# BELARUS

## Ministry of Education

*Chemistry Olympiad*

*National Final*

*Theoretical Examination*

*Gomel, March 29 - April 03, 2010*

### BELARUSIAN CHEMISTRY OLYMPIAD

Belarusian Chemistry Olympiad is an annual science competition held continuously since the early 1970s. The olympiads are organized and coordinated by faculty members of chemistry departments of major Belarusian universities with financial support from the Belarus Ministry of Education. Most participants are high school students of grades 9 through 11. It is not unusual, however, that exceptionally gifted ninth-grade students compete in the National Final.

Selection of nominees for the National Final within each grade 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 provinces 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 Final.

The National Final consists of a theoretical exam and a laboratory practical. The 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 between 4 and 5 hours. The winners of the National Final attend a study camp at the Belarusian State University in Minsk where they undergo additional training in preparation for the International Chemistry Olympiad.

# GRADE 9

## Problem 9-1

The freezing point of a solution is defined as the temperature at which first crystals of the solvent are formed. The freezing point of a pure solvent is equal to its melting point. It is well known that the freezing point of a solution is depressed relative to the freezing point of the pure solvent. The freezing point depression, $\Delta T$, is related to the molality of the solution, $b$, by the equation

$$\Delta T = Kb, \qquad \text{(equation 1)}$$

where $K$ is the cryoscopic constant.

1) *When a pure solvent freezes, how does its temperature change in the process?*
2) *When a solution freezes, how does its temperature change in the process?*
3) *The freezing point of a certain aqueous solution of NaCl is –0.500°C. Calculate the mass percent of NaCl in this solution.*
4) *The cryoscopic constant is related to the enthalpy of fusion of the solvent ($\Delta_m H$)*

   *by the equation $K = RT_m^2 M/\Delta_m H$, where $T_m$ is the melting point of the solvent and $M$ is its molar mass. For water, $K = 1.86$ K·kg·mol$^{-1}$. Calculate the molar enthalpy of fusion of water.*
5) *A more accurate relationship between the freezing point depression and the concentration is*

   $$\Delta T = RT_m^2 x_s/\Delta_m H, \qquad \text{(equation 2)}$$

   *where $x_s$ is the mole fraction of the solute in the solution. Show that for small $x_s$, equation 2 reduces to equation 1.*
6) *The enthalpy of fusion of a certain substance is 10.14 kJ/mol. A sample of this substance contains a small amount of an impurity. When heated at 181.85 K, 28% of the sample is in the liquid phase; at 182.25 K, this fraction increases to 53.0%. Calculate the melting point of the pure substance, the mole fraction of the impurity in the sample, and the melting point of the sample.*

## Problem 9-2

Three different minerals contain the same mole percent of lead. One of these minerals was first characterized by the German chemist Martin Klaproth in 1784, and it was named pyromorphite by the German mineralogist Johann Hausmann in 1813. Pyromorphite is 2.614% chlorine and 6.851% phosphorus by mass. It often occurs naturally with the second mineral called mimetite. This name derives from the Greek word *mimethes* (μιμητής), meaning "imitator". The mass percent of chlorine in mimetite is 2.382%. The third mineral was originally discovered in 1801 in Mexico by the Spanish mineralogist Andrés Manuel del Río. He called the mineral "brown lead" and pointed out that it contained a new element, which he named erythronium. Today, this mineral is the principal source of "erythronium". The mass percent of chlorine in "brown lead" is 2.503%.

1) *Deduce the chemical formulas of the three minerals in question.*
2) *Write balanced equations for the reactions of pyromorphite with excess amounts of dilute and concentrated hydrochloric acid.*
3) *What is the theoretical mass of "erythronium" that can be obtained from 10 metric tons of ore containing "brown lead", given that the ore is 12.0% barren matter? Assume that the process involves four steps, each with a practical yield of 89%.*

## Problem 9-3

The enthalpy change for a chemical reaction is defined as the sum of the enthalpies of formation of the products minus the sum of the enthalpies of formation of the reactants, each

multiplied by the corresponding stoichiometric coefficient. Enthalpies of formation of elementary substances in their standard states are taken to be zero.

Each of three unknown hydrocarbons contains two carbon atoms per molecule. The standard enthalpies of formation ($\Delta_f H^0$) of these hydrocarbons, arranged in the order of increasing number of hydrogen atoms, are 227, 52, and –85 kJ/mol, respectively. From standard tables of thermodynamical properties of compounds, $\Delta_f H^0(CO_2(g)) = -395$ kJ/mol, $\Delta_f H^0(H_2O(g)) = -242$ kJ/mol.

1) *Write the structural formulas of the three hydrocarbons in question. Name these compounds. For each compound, suggest a method of preparation using common reagents available in the chemical laboratory.*
2) *Write balanced equations to describe combustion of each of these hydrocarbons. Calculate the standard enthalpy change for each reaction.*
3) *For a hydrocarbon of the general formula $C_nH_{2n}$, what is the mole ratio of the hydrocarbon and oxygen gas maximizing the heat of combustion?*
4) *Each of the above three hydrocarbons is combined with a stoichiometric amount of oxygen gas. Calculate the ratio of the standard enthalpies of combustion of equal volumes of these stoichiometric mixtures.*
5) *Which of these three stoichiometric mixtures produces the hottest flame? Give your reasoning.*

## Problem 9-4

Compound **A** is a hydroxide of an unknown metal. When **A** is heated in an inert atmosphere, a solid residue (compound **B**) and a mixture of gases are formed. Compound **B** is 27.6% oxygen by mass. The gaseous mixture has a density of $4.20 \times 10^{-4}$ g/cm$^3$ at 400 K and 110 kPa.

1) *Determine the qualitative and quantitative composition of the gaseous mixture (in terms of mass and mole fractions).*
2) *Deduce the chemical composition of compounds **A** and **B**. Write a balanced equation to represent the reaction described in the problem statement.*
3) *What is the shortest synthetic route to the hydroxide **A** starting from the corresponding metal? Write a balanced equation for each step.*

## Problem 9-5

Calcium ions are neither reducing nor oxidizing agents in aqueous solution, so they cannot be detected by redox titration. However, they can be determined indirectly by substitution titration.

A 14.64 g sample of limestone was dissolved in hydrochloric acid. The solution was filtered, transferred quantitatively to a 100 mL graduated flask, and diluted to the mark with distilled water. A 25.00 mL sample of the prepared solution was neutralized with aqueous ammonia (in the presence of methyl orange) and combined with 50.0 mL of a 2.000 M aqueous solution of sodium oxalate, $Na_2C_2O_4$ (the sodium salt of oxalic acid). The resulting white precipitate was separated and rinsed on filter paper. The filtrate was combined with the rinse solution, transferred to a 100 mL graduated flask, and diluted to the mark with distilled water. A 10.00 mL sample of this solution was titrated in the presence of sulfuric acid with 14.85 mL of a 0.1844 M aqueous solution of potassium permanganate.

1) *Write balanced equations to describe the reactions that occur in this analysis, assuming that oxalic acid is oxidized by $KMnO_4$ to carbon dioxide and water.*
2) *Calculate the mass percent of $CaCO_3$ in the initial sample of limestone.*

# GRADE 10

## Problem 10-1
An unknown aromatic hydrocarbon **X** is 89.49% carbon by mass. It is known that the vapor density of **X** at 1 atm and 25°C does not exceed 10 g/L.
1) Determine the molecular formula of X.
2) Draw all possible structural formulas of X, given that free-radical chlorination of X yields only one monochlorosubstituted derivative.
3) Identify compound X, given that it is not readily oxidized with aqueous KMnO4.
4) Compound X can be nitrated with a nitrating mixture, and the product of that reaction can be oxidized with hot aqueous HNO3. These two reactions can also be also carried out in the reverse order. What are the final products in each case? Write the reaction scheme for each case.
5) Are there any optically active arenes isomeric with compound X? If so, write their stereochemical formulas showing the absolute configuration of each isomer. If not, explain why.

## Problem 10-2
A certain aqueous solution contains three oxoacids of phosphorus: **X**, **Y**, and **Z**. Acid **X** is 4.58% hydrogen and 46.9% phosphorus by mass; acid **Y** is 37.8% phosphorus by mass; the total number of atoms in a molecule of **Z** is 14.3% greater than in a molecule of **Y**.
6) Determine the molecular formulas of X, Y, and Z. Show your calculations.
7) Write the structural formulas of X, Y, and Z and arrange these acids in the order of increasing values of their first dissociation constants. Give your reasoning.

The complete neutralization of a 50.0 cm$^3$ sample of the initial solution requires 9.35 cm$^3$ of a 10.0% aqueous solution of NaOH (with a density of 1.07 g/cm$^3$). Two other 50.0 cm$^3$ samples were subjected to the following procedures and then titrated with 0.100 M sodium thiosulfate:

| Sample | Procedure | $V(Na_2S_2O_3)$, cm$^3$ |
|--------|-----------|--------------------------|
| 1 | The sample is treated with 200 mL of a 0.100 M solution of I$_2$, and the mixture is heated for 24 hours | 80.00 |
| 2 | The sample is neutralized with NaOH, the resulting mixture is treated with 200 mL of a 0.100 M solution of I$_2$, and then is allowed to stand for 4 hours | 360.0 |

8) Write balanced equations to describe the reactions that occur in this analysis.
9) What are the molar concentrations of X, Y, and Z in the initial solution?
10) How would you prepare acid X from phosphorus in the chemical laboratory?

