to mankind. For many years, black powder was widely used for military purposes. Nowadays it is employed mostly for pyrotechnic displays (signaling rockets, fireworks) as well as in the manufacture of cartridges for sporting guns.

The composition of black powder may vary but it always contains the following ingredients: saltpeter (potassium nitrate), sulfur, and charcoal. A chemical analysis of a sample of black powder is 75% saltpeter, 13% carbon and 12% sulfur by mass.

- Write a chemical equation for the combustion of the black powder of this composition. Explain the role of each ingredient.
- What combustion products would you expect if the powder had some other quantitative composition? Support your answer with the appropriate chemical equations.
- The combustion of 1.00 g of the same black powder releases 2.15 kJ of heat. Write the balanced thermochemical equation for this reaction.
- Calculate the speed of a 5.0 g bullet shot horizontally out of a cartridge containing 2.0 g of the same black powder. Assume that the cartridge has 35% efficiency.
- Estimate the hitting accuracy if the intended target is 300 m from the shooter at the same elevation. Neglect air resistance.

Problem 10-4.

Carbonic acid is very weak with the first and second ionization constants equal to $4.4 \cdot 10^{-7}$ and $5.6 \cdot 10^{-11}$, respectively. Of all carbonates, only the carbonates of alkali metals and ammonium are water soluble. For example, the solubility product constant for barium carbonate is $5.5 \cdot 10^{-10}$.

- Calculate the solubility of barium carbonate (in g/L) in pure water assuming that no ion hydrolyzes.
- Calculate the actual solubility of BaCO_3 taking into account the hydrolysis of the ions.
- Calculate the actual pH of the saturated BaCO_3 solution.
- Calculate the solubility of BaCO_3 in $1.0 \cdot 10^{-2}$ M NaHCO_3 .

Problem 10-5.

A certain hydrocarbon X (with a specific gravity of 1.93 relative to air) exists in the form of two stereoisomers A and B. Reaction of either one of these stereoisomers with bromine yields a mixture of two diastereomers C and D. Compound C is formed mostly from A, whereas D is formed mostly from B. Spectroscopic investigation of C reveals that at low temperatures this compound may be regarded as a mixture of two isomers.

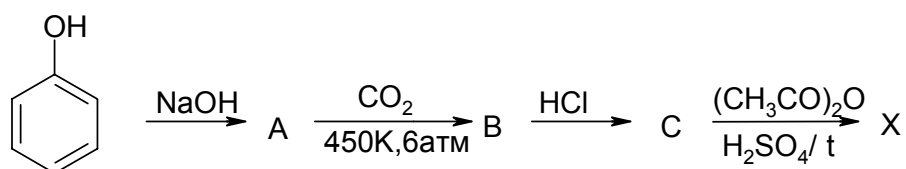
- Identify the hydrocarbon X. Draw the structural formulas of two stereoisomers of X and

give their IUPAC names.

- Identify compounds C and D and write their Fischer projection formulas.
- Explain why compounds A and B predominantly yield C and D, respectively.
- What type of isomerism is exhibited by compound C at low temperatures? Why are these isomers not observed at ordinary temperatures?
- Draw the structures of the two low-temperature isomers of C in a way that clearly shows their difference. Indicate which isomer prevails in an equilibrium mixture.

Problem 10-6.

Phenol is a high-volume commercial product used in the production of many valuable compounds. For instance, the following synthetic sequence leads to compound X which is the starting point in the manufacture of many pharmaceuticals.



Compound C can be obtained by oxidizing compound Y which is 26.20% oxygen (by mass). Treatment of Y with a strong base produces an equimolar mixture of Y1 and Y2. In a weakly acidic medium, compound Y turns into Y3 which is 21.22% oxygen (by mass). The structure Y3 contains four six-membered cycles.

- How was phenol commercially manufactured in the past? What is the modern industrial method of phenol preparation?
- Identify compounds A, B, C, and X and draw their structural formulas.
- Write the structural formulas of compounds Y, Y1, Y2, and Y3 and trace their interconversions.
- When compound Y is treated with aqueous FeCl_3 , a violet-red color is produced. Account for this observation given that the product of the reaction is separable into two enantiomers.