## Problem 10-3
A mixture of nitrogen and hydrogen gases with a total volume of 0.500 dm$^3$ (measured at S.T.P.) was passed over a heated platinum catalyst. One half of the gaseous mixture of products was bubbled through 10 cm$^3$ of a 4.39% aqueous solution of HCl with a density of 1.020 g/cm$^3$. Titration of the excess acid required 18.30 cm$^3$ of 0.5486 M NaOH. The second half of the mixture was burned in an excess of oxygen gas and the combustion products were passed through a column filled with P$_2$O$_5$. As a result, the mass of the column increased by 0.08438 g.
1) Write balanced equations to represent the reactions that occur in this experiment.
2) Calculate the mass percent of HCl in the solution before the titration.
3) Calculate the mass percent of nitrogen gas in the initial mixture.

## Problem 10-4
Phosphorus is an undesirable component of metal alloys because it makes them brittle at

low temperatures. In iron-based alloys, phosphorus normally occurs in the form of iron phosphides or as a solid-state solution. High phosphorus concentrations in Fe-P alloys can be determined by the following method.

A sample of cast iron is dissolved in an excess of hot nitric acid. The resulting solution is replenished with $HNO_3$, and then an excess of aqueous ammonium molybdate is added to the reaction mixture. This causes all of the phosphorus to precipitate in the form of a bright-yellow heteropoly acid $(NH_4)_3H_4[P(Mo_2O_7)_6]$, which is insoluble in nitric acid. The precipitate is separated, rinsed on filter paper, and dissolved in an excess of aqueous ammonia. The resulting solution, which contains ammonium molybdate and ammonium hydrophosphate, is treated with aqueous solutions of magnesium chloride and ammonia. This produces a precipitate of magnesium-ammonium orthophosphate hexahydrate, which is rinsed, filtered off, and heated to constant mass at a high temperature. The mass loss constitutes 54.66%. The resulting solid residue is allowed to cool and then is weighed. It should be noted that if the oxidizing reagent used in the first step of the analysis is not sufficiently strong, a substantial fraction of the phosphorus may be lost, which will distort the final result of the analysis.

1) *Assuming that all of the phosphorus in the sample is in the form of Fe₃P, write balanced equations to represent the reactions that occur in this analysis.*
2) *Explain why the use of a weaker oxidizing reagent in the first step can affect the result of the determination. Write a chemical equation to represent the corresponding reaction.*
3) *Calculate the mass percent of phosphorus in a 14.66 g sample of cast iron, given that the mass of the solid residue in the final step is 179.6 mg.*

## Problem 10-5

A certain crystalline compound **X** can be prepared by fusing calcium metal with boron at 900°C. Compound **X** has a density of 2.44 $g/dm^3$ and finds many industrial applications. For example, it is used as a deoxidation agent in the production of oxygen-free copper. The unit cell of **X** is a cube with a side of 415 pm. The corner of each cube is occupied by a calcium atom while a group of boron atoms occupies the center.

1) *Determine the molecular formula of **X** and name this compound. Show your calculations.*
2) *Write the chemical formulas of the two substances into which compound **X** may transform during the production of "oxygen-free copper".*
3) *Suggest a different method for synthesizing compound **X** in the chemical laboratory. Write chemical equations for the reactions involved in this synthesis and indicate the conditions under which they take place.*
4) *What is the spatial arrangement of the boron atoms occupying the center of the unit cell?*
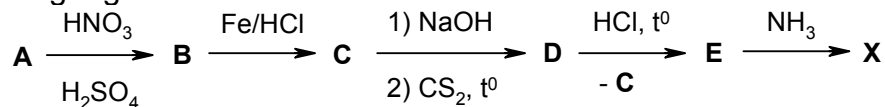
## GRADE 11

## Problem 11-1

> *"There is no disputing about tastes, and therefore there is always bragging, brawling, and rioting about tastes."* G. K. Chesterton

A white crystalline compound **X** draws attentions of scientists working in various fields. Some people find that **X** tastes very bitter even in minute concentrations, while others find it virtually tasteless. Yet another group asserts that **X** tastes sweet. It is believed that the ability to perceive **X** determines whether an individual can become a professional taster. Studies have shown that the ability to taste **X** depends on the genetic makeup of

the person, and so it is hereditary.

Compound **X** can be synthesized according to the following scheme. The starting material is a certain hydrocarbon **A** which is 92.3% carbon by mass and has a vapor density not exceeding 4 g/L.

$$A \xrightarrow[H_2SO_4]{HNO_3} B \xrightarrow{Fe/HCl} C \xrightarrow[2) CS_2, t^0]{1) NaOH} D \xrightarrow[-C]{HCl, t^0} E \xrightarrow{NH_3} X$$

1) *Deduce the structural formulas of compounds **A** – **E** and **X**, given that **D** is 14.05% sulfur and 12.27% nitrogen by mass, and that compound **X** is 55.24% carbon by mass.*
2) *Name the compound **X**.*
3) *What is the theoretical mass of **X** that can be obtained from 1.00 kg of **A**?*
4) *Compound **X** can be also prepared by heating **C** with a certain potassium salt (compound **Y**), which is 12.36% carbon by mass. Identify compound **Y** and write a balanced equation for this reaction. What historically significant synthesis is analogous to this method of preparation of **X**?*

## Problem 11-2

An unknown binary compound **A** is a solid at S.T.P and contains more than 10% hydrogen by mass. A strong reducing agent, compound **A** reacts with water to give an elementary substance **B**. When **A** is heated under pressure in an atmosphere of $CO_2$, the only product is a colorless crystalline compound **C**, which is 61.6% oxygen by mass. When **C** reacts with dilute sulfuric acid, the product is an organic compound **D**. However, when **C** reacts with concentrated $H_2SO_4$, the product is a gas **E** which has a lower density than air.

1) *Identify the lettered compounds and give their names.*
2) *Write chemical equations to describe the reactions that occur in this experiment.*
3) *Write an equation for the reaction of $AlCl_3$ with an excess of **A**. What is the practical use of the product of this reaction?*
4) *Assuming that each of the two elements comprising compound **A** occurs naturally in the form of two isotopes with relative isotopic masses differing by 1, calculate the relative abundances of the four possible isotopomers of **A**.*

## Problem 11-3

When organizing safe storage and handling of combustible solid materials, it is important to take into account their calorific values. These values are routinely included in material safety data sheets. The questions below refer to the following table.

| Substance | Calorific value Q, MJ/kg |
|---|---|
| Polyethylene | 47.14 |
| Natural rubber | 44.73 |

1) *What is the definition of the calorific value?*
2) *Using the data provided in the table, estimate the calorific value of butadiene-based synthetic rubber. Indicate all the assumption you have made.*
3) *Arrange the following substances in the order of increasing calorific value: cellulose, polymethyl methacrylate, natural rubber (polyisoprene), and polystyrene. Give your reasoning.*

A common model of fire extinguishers consists of two chambers. The main chamber contains 8 kg of a 5% aqueous solution of sodium bicarbonate and a small amount of a surfactant additive, while the auxiliary chamber contains 400 g of aqueous sulfuric acid. When the fire extinguisher is activated, the acid flows into the main chamber. The evolving gas causes the mixture to stir vigorously. Due to a pressure build-up, the foam is expelled from the main chamber and can be directed on a fire.

4) *Write balanced equations to describe the action of this particular fire extinguisher. What is the role of the surfactant additive?*

5) *Calculate the minimum mass percent concentration of sulfuric acid needed for the reaction with the gas-forming substance in the main chamber.*

6) *Estimate the volume of foam (in $dm^3$ at 20°C and 1 atm) that would be produced by a fire extinguisher of this particular model.*

## Problem 11-4

The following method is used for quantitative determination of hydrogen sulfide in air. The analyzed sample is bubbled through an excess of aqueous cadmium acetate. The resulting precipitate is treated with an excess of aqueous iodine whose concentration is known. This reaction proceeds quantitatively. The unreacted iodine is then titrated with a standardized solution of sodium thiosulfate using starch as an indicator.

In one particular experiment, a 2.68 $dm^3$ sample of air (measured at 24.0°C and 98.0 kPa) was bubbled through an excess of aqueous cadmium acetate. The resulting precipitate was treated with 20.0 $cm^3$ of a 0.08226 M solution of iodine. Titration of this mixture required 15.80 $cm^3$ of a 0.1085 M aqueous solution of sodium thiosulfate.

1) *Write balanced ionic equations to represent the reactions that occur in this analysis.*

2) *What changes of color can be observed in the course of this analysis? How would you explain each of them?*

3) *Calculate the volume of $H_2S$ (at S.T.P.) in the air sample.*

4) *Calculate the mass percent of $H_2S$ in the analyzed air.*

5) *Express the concentration of $H_2S$ in the analyzed air in parts per million (ppm).*

## Problem 11-5

Many properties of atoms and molecules can be rationalized by introducing the concept of an effective nuclear charge felt by an electron in a particular orbital. This charge, denoted by $Z_{eff}$, can be determined by a set of rules developed by John Slater.