Grade 11.

Problem 11-1.

A 12.2 g sample containing rock salt (NaCl) and sylvinite ($\text{KCl} \cdot \text{NaCl}$) was dissolved in 100 mL of water. After the insoluble impurities were removed by filtering, the solution had a volume of 104 mL. A 10.0 mL aliquot of this solution was added to an excess of acidified aqueous silver nitrate. The resulting precipitate was filtered, dried, and weighed. Its mass was found to be 2.53 g. Another 5.00 mL aliquot of the solution was evaporated to dryness to

yield 0.543 g of a solid residue.

- Calculate the mass percentage of impurities in the sample.
- Calculate the mass percentage of NaCl and $\text{KCl} \cdot \text{NaCl}$ in the sample.
- Write chemical equations for the reactions that you would expect to occur when a direct electric current flows through the filtered solution.
- How many liters (at STP) of what gas are produced by the electrolysis of this solution with a current of 5 A after 3 hours?

Problem 11-2.

Each of the six labeled flasks contains 250 mL of a solution of one of the following substances: hydrogen chloride, sodium hydroxide, ammonium chloride, silver nitrate, cesium hydroxide, and copper dichloride. The mass content of solute in each flask is 5%.

- Describe how you would identify each of these six substances using no other reagents (including indicators) or specialized laboratory equipment. Briefly explain your reasoning.
- Write the net ionic equations for the reactions that occur in the proposed tests.

Problem 11-3.

Alkanes are relatively inert and react with only a few other substances. At elevated temperatures or under UV light they undergo oxidation and substitution reactions. For example, methane reacts with chlorine when heated or exposed to light. One of the products of this reaction is tetrachloromethane, a colorless liquid (b.p. $76.8\text{ }^\circ\text{C}$) with a density of 1.595 g/mL and a characteristic odor. Tetrachloromethane is slightly soluble in water (1.05 g per 100 g of water).

- What other compounds are formed when methane reacts with chlorine?
- What is the mechanism of the chlorination of methane? Explain.
- Estimate the C-Cl bond length in the tetrachloromethane molecule. State all the assumptions that you make.
- Indicate the type of chemical bond in the CCl_4 molecule.
- Tetrachloromethane is an excellent solvent for many compounds. Using the alchemist's rule that "like dissolves like" ("similia similibus solvuntur"), predict which of the following five substances---soot, fat, rust, gasoline, and chalk---should readily dissolve in CCl_4 . Rationalize your answer in terms of bond types and molecular structure.

Problem 11-4.

Silver acetate is a slightly soluble salt of a weak acid ($K_a = 1.75 \cdot 10^{-5}$). At $20\text{ }^\circ\text{C}$, 100 g of water dissolves 1.04 g of crystalline silver acetate. The solubility of the salt can be in-

creased by acidifying the solution (using, for example, nitric acid).

- Calculate the molar concentration of silver acetate in a solution saturated at 20° C, if the density of the solution is 1.01 g/cm³.
- Calculate the solubility product constant for silver acetate.
- What is the pH of a solution of silver acetate saturated at 20 °C?
- Compare the solubility of silver acetate in pure water with that in 0.10 M nitric acid.
- Calculate the pH of the saturated solution of silver acetate in 0.10 M nitric acid.

Problem 11-5.

A 1.34 g sample of a certain gaseous (at STP) organic compound X was burned completely in a vessel containing 2.50 L (at 295 K and 100.2 kPa) of nitrogen dioxide. The desiccated volatile combustion products were passed through heated copper filings and then bubbled through an excess of aqueous alkali. As a result, the volume of the gaseous mixture on exit decreased to 1.63 L (at STP).

- According to an elemental analysis, X does not contain either sulfur or any of the halogens. Using this information determine the molecular formula of X.
- Write the structural formula of X and give its IUPAC name.
- Write equations for the reactions that occur in this experiment.
- What qualitative tests can support the proposed structure of X?
- How would you establish the absence of sulfur and halogens in the composition of X?