According to Slater's rules, the electrons are divided into groups that keep s- and p- orbitals with the same principal quantum number together, but otherwise are made up of individual subshells: [1s][2s,2p][3s,3p][3d][4s,4p][4d][4f][5s,5p][5d], and so on. Each group is assigned a different shielding constant which depends upon the number and types of electrons in the groups preceding it. The shielding constant for each group is formed as the *sum* of the following contributions: (i) An amount of 0.35 from each *other* electron within the *same* group except for the [1s] group, where the other electron contributes only 0.30. (ii) If the group is of the [ns,np] type, an amount of 0.85 from each electron with a principal quantum number (n–1) and an amount of 1.00 for each electron with principal quantum numbers (n–2) and smaller. (iii) If the group is of the [nd] or [nf], type, an amount of 1.00 for each electron with a principal quantum number (n−1) and smaller. The effective charge is the difference between the actual nuclear charge and the sum of these shielding constants.

For example, the nuclear charge of the carbon atom is 6 and the electrons belong to one of the two groups, [1s] and [2s,2p]. The effective nuclear charges experienced by the electrons in the 1s, 2s, and 2p orbitals are as follows:

$Z_{eff}(1s) = 6 – (1 × 0.3) = 5.7$
$Z_{eff}(2s) = 6 – (2 × 0.85 + 3 × 0.35) = 3.25$
$Z_{eff}(2p) = 6 – (2 × 0.85 + 3 × 0.35) = 3.25$

1) *Write the electron configurations of the oxygen, sodium, and titanium atoms.*

2) *Calculate the effective nuclear charge experienced by electrons occupying the highest and next-to-highest energy levels in each of these atoms.*

The relative ability of an atom to attract valence electrons is called electronegativity. Quan-

titatively, an atom's electronegativity $\chi$ can be estimated using a formula proposed by Allred and Rochow: $\chi = 0.359 Z^* / r^2_{cov} + 0.744$, where $Z^*$ is the effective nuclear charge experienced by valence electrons and $r_{cov}$ is the covalent radius of the atom expressed in Ångstrøms (Å). (1 Å = $10^{-10}$ m).

3) *Calculate the Allred–Rochow electronegativity of the atoms H, O, F, and Na..*

| Atom | H | O | F | Na |
|------|---|---|---|----|
| $r_{cov}$, pm | 42 | 74 | 72 | 167 |

4) *Estimate the polarity of the O–H bond in a water molecule relative to NaF by assuming that (a) the polarity of a bond is proportional to the difference in the electronegativities of the bonded atoms; (b) the valence electron of the sodium atom in the NaF molecule is completely transferred to the fluorine.*

5) *Estimate the dipole moment of the water molecule relative to the dipole moment of NaF. The dipole moment of a molecule is the vector sum of the dipole moments of the individual bonds. The dipole moment $\mu$ of a bond is $\mu_{bond} = l_{bond} q$, where the charge $q$ is equal to the relative polarity of the bond. The H–O–H angle in the water molecule is 105°. The relative dipole moment of NaF is 7.2 arbitrary units.*

**SOLUTIONS**

**GRADE 9**

**Problem 9-1**

1) When a pure solvent freezes, the temperature remains constant until all of the solvent has crystallized.

2) As the solvent precipitates, the molality of the solution increases, so the freezing point becomes depressed even lower. Therefore, when the solvent crystallizes, the temperature of the solution decreases.

3) Since NaCl is completely ionized in aqueous solution, the number of particles is doubled: $NaCl = Na^+ + Cl^-$.

   Therefore, the molality of the solution is $\dfrac{0.500}{1.86} \times \dfrac{1}{2} = 0.1344$ mol/kg, that is, the solution contains 0.1344 mol of NaCl per 1 kg of water.
   $M(NaCl) = 58.5$ g/mol.

   The mass percent of NaCl in the solution is $\dfrac{0.1344 \times 58.5}{1000 + 0.1344 \times 58.5} \times 100\% = 0.780\%$.

4) The enthalpy of fusion is $\Delta_m H = R T_m^2 M/K$.
   The melting point of pure water is $0^\circ$C or 273 K.
   $M(H_2O) = 18$ g/mol $= 0.018$ kg/mol. Therefore,

   $$\Delta_m H = R T_m^2 M/K = \frac{8.314 \times (273)^2 \times 0.018}{1.86} = 5996 \text{ J/mol} \approx 6 \text{ kJ/mol}$$

5) Let us relate the mole fraction of the solute, $x$, to the molality of the solution, $b$. By definition,
   $x = n(\text{solute})/[n(\text{solute}) + n(\text{solvent})]$.
   For dilute solutions, $n(\text{solute}) \ll n(\text{solvent})$, so we can write
   $x \approx n(\text{solute})/n(\text{solvent}) = n(\text{solute}) \times [M(\text{solvent})/m(\text{solvent})] = [n(\text{solute})/m(\text{solvent})]M = bM$,
   where $b$ is the molality of the solution and $M$ is the molar mass of the solvent.
   Combining equation 2 with the equation for the cryoscopic constant we have

   $$\Delta T = \frac{R T_m^2}{\Delta_m H} x_s = \frac{K}{M} x_s = \frac{K}{M} bM = Kb.$$

6) Let the mole fraction of the impurity in the sample be $x$. Then the mole fraction of the impurity in the liquid phase is $x/y$, where $y$ is the fraction of the fused substance. We have following system of equations:

   $$(T_m - 181.85) = \frac{R T_m^2}{\Delta_m H} \frac{x_s}{0.28}.$$

   $$(T_m - 182.25) = \frac{R T_m^2}{\Delta_m H} \frac{x_s}{0.53},$$ where $T_m$ is the melting point of the pure substance.

   Solution of this system of equations yields the melting point of the pure substance,
   $T_m(\text{pure}) = 182.70$ K, and the mole fraction of the impurity, $x = 0.0087$ or 0.87%.
   The melting point of the sample corresponds to $y = 1.00$. Therefore,
   $T_m(\text{sample}) = 182.25 + (R T_m^2/\Delta_m H) \times (x/1.00) = 182.46$ K.

**Problem 9-2**

1) Mineral phosphorus occurs in the form of $PO_4^{3-}$ anions. Therefore, we can write the composition of pyromorphite as $Pb_x(PO_4)_yCl_z$.
   $M(P) = 30.97$ g/mol.
   $M(Cl) = 35.45$ g/mol.
   $y : z = \dfrac{6.851}{30.97} : \dfrac{2.614}{35.45} = 0.22121 : 0.07374 = 3 : 1.$

This gives $Pb_x(PO_4)_3Cl$. Assuming that lead in pyromorphite is bivalent we obtain $x = 5$.
Thus, the composition of pyromorphite is $Pb_5(PO_4)_3Cl$. Let us assume that the two other minerals have the composition $Pb_5X_3Cl$, where X is a trivalent atom or a group of atoms.

The molar mass of mimetite ($Pb_5X_3Cl$) is $\dfrac{35.45}{0.02382} = 1488.2$ g/mol.

$M(Pb) = 207.2$ g/mol.

Thus, the molar mass of the group X is $\dfrac{1488.2 - 5 \times 207.2 - 35.45}{3} = 138.91$ g/mol.

The group X is $AsO_4$. The formula of mimetite is $Pb_5(AsO_4)_3Cl$.

The molar mass of the third mineral, $Pb_5Y_3Cl$, is $\dfrac{35.45}{0.02503} = 1416.3$ g/mol.

The molar mass of the group Y is $\dfrac{1416.3 - 5 \times 207.2 - 35.45}{3} = 114.95$ g/mol.

The group Y is $VO_4$; "brown lead" is $Pb_5(VO_4)_3Cl$.

2) Reaction of pyromorphite with an excess of dilute hydrochloric acid:
$Pb_5(PO_4)_3Cl + 9HCl = 5PbCl_2\downarrow + 3H_3PO_4$.
Reaction with an excess of concentrated HCl:
$Pb_5(PO_4)_3Cl + 19HCl = 5H_2[PbCl_4] + 3H_3PO_4$.
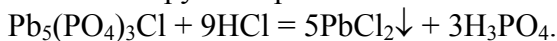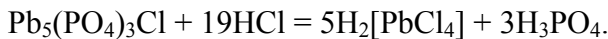
3) $Pb_5(VO_4)_3Cl \rightarrow 3V$.
$M(V) = 50.94$ g/mol.
$M(Pb_5(VO_4)_3Cl) = 1416.3$ g/mol.

The ore contains $10(0.88) = 8.8$ tons or $\dfrac{8.8 \times 10^6}{1416.3} = 6.21 \times 10^3$ mol of $Pb_5(VO_4)_3Cl$.

The ideal yield is $6.21 \times 10^3 \times 3 = 1.86 \times 10^4$ mol of vanadium metal.
The overall practical yield is $1.86 \times 10^4 (0.86)^4 = 1.167 \times 10^4$ mol or
$1.167 \times 10^4 \times 50.94 = 5.94 \times 10^5$ g $= 594$ kg of vanadium metal.

## Problem 9-3

1) The three hydrocarbons are

$H_3C—CH_3$        $H_2C = CH_2$        $HC \equiv CH$
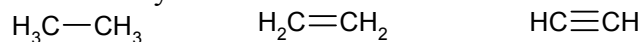
   ethane              ethylene              acetylene.

Acetylene can be prepared by treating calcium carbide with water:
$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$.
Ethylene can be obtained by treating ethanol with concentrated sulfuric acid:
$C_2H_5OH \rightarrow C_2H_4 + H_2O$.
Ethane can be prepared by heating a salt of propionic acid with an alkali, e.g.,
$C_2H_5CO_2Na + NaOH \rightarrow Na_2CO_3 + C_2H_6$.
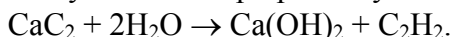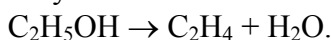
2) The combustion reactions are:

$C_2H_2 + \dfrac{5}{2}O_2 \rightarrow 2CO_2 + H_2O$;

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$;

$C_2H_6 + \dfrac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$.
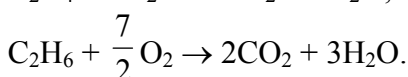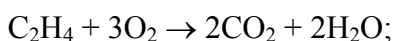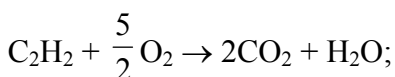
The enthalpy change for the first reaction is

$\Delta_r H^0 = 2\Delta_f H^0(CO_{2(г)}) + \Delta_f H^0(H_2O_{(г)}) - \Delta_f H^0(C_2H_{2(г)}) - \dfrac{5}{2}\Delta_f H^0(O_{2(г)}) =$

$= 2 \times (-395) + (-242) - 227 - \dfrac{5}{2} \times 0 = -1259$ kJ.

Similarly, for the second and the third reactions,

$\Delta_r H^0 = 2\Delta_f H^0(CO_{2(r)}) + 2\Delta_f H^0(H_2O_{(r)}) - \Delta_f H^0(C_2H_{4(r)}) - 3\Delta_f H^0(O_{2(r)}) =$
$= 2 \times (-395) + 2 \times (-242) - 52 - 3 \times 0 = -1326$ kJ.

$\Delta_r H^0 = 2\Delta_f H^0(CO_{2(r)}) + 3\Delta_f H^0(H_2O_{(r)}) - \Delta_f H^0(C_2H_{6(r)}) - \dfrac{7}{2}\Delta_f H^0(O_{2(r)}) =$

$= 2 \times (-395) + 3 \times (-242) - (-85) - \dfrac{7}{2} \times 0 = -1431$ kJ.

3) We write

$$C_nH_{2n} + \frac{3n}{2} O_2 \rightarrow nCO_2 + nH_2O + Q.$$
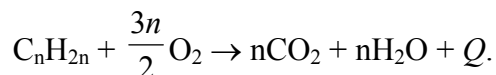
The optimal mole ratio of the reagents is $C_nH_{2n} : O_2 = 1 : \dfrac{3n}{2}$.

4) The thermochemical equations are

$$C_2H_2 + \frac{5}{2} O_2 \rightarrow 2CO_2 + H_2O + 1259 \text{ kJ}$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O + 1326 \text{ kJ}$$

$$C_2H_6 + \frac{7}{2} O_2 \rightarrow 2CO_2 + 3H_2O + 1431 \text{ kJ}$$
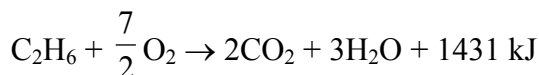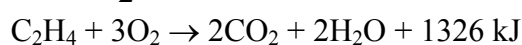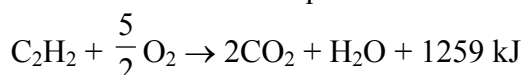
The amount of heat produced by combustion of 1 mol of a stoichiometric mixture is

$C_2H_2$: $\quad \dfrac{1}{1+\dfrac{5}{2}} \times 1259 = 359.7$ kJ

$C_2H_4$: $\quad \dfrac{1}{1+3} \times 1326 = 331.5$ kJ

$C_2H_6$: $\quad \dfrac{1}{1+\dfrac{7}{2}} \times 1431 = 318$ kJ

Therefore, the ratio of the amounts of heat is
acetylene : ethylene : ethane = 1.00 : 1.04 : 1.13.

5) Acetylene, because it produces the least amount of water.

**Problem 9-4**

1) Metal hydroxides decompose when heated:
$2Me(OH)_n \rightarrow Me_2O_n + nH_2O\uparrow$.
If the resulting oxide is not very stable, the metal can change its oxidation state. There are two possibilities to consider. Decomposition of the oxide lowers the oxidation number:

$$Me_2O_n \rightarrow Me_2O_m + \frac{n-m}{2} O_2\uparrow;$$
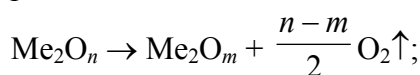
Reaction of the oxide with water vapors increases the oxidation number of the metal:
$Me_2O_n + (p-n)H_2O \rightarrow Me_2O_p + (p-n)H_2\uparrow$.
At 400 K and 110 kPa, water is in the gas phase, so the gaseous products can be either
$(O_2 + H_2O)$ or $(H_2 + H_2O)$.
$M(H_2) = 2.02$ g/mol.
$M(H_2O) = 18.02$ g/mol.
$M(O_2) = 32.00$ g/mol.
From the ideal gas equation of state
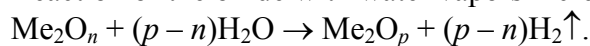
$$M = \frac{m}{n} = \frac{mRT}{pV} = \frac{\rho RT}{p} = \frac{(4.20\times10^{-4}\times10^3)\times8.314\times400}{110} = 12.70 \text{ g/mol},$$

which means that the gaseous mixture is $(H_2 + H_2O)$.

Let the mole fraction of water vapor in this mixture be $x$. Then we have the equation

$18.02x + 2.02(1 - x) = 12.70$,

from which $x = 0.667$

$x(H_2O) = 0.667$

$x(H_2) = (1 - 0.667) = 0.333$

The mass fractions of the ingredients are

$w(H_2O) = \dfrac{18.02 \times 0.667}{12.70} = 0.947$

$w(H_2) = (1 - 0.947) = 0.053$

2) On the basis of the analysis of part (1) we can conclude that the hydroxide undergoes the reaction

$x Me(OH)_a \rightarrow x MeO_b + 2H_2O\uparrow + H_2\uparrow$

The oxidation number of Me in the oxide is higher than in the hydroxide. Let us write the formula of the oxide as $Me_2O_n$, where $n$ is the oxidation number of the metal in the oxide. Then

$0.276 = \dfrac{16.00n}{16.00n + A_r(Me) \times 2}$,

which gives $A_r(Me) = 21.0n$.

There are no metals with relative atomic masses equal to $21n$, where $n$ is an integer. Therefore, the oxide must be mixed, for instance, $Me_3O_4$. Assuming this composition, we have

$0.276 = \dfrac{16.00 \times 4}{16.00 \times 4 + A_r(Me) \times 3}$,

from which $A_r(Me) = 55.9$, so that $Me = Fe$.

If **B** is $Fe_3O_4$, then **A** is $Fe(OH)_2$.

The reaction of thermal decomposition of iron(II) hydroxide is

$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O\uparrow + H_2\uparrow$.
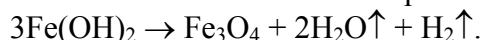
3) $Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$;

$FeCl_2 + 2NaOH \rightarrow 2NaCl + Fe(OH)_2\downarrow$.


**Problem 9-5**

1) $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2\uparrow$;

$HCl + NH_3 = NH_4Cl$;

$CaCl_2 + Na_2C_2O_4 =- CaC_2O_4\downarrow + 2NaCl$;

$Ca_2C_2O_4 + H_2SO_4 = CaSO_4\downarrow + H_2C_2O_4$;

$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2\uparrow + 8H_2O$.

2) The titration of the 10.00 mL sample required

$0.1844 \times \dfrac{14.85}{1000} = 2.738$ mmol of $KMnO_4$.

The sample contains $2.738 \times \dfrac{5}{2} = 6.846$ mmol of oxalic acid, $H_2C_2O_4$.

100 mL of the solution contains $6.846 \times 10 = 68.46$ mmol of $H_2C_2O_4$.

The amount of sodium oxalate added to the 25.00 mL sample is

$2.000 \times \dfrac{50}{1000} = 0.1000$ mol $= 100.0$ mmol of $Na_2C_2O_4$.

Of this amount, $(100.0 - 68.46) = 31.54$ mmol of $C_2O_4^{2-}$ anions reacted with calcium ions. Therefore, the 25.00 mL sample contained 31.54 mol of $Ca^{2+}$.

$M(CaCO_3) = 100.1$ g/mol.

100 mL of the solution contains $31.54 \times 4 = 126.2$ mmol of $Ca^{2+}$ or 126.2 mmol

or $0.1262 \times 100.1 = 12.63$ g of $CaCO_3$.