Problem 11-6.

Monosaccharide A (one of the intermediate products of plant photosynthesis) exists in the form of two stereoisomers. Oxidation of A with Tollens' reagent (a solution of Ag₂O in aqueous ammonia) produces an acid B which is 60.3% oxygen by mass. The reduction of A with sodium amalgam in a weakly acidic medium yields compound C.

- Identify compounds A, B, and C.
 - Draw the two stereoisomers of A and give their IUPAC names.
 - Draw the structures of B, C, and their stereoisomers, if any.
-

KEY SOLUTIONS

GRADE 9.

Problem 9-1.

- The mass fraction of the salt in the final solution is given by $w = (M-1)/(M+8)$, where M is the molar mass of the alkali metal.
- Moving down the periodic table we obtain: $w(\text{Li}) = 0.40$, $w(\text{Na}) = 0.71$, $w(\text{K}) = 0.81$,

$w(\text{Rb}) = 0.90$, $w(\text{Cs}) = 0.94$. The mass fraction of the hydrohalic acid has a realistic value only in the first case, hence, the metal is lithium. Any of the following acids may have been used: HCl, HBr, HI.

Hydrofluoric acid can be ruled out because LiF is sparingly soluble.

Problem 9-2.

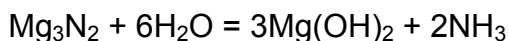
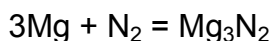
- a) The chemical formula of zircon is ZrSiO_4 .
- b) The following reactions occur in the preparation of Zr metal:
- $$\text{ZrSiO}_4 + 4\text{C} + 4\text{Cl}_2 = \text{ZrCl}_4 + \text{SiCl}_4 + 4\text{CO}$$
- $$\text{ZrSiO}_4 + 2\text{C} + 2\text{Cl}_2 = \text{ZrCl}_4 + \text{SiO}_2 + \text{CO}$$
- $$\text{ZrCl}_4 + 2\text{Mg} = 2\text{MgCl}_2 + \text{Zr}$$
- c) 13.52 metric tons of Zr.
- d) Zirconium always occurs together with its "double" hafnium. Zr and Hf have practically indistinguishable chemical properties.

Problem 9-3.

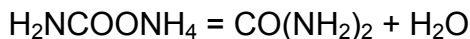
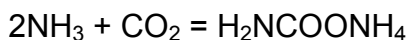
- a) The substance X is gold (Au).
- b) The density of gold is 19.41 g/cm^3 .
- c) The following reactions have occurred:
- $$3\text{Zn} + 2\text{AuCl}_3 = 3\text{ZnCl}_2 + 2\text{Au}$$
- $$2\text{Au} + 3\text{Cl}_2 = 2\text{AuCl}_3$$
- $$\text{HCl} + \text{AuCl}_3 = \text{H}[\text{AuCl}_4]$$
- d) The yellow crystals are chloroauric acid, $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$.

Problem 9-4.

- a) The lettered compounds are:
- A** – CO_2
- B** – MgO
- C** – C
- D** – N_2
- E** – Mg_3N_2
- F** – NH_3
- b) The following reactions occur:
- $$\text{Mg} + \text{CO}_2 = \text{MgO} + \text{C}$$
- $$\text{C} + \text{O}_2 = \text{CO}_2$$

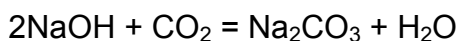
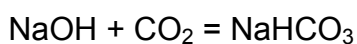


c) Urea (carbamide).



Problem 9-5.