The mass percent of calcium carbonate in the limestone sample is $\dfrac{12.63}{14.64} \times 100\% = 86.3\ \%$

# GRADE 10

## Problem10-1

1) The empirical formula of the hydrocarbon **X** is

$$N(C) : N(H) = \frac{89.49}{12.01} : \frac{100 - 89.49}{1.008} = 7.45 : 10.43 = 5 : 7.$$

The number of hydrogen atoms in a hydrocarbon cannot be odd. Therefore, the simplest molecular formula of **X** is $C_{10}H_{14}$.
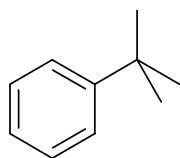
$M(C_{10}H_{14}) = 134$ g/mol

From the vapor density data, the molecular mass of **X** does not exceed

$$M = \frac{m}{n} = \frac{mRT}{pV} = \frac{\rho RT}{p} = \frac{10 \times 8.314 \times (273 + 25)}{101.3} = 245 \text{ g/mol}.$$

Therefore, **X** is $C_{10}H_{14}$.

2) The two possible structures of **X** are
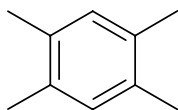


*tert*-butyl benzene          durene

.

3) Only arenes with hydrogen atoms in the α-position can be oxidized with $KMnO_4$. Therefore, durene can be ruled out. Compound **X** is *tert*-butyl benzene

4) The *tert*-butyl group directs the entering nitro group to the *para*-position (the *ortho*-position is sterically hindered). The carboxyl group is a *meta*-director. Thus, the reactions are
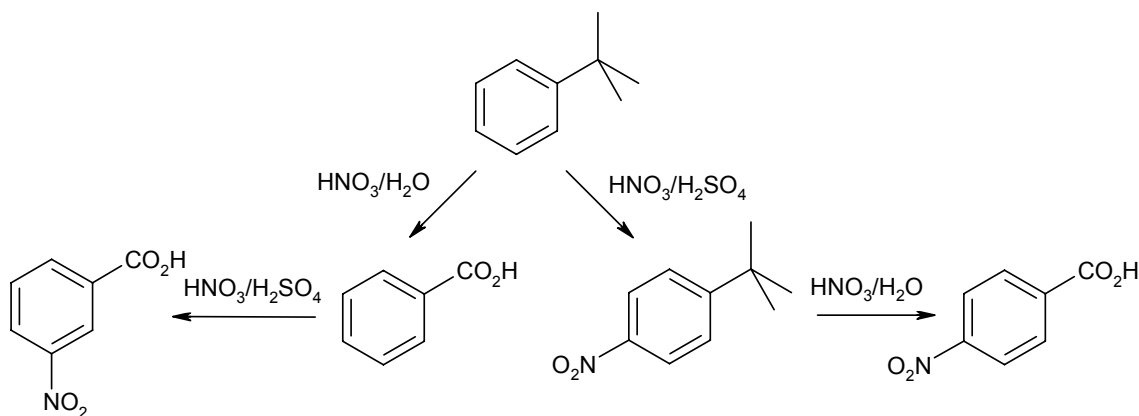


5) The only isomer of **X** that exhibits optical activity is 2-phenyl butane:



.
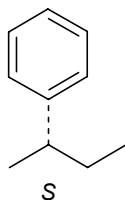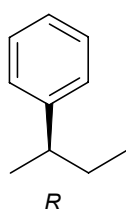
## Problem 10-2

1) The general formula of oxoacids of phosphorus is $H_h P_p O_o$.
   The empirical formula of **X** is:

$$N(H) : N(P) : N(O) = \frac{4.58}{1.01} : \frac{46.9}{31.0} : \frac{100 - 4.58 - 46.9}{16.0} = 4.53 : 1.51 : 3.03 = 3 : 1 : 2.$$

Thus, **X** is $H_3PO_2$ (hypophosphorous acid).

Assuming that **Y** has the composition $H_h P_p O_o$ and using the data of the elemental analysis we have

$$1.0h + 31.0p + 16.0o = \frac{31.0}{0.378} p = 82.0p,$$

from which $1.0h + 16.0o = 51.0p$.

The only solution in integers is

$h = 3, p = 1, o = 3$.

Thus, **Y** is $H_3PO_3$ (phosphorous acid).

The molecule of **Z** contains $7(1 + 0.143) = 8$ atoms.

**Z** is $H_3PO_4$ (phosphoric acid).

2) The structural formulas of the three acids are



        **Z**              **Y**    (\*)            **X**
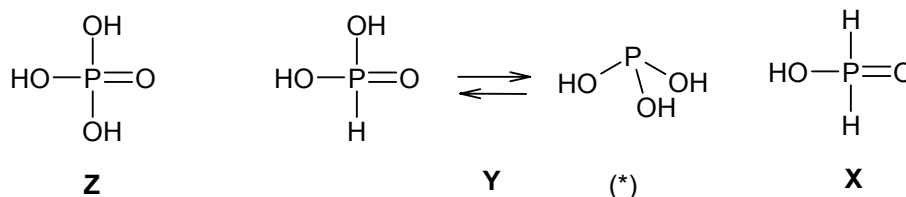
The first dissociation constants of these acids decrease in the order **X** > **Y** ~ **Z**. (The actual $pK_a$ values are 1.2, 2.1, and 2.1, respectively.)

3) Complete neutralization of the three acids is described by the equations

$H_3PO_2 + NaOH = NaH_2PO_2 + H_2O$;

$H_3PO_3 + 2NaOH = Na_2HPO_3 + 2H_2O$;

$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O$.
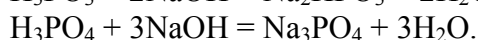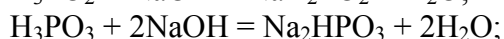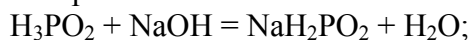
Acids **X** and **Y** react with iodine according to the equations:

$H_3PO_2 + 2I_2 + 2H_2O = H_3PO_4 + 4HI$;
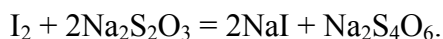
$H_3PO_3 + I_2 + H_2O = H_3PO_4 + 2HI$.
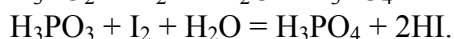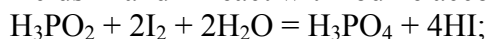
One of these reactions is fast at room temperature, but the other requires heating.

Another possibility to consider is the stepwise oxidation:

$H_3PO_2 + I_2 + H_2O = H_3PO_3 + 2HI$;

$H_3PO_3 + I_2 + H_2O = H_3PO_4 + 2HI$.
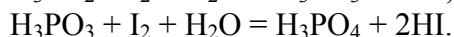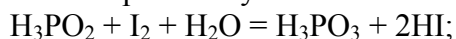
Titration of iodine with thiosulfate is based on the reaction

$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$.

4) Let the amounts of acids **X**, **Y**, and **Z** in the 50 mL sample be $x$, $y$, and $z$ mmol, respectively.

$M(NaOH) = 40.0$ g/mol.

The complete neutralization requires

$$9.35 \times 1.07 \times 0.100 = 1.00 \text{ g of NaOH, or } \frac{1.00}{40.0} = 0.0250 \text{ mol} = 25.0 \text{ mmol}$$

Then $(x + 2y + 3z) = 25.0$

The amount of iodine added to samples 1 and 2 is $200 \times 0.100 = 20.0$ mmol.

The titration required:

For sample 1:   $80 \times 0.100 = 8.00$ mmol of sodium thiosulfate;

For sample 2:   $360 \times 0.100 = 36.0$ mmol of sodium thiosulfate

The amounts of iodine reacted with the acids are:

Sample 1:   $(20.0 - \frac{8.00}{2}) = 16.0$ mmol

Sample 2:   $(20.0 - \frac{36.0}{2}) = 2.0$ mmol

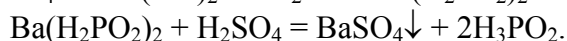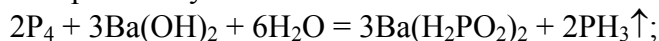It is known that **Y** reacts with iodine fast, whereas **X** reacts slowly and only when the reaction

mixture is heated. Thus, we have

$x + 2y + 3z = 25.0$

$y = 2.0$

$2x + y = 16.0$

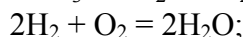The solution of this system of equations is $x = 7.0$, $y = 2.0$, $z = 4.67$.

The concentrations of the acids in the sample are

$$c(H_3PO_2) = \frac{7.0}{50} = 0.14 \text{ M}; \quad c(H_3PO_3) = \frac{2.0}{50} = 0.040 \text{ M}; \quad c(H_3PO_4) = \frac{4.67}{50} = 0.093 \text{ M}.$$

Let us now show how one can arrive at the same conclusion even without knowing relative oxidation rates for the acids. Suppose **X** is oxidized by iodine fast and that **Y** is oxidized slowly. This assumption leads to the system of equations
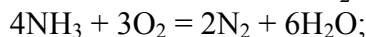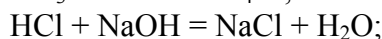
$x + 2y + 3z = 25.0$

$2x = 2.0$

$2x + y = 16.0$

Solution of this system yields $z < 0$, which means that the starting assumption is incorrect. Assuming that the oxidation of **X** to **Y** is fast, while the oxidation of **Y** to **Z** is slow, we have

$x + 2y + 3z = 25.0$

$x = 2.0$

$2x + y = 16.0$

This also gives $z < 0$.