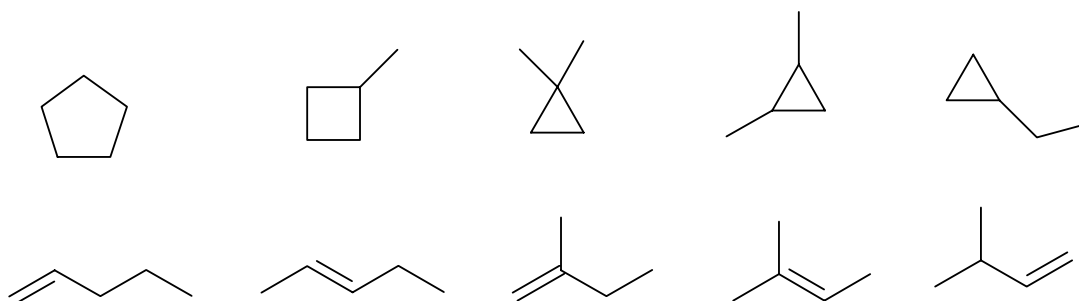
- a) The initial mass of the gaseous mixture is 5.45 g.
b) At the specified conditions, the volume of the resulting CO_2 is 9.38 dm^3 .
c) When the CO_2 gas is bubbled through aqueous NaOH , the following reactions occur:



The resulting solution contains 5.53% NaHCO_3 and 2.64% Na_2CO_3 by mass.

Problem 9-6.

- a) CH_2 .
b) Taking into account the specific gravity of vapors of the unknown compound, the molecular formula is C_5H_{10} . There exist 10 isomers of this composition:



- c) Example: cyclopentane and 1-pentene.
d) 120 dm^3 .

GRADE 10

Problem 10-1.

- a) The stopper is shot out because of the pressure build-up inside the test tube which is caused by the heat released in the reaction.
b) A free radical (chain) mechanism.
c) Since the number of moles of the gases is unchanged in the course of the reaction, the pressure build-up is an isochoric process. The degree of conversion is 0.953%.

Problem 10-2.

- a) X is FeCO_3 , Y is CO_2 , Z is FeCl_3 .
- b) The following reactions occur:
- $$\text{FeCO}_3 = \text{FeO} + \text{CO}_2$$
- $$3\text{FeCO}_3 + 2\text{NH}_3 = 3\text{Fe} + 3\text{CO}_2 + 3\text{H}_2\text{O}$$
- $$4\text{FeCO}_3 = 2\text{Fe}_2\text{O}_3 + 4\text{CO}_2$$
- $$\text{FeCO}_3 + 2\text{HCl} = \text{FeCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$$
- $$2\text{FeCO}_3 + 4\text{HCl} + \text{Cl}_2 = 2\text{FeCl}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O}$$
- c) At moderate temperatures, ferrous chloride (FeCl_3) exists in the gas phase as the dimer $(\text{FeCl}_3)_2$.

Problem 10-3.

- a) The molar ratio of the ingredients is $\text{KNO}_3 : \text{C} : \text{S} = 0.743 : 1.08 : 0.375 = 2 : 3 : 1$. This corresponds to the following reaction:
- $$2\text{KNO}_3 + 3\text{C} + \text{S} = \text{K}_2\text{S} + \text{N}_2 + 3\text{CO}_2$$
- KNO_3 is the oxidizing agent, S is the binder, C is the fuel (the reducing agent).
- b) Other plausible combustion products: KNO_2 , SO_2 , K_2CO_3 , K_2SO_3 , K_2SO_4 .
- $$4\text{KNO}_3 + \text{C} + \text{S} = 4\text{KNO}_2 + \text{CO}_2 + \text{SO}_2$$
- $$4\text{KNO}_3 + 2\text{C} + 3\text{S} = 2\text{K}_2\text{CO}_3 + 3\text{SO}_2 + 2\text{N}_2$$
- $$2\text{KNO}_3 + \text{C} + \text{S} = \text{K}_2\text{SO}_4 + \text{CO}_2 + \text{N}_2$$
- $$4\text{KNO}_3 + 3\text{C} + 2\text{S} = 2\text{K}_2\text{SO}_3 + 3\text{CO}_2 + 2\text{N}_2$$
- c) The stoichiometric mixture of the specified composition ($2\text{KNO}_3 + 3\text{C} + \text{S}$) weighs 270 g. Hence, the thermochemical equation is:
- $$2\text{KNO}_3 + 3\text{C} + \text{S} = \text{K}_2\text{S} + \text{N}_2 + 3\text{CO}_2 + 580.5 \text{ kJ}$$
- d) Assuming 35% efficiency, the combustion of 2.0 g of the powder transfers 1505 J of energy to the bullet. From the formula $E = mv^2/2$, the speed is $v = 7.8 \cdot 10^2 \text{ m/s}$. The flight time of the bullet is $t = s/v = 0.39 \text{ s}$.
- e) The fall (caused by gravity) is $r = gt^2/2 = 0.73 \text{ m}$.