5) One possibility is

$2P_4 + 3Ba(OH)_2 + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3\uparrow;$

$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4\downarrow + 2H_3PO_2.$

## Problem 10-3

1) The reactions are

$3H_2 + N_2 = 2NH_3;$

$NH_3 + HCl = NH_4Cl;$

$HCl + NaOH = NaCl + H_2O;$

$4NH_3 + 3O_2 = 2N_2 + 6H_2O;$

$2H_2 + O_2 = 2H_2O;$

$3H_2O + P_2O_5 = 2H_3PO_4.$
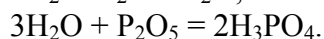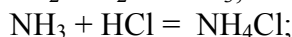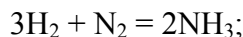
2) $M(HCl) = 36.46$ g/mol.

The initial solution contains $0.0439 \times 10 \times 1.020 = 0.4478$ g or

$\dfrac{0.4478}{36.46} = 12.28$ mmol of HCl. The neutralization of the excess of HCl required

$0.5486 \times \dfrac{18.30}{1000} = 10.04$ mmol of NaOH.

The amount of HCl reacted with ammonia is $(12.28 - 10.04) = 2.24$ mmol HCl.

The amount of $NH_3$ absorbed by the solution is also 2.24 mmol.

$M(NH_3) = 17.03$ g/mol.

Therefore, the mass of the solution increased by $0.00224 \times 17.03 = 0.0381$ g and became $(10 \times 1.020 + 0.0381) = 10.24$ g.

The amount of HCl remaining in the solution is 10.04 mmol.

The mass percent of the remaining HCl is $\dfrac{36.46 \times \dfrac{10.04}{1000}}{10.24} \times 100\% = 3.57\%$.

3) The mass of the column filled with $P_2O_5$ increased due to absorption of water.

$M(H_2O) = 18.02$ g/mol.

The amount of water in one half of the reaction mixture is $\dfrac{0.08438}{18.02} = 4.683$ mmol.

Therefore, the whole mixture contains $4.683 \times 2 = 9.366$ of hydrogen gas.

The initial mixture contained a total of $\dfrac{0.500}{22.4} = 22.32$ mmol of $N_2$ and $H_2$.

The amount of $N_2$ is $(22.32 - 9.366) = 12.95$ mmol.

$M(H_2) = 2.016$ g/mol

$M(N_2) = 28.01$ g/mol.

The mass percent of hydrogen gas in the initial gaseous mixture is

$$\frac{2.016 \times 9.366}{2.016 \times 9.366 + 28.01 \times 12.95} \times 100\% = 4.95\ \%.$$

## Problem 10-4

1) $3Fe_3P + 41HNO_3 = 3H_3PO_4 + 9Fe(NO_3)_3 + 14NO\uparrow + 16H_2O$  or
   $Fe_3P + 23HNO_3 = H_3PO_4 + 3Fe(NO_3)_3 + 14NO_2\uparrow + 10H_2O$;
   $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = (NH_4)_3H_4[P(Mo_2O_7)]_6\downarrow + 21NH_4NO_3 + 10H_2O$;
   $(NH_4)_3H_4[P(Mo_2O_7)]_6 + 23NH_3 \cdot H_2O = 12(NH_4)_2MoO_4 + (NH_4)_2HPO_4 + 13H_2O$;
   $(NH_4)_2HPO_4 + NH_3 \cdot H_2O + MgCl_2 = MgNH_4PO_4 \cdot 6H_2O\downarrow + 2NH_4Cl + H_2O$;
   $2MgNH_4PO_4 \cdot 6H_2O = Mg_2P_2O_7 + H_2O\uparrow$.

2) If the oxidizing agent is not sufficiently strong, the following reaction can occur
   $2Fe_3P + 12H^+ = 6Fe^{2+} + 2PH_3\uparrow + 3H_2\uparrow$.
   Some phosphorus can escape in the form of $PH_3$ gas.

3) $M(Mg_2P_2O_7) = 222.6$ g/mol

   The amount of $Mg_2P_2O_7$ is $\dfrac{0.1796}{222.6} = 0.8068$ mmol

   Therefore, the initial sample contained $0.8068 \times 2 = 1.614$ mmol of phosphorus.

   $M(P) = 30.97$ g/mol.

   The mass percent of elemental phosphorus in the initial sample of cast iron is

   $$\frac{30.97 \times (1.614/1000)}{14.66} \times 100\% = 0.3410\%.$$

## Problem 10-5

1) Let us write the empirical formula of **X** as $CaB_y$.

   Each cubic unit cells contains $8 \times \dfrac{1}{8} = 1$ calcium atom and $y$ boron atoms.

   The volume of the unit cell is $(415 \times 10^{-10}\ cm)^3 = 7.15 \times 10^{-23}\ cm^3$.
   Given the density of 2.44 g/cm$^3$, the mass of the unit cell is
   $2.44 \times (7.15 \times 10^{-23}) = 1.744 \times 10^{-22}$ g.
   $M(Ca) = 40.08$ g/mol.

   The mass of one calcium atom is $\dfrac{40.08}{6.02 \times 10^{23}} = 6.658 \times 10^{-23}$ g.

   The mass of $y$ boron atoms is $(1.744 \times 10^{-22} - 6.658 \times 10^{-23}) = 1.078 \times 10^{-22}$ g.
   $M(B) = 10.81$ g/mol.

   The mass of one boron atom is $\dfrac{10.81}{6.02 \times 10^{23}} = 1.796 \times 10^{-23}$ h.

   Therefore, $y = \dfrac{1.078 \times 10^{-22}}{1.796 \times 10^{-23}} = 6$.

   **X** is $CaB_6$, calcium hexaboride.

2) Calcium metaborate, $Ca(BO_2)_2$, and calcium tetraborate, $CaB_4O_7$. These compounds have a

lower density than copper, so they float and can be easily removed.

3) $CaO + 3B_2O_3 + 10Mg = CaB_6 + 10MgO$ (~1100 °C);
   $Ca(OH)_2 + 7B = CaB_6 + BO\uparrow + H_2O\uparrow$ (~1000 °C);
   $CaCl_2 + 6NaBH_4 = CaB_6 + 2NaCl + 12H_2\uparrow$ (~500 °C).

4) The six boron atoms at the center of the unit cell are arranged in the form of an octahedron.

## GRADE 11

### Problem 11-1

1) The empirical formula of the hydrocarbon **A** is

$$N(C) : N(H) = \frac{92.3}{12.0} : \frac{100 - 92.3}{1.01} = 7.69 : 7.63 = 1 : 1.$$

Therefore, the molecular formula of **A** is $(CH)_{2n}$.
$M[(CH)_{2n}] = 26n$ g/mol.
Since $M$ does not exceed $4 \times 22.4 = 90$ g/mol, we conclude that $n \leq 3$. Because **A** reacts with a nitrating mixture, it is probably an arene. This implies that $n$ is at least 3.
Therefore, $A = C_6H_6$ (benzene), **B** is nitrobenzene, and **C** is aniline hydrochloride:
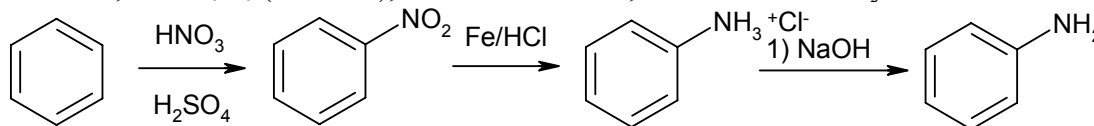


**A** - benzene          **B** - nitrobenzene          **C** - aniline hydrochloride

Assuming that **D** contains $s$ atoms of sulfur, we write

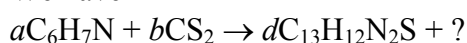$$M(\mathbf{D}) = \frac{32.07}{0.1405} s = 228.3s \text{ (g/mol)}.$$

For each sulfur atom in **D**, there are $228.8 \times \dfrac{0.1227}{14.01} = 2$ nitrogen atoms. Since **D** is produced by the reaction of aniline and hydrogen sulfide, the other elements comprising **D** can be only carbon and hydrogen. We have:
$M(\mathbf{D}) = 228.3 = 1 \times 32.07 + 2 \times 14.01 + N(C) \times 12.01 + N(H) \times 1.01$.
The only solution in integers is $C_{13}H_{12}N_2S$.
We have
$aC_6H_7N + bCS_2 \rightarrow dC_{13}H_{12}N_2S + ?$
Assuming that the second product is $H_2S$, the equation becomes balanced if $a = 2$, $b = d = 1$.
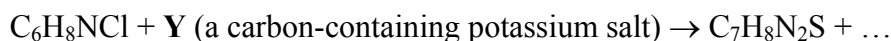This reaction is similar to the reaction of ammonia with carbon dioxide. This suggests that **D** is N,N'-diphenylthiourea.
The next step is $C_{13}H_{12}N_2S + HCl \rightarrow C_6H_8NCl + \mathbf{E}$.
Compound **E** must be phenyl isothiocyanate. The latter reacts with ammonia to give the final product, phenylthiourea (the mass percent of carbon is 7(12.01)/152.2=0.5524):



.
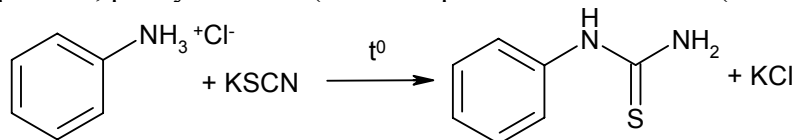
2) **X** is phenylthiourea.