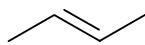
Problem 10-4.

- a) The solubility of BaCO_3 in pure water is $4.63 \cdot 10^{-3} \text{ g/L}$.
- b) If the hydrolysis is taken into account, the solubility increases by a factor of 2.27 to $1.05 \cdot 10^{-2} \text{ g/L}$.
- c) In the saturated BaCO_3 solution $\text{pH} = 9.63$.

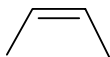
d) The solubility of BaCO_3 in 0.01 M NaHCO_3 is $9.46 \cdot 10^{-4}$ g/L.

Problem 10-5.

a) The molar mass of X is 56 g/mol. Hence, the hydrocarbon has the composition C_4H_8 . Of all the isomers of C_4H_8 , only 2-butene exists in the form of two stereoisomers:

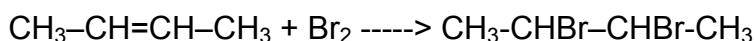


trans-2-butene

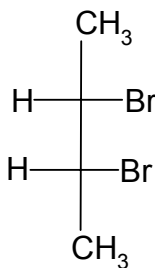


cis-2-butene

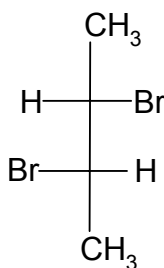
b) The reaction with bromine:



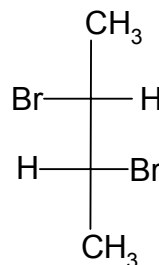
Two stereoisomeric 2,3-dibromobutanes are possible:



erythro-

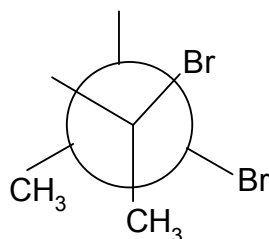
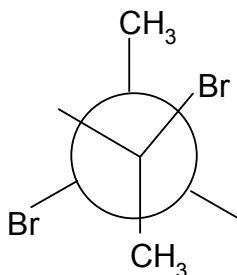


threo- (enantiomers)



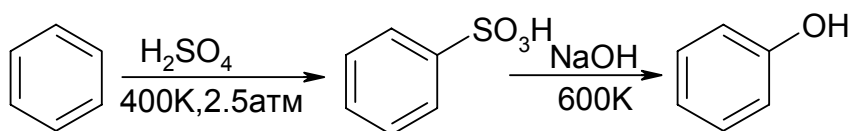
One of the isomers is C, the other is D.

- c) Considering the reaction mechanism, the threo-isomer is formed predominantly from cis-2-butene, while the erythro-isomer is the principal product of bromination of trans-2-butene.
- d) At low temperatures compound C exhibits conformational isomerism. Thus, C is the erythro-, D is the threo-isomer, A is trans-2-butene, and B is cis-2-butene.
- e) The difference between the conformational isomers of C is best represented by their Newman projection formulas:

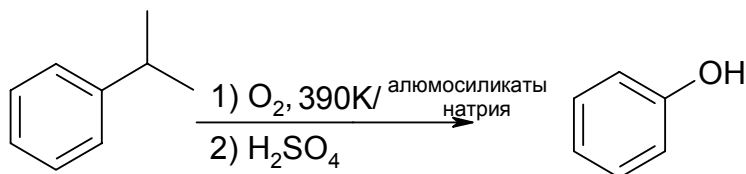


Problem 10-6.