3) $M(\mathbf{A}) = 78.1$ g/mol.
   $M(\mathbf{X}) = 152$ g/mol.
   Synthesis of 1 mol of phenylthiourea requires 2 mol of benzene. Thus, the ideal yield of **X** is

   $$\frac{1.00}{78.1} \times \frac{1}{2} \times 152 = 0.973 \text{ kg}.$$

4) The reaction is of the type:

$C_6H_8NCl + Y$ (a carbon-containing potassium salt) $\rightarrow C_7H_8N_2S + \ldots$
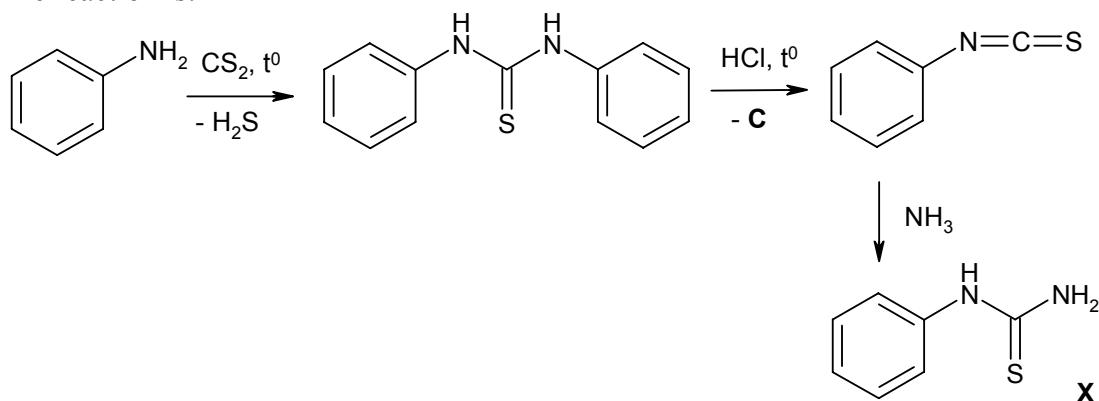
It is obvious that the salt **Y** contains sulfur in addition to K and C, and that the reaction products contain potassium and chlorine.

If each formula unit of **Y** contains $x$ carbon atoms, then the molecular mass of this compound is

$$M(Y) = \frac{12.01}{0.1236} x = 97.1x \text{ (g/mol)}$$

The only possibility is that **Y** is potassium thiocyanate, KSCN.

The reaction is:



This process is similar to the first synthesis of an organic substance from inorganic reagents: the preparation of urea from silver cyanate and ammonium chloride by Friedrich Wöhler in 1828.

## Problem 11-2

*1)* The binary compound **A** contains hydrogen and is a strong reducing agent. Therefore, it is some hydride. Reaction of **A** with water produces hydrogen gas (compound **B**). Let the mass of one equivalent of the unknown element X be $M_e(X)$. From the condition that

$1.0/(1.0 + M_e(X)) > 0.10$

we obtain the inequality $M_e(X) < 9.0$. Since the hydride is solid, the only possibilities are the metals lithium and beryllium. Since **C** is the only product of the reaction of **A** and **B**, we can write

$XH_x + aCO_2 = XH_x \cdot aCO_2$,
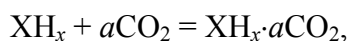
from which $\dfrac{2a \times 16.0}{x \times 1.0 + M_e(X) + a \times 44.0} = 0.616$, so $M_e(X) = (7.94a - 1.0x)$ g/mol.

The value of $x$ must be a small integer, while $a$ must be a rational number. The physically acceptable solution is $a = x = 1$.

Then $M_e(X) = 6.94$ g/mol, which means that X is lithium.
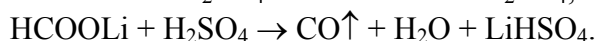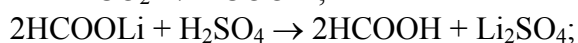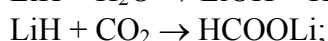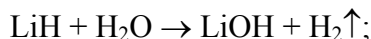
**A** is LiH (lithium hydride).

**B** is $LiH \cdot CO_2$ (or, more correctly, HCOOLi), lithium formate.

Reaction of a formate with dilute sulfuric acid produces formic acid (compound **D**). Concentrated sulfuric acid dehydrates HCOOH and yields carbon monoxide (compound **E**).
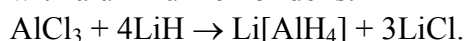
**D** is HCOOH (formic acid);

**E** is CO (carbon monoxide).

*2)* The reactions are as follows:

$LiH + H_2O \rightarrow LiOH + H_2\uparrow$;

$LiH + CO_2 \rightarrow HCOOLi$;

$2HCOOLi + H_2SO_4 \rightarrow 2HCOOH + Li_2SO_4$;

$HCOOLi + H_2SO_4 \rightarrow CO\uparrow + H_2O + LiHSO_4$.

*3)* Lithium hydride is an ionic compound, so its formula may be written as $Li^+H^-$. Reaction of LiH with aluminum chloride is:

$AlCl_3 + 4LiH \rightarrow Li[AlH_4] + 3LiCl$.

Lithium aluminum hydride, Li[AlH₄], is widely used as a reducing agent in chemical synthesis.

*4)* The relative atomic masses of the elements that constitute compound **A** are

$A_r(H) = 1.008$.

$A_r(Li) = 6.94$.

The isotopes in question are $^1H$, $^2H$, $^6Li$, $^7Li$.

Let the natural abundance of $^1H$ be $x$. Then we have

$1x + 2(1 - x) = 1.008$, which gives $x = 0.992$.

Let the natural abundance of $^6Li$ be $y$. Then we have the equation

$6y + 7(1 - y) = 6.94$, whose solution is $y = 0.06$.

Assuming that the probability of finding a particular isotope is proportional to its abundance, the relative abundances of the four isotopomers $^aLi^bH$ are

$^6Li^1H$: $0.06 \cdot 0.992 = 0.0595$

$^6Li^2H$: $0.06 \cdot 0.008 = 0.00048$

$^7Li^1H$: $0.94 \cdot 0.992 = 0.932$

$^7Li^2H$: $0.94 \cdot 0.008 = 0.0075$

The relative abundances of these four isotopomers are

$0.0595 : 0.00048 : 0.932 : 0.0075 \approx 124 : 1 : 1942 : 16$.

**Problem 11-3**

*1)* The calorific value of a compound is the energy released as heat when a unit mass of the compound undergoes complete combustion with oxygen under standard conditions.

*2)* We assume that chemical bonds of the same type make equal contributions to the calorific value of a compound. The repeating unit of polyethylene (-CH₂–CH₂-) contains two C–C bond and 4 C–H bonds. The repeating unit of natural rubber, -CH₂–C(CH₃)=CH–CH₂-, contains one C=C bond, four single C–C bonds and eight C–H bonds. The repeating unit of poly-1,3-butadiene, -CH₂–CH=CH–CH₂-, contains one C=C bond, three single C–C bonds, and six C–H bonds.

$M(C_2H_4) = 28.06$ g/mol

$M(C_5H_8) = 68.12$ g/mol

$M(C_4H_6) = 54.09$ g/mol

The heat of combustion per 1 mol of repeating units is

for polyethylene: $47.14 \times \dfrac{28.06}{1000} = 1.323$ MJ per 1 mol of repeating units

for natural rubber: $44.73 \times \dfrac{68.12}{1000} = 3.047$ MJ per 1 mol of repeating units

Let us denote the number of C–C bonds by $s$, the number of C=C bonds by $d$, and the number of C–H bonds by $h$. Then we can write for polyethylene and for polyisoprene
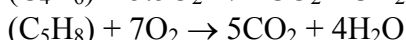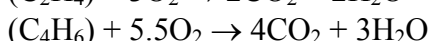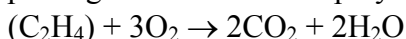
$1.323 = 2s + 4h$

$3.047 = 4s + d + 8h$.

Then the heat of combustion of polybutadiene is

$3s + d + 6h = 3.047 - \dfrac{1.323}{2} = 2.386$ MJ per 1 mol of repeating units.

Therefore, the calorific value of polybutadiene is $2.386 \times \dfrac{1000}{54.09} = 44.10$ MJ/kg.