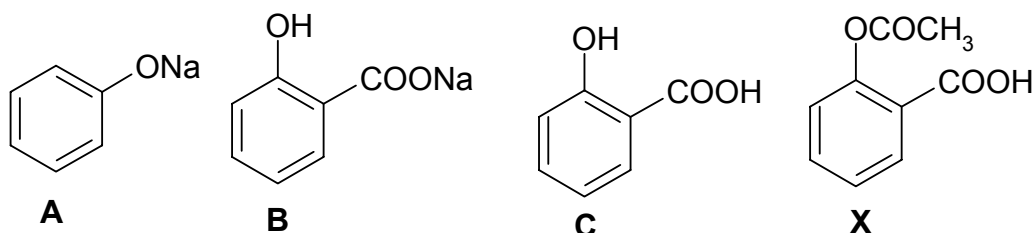
a) In the past, phenol was synthesized by the following method:



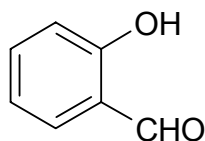
Nowadays phenol is manufactured mostly from cumene:



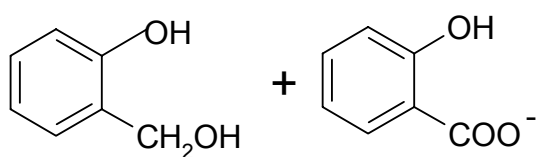
b) The lettered compounds are:



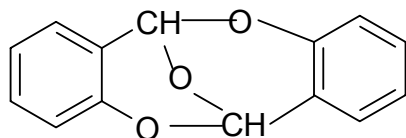
c) Since the oxidation of Y results in C, compound Y must have the molecular formula $C_7H_6O_2$. This is hydroxyaldehyde:



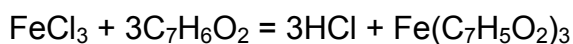
In the presence of a base, hydroxyaldehyde undergoes the Cannizzaro reaction to produce an equimolar mixture of o-hydroxybenzyl alcohol and a salt of o-hydroxybenzoic (salicylic) acid (Y1 and Y2):



d) In a weakly acidic medium Y turns into acetal Y3 which has the stated oxygen content:



The reaction:



produces a chelate complex which is responsible for the color. The three bidentate ligands give rise to the enantiomers.

Problem 11-1.

- a) The mass percentage of the impurities is $0.900/12.2 \cdot 100\% = 7.38\%$.
- b) The mixture contains 55.8% NaCl and 37.2% KCl·NaCl.
- c) The reaction that occurs during the electrolysis is:
$$\text{NaCl} + \text{KCl} + 2\text{H}_2\text{O} = \text{NaOH} + \text{KOH} + \text{Cl}_2 + \text{H}_2$$
When all chloride ions are exhausted, the electrolysis proceeds to decompose water:
$$2\text{H}_2\text{O} = \text{H}_2 + \text{O}_2.$$
- d) The mixture contains 0.112 mol of NaCl and 0.0358 mol of KCl·NaCl.
The electrolysis generates 2.06 L of Cl₂ and 2.10 L of O₂.

Problem 11-2.

- a) The CuCl₂ solution may be identified by its bluish color. The remaining five solutions fall into three groups:
- (i) the hydroxides which produce a blue precipitate with CuCl₂;
 - (ii) AgNO₃ which gives a white precipitate;
 - (iii) NH₄Cl and HCl which do not react with CuCl₂.
- The solution of NH₄Cl may be identified by the reaction with a hydroxide which produces the pungent ammonia gas.
- Therefore, the other solution in the same group must be HCl.
- The solutions of NaOH and CsOH may be distinguished by mixing equal volumes of each with HCl and manually comparing the amounts of heat released. (The neutralization of NaOH releases almost 4 times as much heat as that of CsOH. When equal volumes of 5% NaOH and HCl and mixed, the temperature rises by 8.5 K).
- An alternative method: If n mL samples of 5% NaOH and CsOH are mixed with n/2 mL of 5% HCl, the NaOH solution will remain basic whereas the solution of CsOH will become acidic. They may be distinguished by the above test with NH₄OH.
- b) The following reactions take place:
- $$\text{Ag}^+ + \text{Cl}^- = \text{AgCl}$$
- $$\text{Cu}^{2+} + 2\text{OH}^- = \text{Cu}(\text{OH})_2$$
- $$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$$
- $$\text{NH}_4^+ + \text{OH}^- = \text{NH}_3 + \text{H}_2\text{O}.$$

Problem 11-3.