There is a different way of solving this problem. Consider the combustion reactions for the repeating units of the three polymers in question:

$(C_2H_4) + 3O_2 \rightarrow 2CO_2 + 2H_2O$

$(C_4H_6) + 5.5O_2 \rightarrow 4CO_2 + 3H_2O$

$(C_5H_8) + 7O_2 \rightarrow 5CO_2 + 4H_2O$

The first reaction involves the rupture of 2 C–C bonds, 4 C–H bonds, and 3 O–O bonds, and the formation of 4 C=O bonds and 4 O–H bonds. Therefore, the heat of combustion for this reac-

tion can be written as

$Q_1 = 4E_{C=O} + 4E_{O-H} - 2E_{C-C} - 4E_{C-H} - 3E_{O=O}.$

Similarly, for the two other reactions we can write

$Q_2 = 8E_{C=O} + 6E_{O-H} - 3E_{C-C} - E_{C=C} - 6E_{C-H} - 5,5E_{O=O};$
$Q_3 = 10E_{C=O} + 8E_{O-H} - 4E_{C-C} - E_{C=C} - 8E_{C-H} - 7E_{O=O}.$

A moment's thought shows that $Q_2 = Q_3 - \dfrac{Q_1}{2}$.

3) The repeating unit of cellulose is $C_6H_{10}O_5$, for polymethyl methacrylate it is $C_5H_8O_2$, for natural rubber (polyisoprene) it is $C_5H_8$, and for polystyrene it is $(C_8H_8)$. The composition of all these units can be written as $C_xH_yO_z$. The combustion reaction is

$$C_xH_yO_z + \dfrac{2x + \dfrac{y}{2} - z}{2} O_2 \rightarrow xCO_2 + \dfrac{y}{2} H_2O.$$
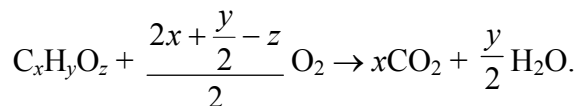
The calorific value of $C_xH_yO_z$ is

$$Q = \dfrac{xQ_f^m(CO_2) + \dfrac{y}{2}Q_f^m(H_2O) - Q_f^m(C_xH_yO_z)}{12x + y + 16z},$$

where $Q_f^m$ is the heat of formation of a substance. As a rule, heats of formation of organic compounds are relatively small. Also, the higher the oxygen content, the higher the heat of formation. This allows us to conclude that the calorific value of a compound should decrease as the fraction of oxygen atoms in the repeating unit increases. For hydrocarbon-based polymers, the calorific value increases with increasing hydrogen content (this is because the molar heats of combustion of atomic carbon and hydrogen are similar, but carbon is an order of magnitude heavier than hydrogen). Thus, the order of increasing calorific value is: cellulose, polymethyl methacrylate, polystyrene, natural rubber. The reference values are, respectively (in MJ/kg): 13.4, 27.7, 39.0, and 44.7.

4) $H_2SO_4 + 2NaHCO_3 = Na_2SO_4 + 2H_2O + 2CO_2\uparrow.$
The surfactant is added to increase the amount of soapy foam.

5) $M(H_2SO_4) = 98$ g/mol
$M(NaHCO_3) = 84$ g/mol.

The main chamber contains $8 \times 0.05 = 0.4$ kg $= 400$ g or $\dfrac{400}{84} = 4.76$ mol of $NaHCO_3$.

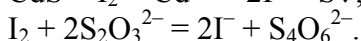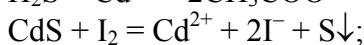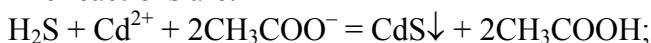The stoichiometric quantity of $H_2SO_4$ is $98 \times \dfrac{4.76}{2} = 233$ g

Therefore, the minimum mass percent of sulfuric acid is $\dfrac{233}{400} \times 100\% = 58\%.$

6) The volume of foam is approximately equal to the volume of carbon dioxide produced by the reaction of $NaHCO_3$ and $H_2SO_4$. Since $n(CO_2) = n(NaHCO_3)$, we have

$$V = \dfrac{nRT}{p} = \dfrac{4.76 \times 8.314 \times (20 + 273)}{101.3} = 114 \text{ dm}^3.$$

**Problem 11-4**
1) The reactions are:
$H_2S + Cd^{2+} + 2CH_3COO^- = CdS\downarrow + 2CH_3COOH;$
$CdS + I_2 = Cd^{2+} + 2I^- + S\downarrow;$
$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}.$
2) A yellow precipitate of CdS is produced; milky-yellow colloidal sulfur is formed; the color of molecular iodine disappears during the titration.

*3)* The amount of added iodine is $0.08226 \times \dfrac{20.0}{1000} = 1.645$ mmol.

The titration of the excess iodine required $0.1085 \times \dfrac{15.80}{1000} = 1.714$ mmol of $Na_2S_2O_3$,

which corresponds to $\dfrac{1.714}{2} = 0.8570$ mmol of $I_2$.

The amount of $I_2$ reacted with CdS is $(1.645 - 0.8570) = 0.7880$ mmol.
Therefore, the initial air sample contained 0.7880 mmol of $H_2S$.

This amount of $H_2S$ occupies the volume $22.4 \times \dfrac{0.7880}{1000} = 17.65$ dm$^3$.

*4)* $M(H_2S) = 34$ g/mol.

The mass of hydrogen sulfide is $34 \times \dfrac{0.7880}{1000} = 2.68 \times 10^{-2}$ g.

The amount of air in the sample is

$\dfrac{98.0 \times 2.68}{8.314 \times (273 + 24)} = 0.1064$ mol.

The average molar mass of air is $M(air) = 29$ g/mol.
Therefore, the mass of the air sample is $0.1064 \times 29 = 3.08$ g.

The mass percent of $H_2S$ in the sample is $\dfrac{0.0268}{3.08 + 0.0268} \times 100\% = 0.863\%$.

*5)* $86.3 \times 10^3$ ppm by mass and $7.4 \times 10^3$ ppm by mole.

## Problem 11-5
1) O: $1s^2 2s^2 2p^4$;
   Na: $1s^2 2s^2 2p^6 3s^1$;
   Ti: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$.
2) Oxygen atom:
   $Z_{eff}(2s,2p) = 8 - (5 \times 0.35 + 2 \times 0.85) = 4.55$
   $Z_{eff}(1s) = 8 - (1 \times 0.30) = 7.70$
   Sodium atom:
   $Z_{eff}(3s) = 11 - (8 \times 0.85 + 2 \times 1.00) = 2.20$
   $Z_{eff}(2s,2p) = 11 - (7 \times 0.35 + 2 \times 0.85) = 6.85$
   Titanium atom:
   $Z_{eff}(4s) = 22 - (1 \times 0.35 + 10 \times 0.85 + 8 \times 1.00 + 2 \times 1.00) = 3.15$
   $Z_{eff}(3d) = 22 - (1 \times 0.35 + 8 \times 1.00 + 8 \times 1.00 + 2 \times 1.00) = 3.65$
   $Z_{eff}(3s,3p) = 22 - (7 \times 0.35 + 8 \times 0.85 + 2 \times 1.00) = 10.75$
3) The Allred–Rochow electronegativities are

H: $0.359 \times \dfrac{1 - (1 \times 0.30)}{\left(\dfrac{42 \times 10^{-12}}{10^{-10}}\right)^2} + 0.744 = 2.17$

O: $0.359 \times \dfrac{8 - (6 \times 0.35 + 2 \times 0.85)}{\left(\dfrac{74 \times 10^{-12}}{10^{-10}}\right)^2} + 0.744 = 3.50$

F: $0.359 \times \dfrac{9 - (7 \times 0.35 + 2 \times 0.85)}{\left(\dfrac{72 \times 10^{-12}}{10^{-10}}\right)^2} + 0.744 = 4.10$

Na: $0.359 \times \dfrac{11 - (1 \times 0.35 + 8 \times 0.85 + 2 \times 1.00)}{\left(\dfrac{167 \times 10^{-12}}{10^{-10}}\right)^2} + 0.744 = 0.98$

4) We assume that the polarity of the chemical bond in NaF is 100 %. The difference in the electronegativities of the F and Na atoms is (4.10 – 0.98) = 3.12.
   The difference in the electronegativities of the O and H atoms is (3.50 – 2.17) = 1.33.
   The polarity of the OH bond relative to the HF bond is, therefore, $\dfrac{1.33}{3.12} \times 100\% = 42.6\ \%$.

5) The bond length in NaF is (167 + 72) = 239 pm. Let us assume that the charge flow in the NaF molecule is 1.00. Therefore, our unit of the dipole moment is $\dfrac{239}{7.2}\ e{\cdot}\text{pm}$.

   The O–H bond in the water molecule has a length of (42 + 74) = 116 pm.
   From part (4), the charge flow for the O–H bond is 0.426.
   The dipole moment of the O–H bond is (116 pm)(0.426) = 49.4 $e{\cdot}$pm, which is equivalent to 49.7/(239/7.2) = 1.49 arbitrary units.
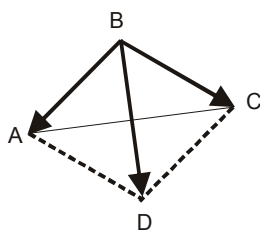
According to the figure shown below, the magnitude of the dipole moment of $H_2O$ is equal to *BD*, the magnitude of the vector sum of the dipole moments of the two OH bonds.
Since the angle *DBC* is 52.5°, we have *BD* = 2(*BC*)cos 52.5° = 2(1.49)(0.609) = 1.81 arbitrary units.

Translated by **V.Staroverov**