- a) Chloromethane (CH₃Cl), dichloromethane (CH₂Cl₂), and trichloromethane (CHCl₃).

- b) The light-induced chlorination of methane occurs by a free radical (chain) mechanism.
- c) The estimated C-Cl bond length is 337 pm. (The actual value is 177 pm).
- d) The C-Cl bond in the CCl₄ molecule is polar covalent.
- e) The substances soluble in CCl₄ either have large nonpolar fragments (fats) or are themselves nonpolar (gasoline).

Problem 11-4.

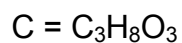
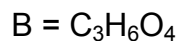
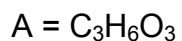
- a) The molar concentration of silver acetate is 0.0623 mol/L.
- b) $K_s = 3.88 \cdot 10^{-3}$.
- c) pH = 8.78.
- d) The solubility will increase by a factor of 2.09 to 0.130 mol/L.
- e) pH = 4.23

Problem 11-5.

- a) The molar ratio of the elements constituting X is: C : H : N = 1 : 5 : 1.
The empirical formula is CH₅N.
- b) There exists only one compound of this composition: methylamine, CH₃NH₂.
- c) The following reactions occur:
$$8\text{CH}_3\text{NH}_2 + 18\text{NO}_2 = 8\text{CO}_2 + 20\text{H}_2\text{O} + 13\text{N}_2$$
$$2\text{CH}_3\text{NH}_2 + 9\text{NO}_2 = 2\text{CO}_2 + 5\text{H}_2\text{O} + \text{N}_2 + 9\text{NO}$$
$$2\text{CH}_3\text{NH}_2 + 6\text{NO}_2 = 2\text{CO}_2 + 5\text{H}_2\text{O} + \text{N}_2 + 3\text{N}_2\text{O}$$
$$2\text{NO}_2 + 4\text{Cu} = 4\text{CuO} + \text{N}_2$$
$$2\text{NO} + 2\text{Cu} = 2\text{CuO} + \text{N}_2$$
$$\text{N}_2\text{O} + \text{Cu} = \text{CuO} + \text{N}_2$$
$$\text{CO}_2 + 2\text{NaOH} = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$
- d) The presence of the amine function manifests itself in the basicity of X. For example, an aqueous solution of X has pH > 7.
$$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} = \text{CH}_3\text{NH}_3^+ + \text{OH}^-$$
- e) Halogens may be detected by the Beilstein test. Sulfur may be discovered by oxidizing the sample with hot concentrated HNO₃ and precipitating the resulting sulfate anions with barium ions. To facilitate these tests, it is convenient to convert X into a crystalline salt which contains neither sulfur nor halogens, such as nitrate or acetate.

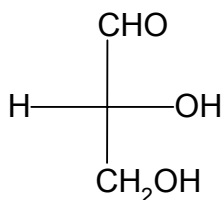
Problem 11-6.

- a) The molecular formulas of the lettered compounds are:

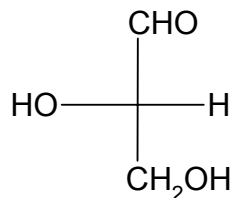


b) Only one monosaccharide – glyceraldehyde – can have the stated composition.

Glyceraldehyde exists as two stereoisomers:

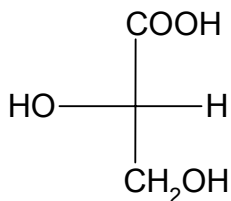
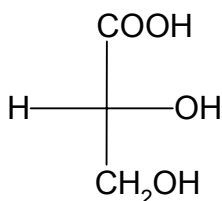


R-2,3-dihydroxypropanal



S-2,3-dihydroxypropanal

c) Compound B exists as two stereoisomers:



Compound C (glycerol) has no stereocenters and, therefore, no stereoisomers:

