BELARUS

Ministry of Education

Chemistry Olympiad

National Final

Theoretical Examination

Minsk, March 30 - April 03, 2009

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.

PROBLEMS

Grade 9

Problem 9-1
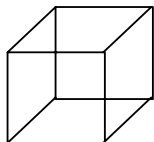
In the middle of the 20th century, chemists debated whether it was possible to synthesize cubane, a hydrocarbon whose structure is shown on the left. The first successful synthesis of cubane was reported in 1964 by American researchers Philip Eaton and Thomas Cole.

1) *Draw the structures and give the IUPAC names of three hydrocarbons that are isomeric with cubane.*
2) *How many chloro-substituted cubanes have a vapor density of less than 6.0 g/L at 200 °C and 100 kPa? Draw the chemical structures of these compounds.*
3) *Compound **X** is a certain derivative of cubane. The relative vapor density of **X** with respect to air does not exceed 6. When a 150 mg sample of **X** is burned in excess oxygen, only two products are formed with a total mass of 544 mg. Deduce the molecular formula of compound **X**. Draw the structures of all isomers of **X** that are consistent with the above data.*

Problem 9-2

Below is a description of the synthesis of a certain inorganic compound.

A 40 g sample of commercial-grade iron in the form of filings and small cuts of wire is added to 415 mL of 15% sulfuric acid with a density of 1.10 g/cm^3 and the mixture is refluxed until all the iron is dissolved. The resulting solution is filtered, transferred to a flask, acidified with a few drops of sulfuric acid, cooled to room temperature, and saturated with hydrogen sulfide. The flask is then sealed and left standing for 2 days. Upon standing, the reaction mixture is filtered, evaporated to half mass in the atmosphere of CO_2 and left to crystallize at 20 °C in a tightly sealed vessel. The next day, the mother liquid is drained, the crystals are rinsed with alcohol and dried quickly between filter paper. This yields 140 g of blue crystals which are 11.54% sulfur by mass.

1) *What is the final product of this synthesis? Write the chemical equation for the principal reaction.*
2) *Can the 15% sulfuric acid solution be replaced with 60% H_2SO_4 to accelerate the reaction? Why is it necessary to saturate the solution with hydrogen sulfide and then to filter it? Why should the solution be evaporated in the atmosphere of carbon dioxide? What will happen if the solution is evaporated in open air? Give your reasoning and supply the relevant chemical equations.*
3) *Explain the choice of the drying method in the final step of the synthesis. Can the drying be accelerated by using an oven? Give your reasoning.*
4) *Calculate the overall theoretical yield of the final product given that its saturated aqueous solution at 20 °C is 78% water by mass.*
5) *A mixture of concentrated nitric and sulfuric acids is added by small portions to a hot solution of the final product and the resulting mixture is evaporated until it becomes much more viscous. When the evaporated mixture is cooled, yellowish crystals are formed which contain 17.12% sulfur by mass. Deduce the molecular formula of the crystalline compound and write the chemical equation to represent its formation.*

Problem 9-3

Hydrocarbons represent the simplest class of organic compounds. Traditionally, the study of organic chemistry begins with hydrocarbons.

1) *An unknown hydrocarbon is a gas under standard temperature and pressure. When a sample of this hydrocarbon was burned in oxygen gas, the total volume of gaseous reaction products, measured at 99 °C u 101 Pa, turned out to be equal to the total volume of the reactants. Deduce the possible structures of the hydrocarbon used in this experiment.*

2) *In a second experiment, a sample of another unknown hydrocarbon was burned completely and the combined mass of the reaction products was found to be 4.43 times greater than the mass of the initial sample. To what type(s) of hydrocarbons may the unknown compound belong?*

3) *Propose a synthesis from inorganic reagents of the simplest possible hydrocarbon (i.e., the hydrocarbon containing the smallest possible number of carbon atoms) for which the mass ratio defined in question 2 is equal to 4.26.*

4) *What hydrocarbon is characterized by the smallest possible mass ratio as defined in question 2? Support your answer with calculations.*

5) *The mass of the product of complete hydrogenation of a certain hydrocarbon is 1.042 times greater than the initial mass of the hydrocarbon. Write the chemical equation for this reaction.*

Problem 9-4

A 500 mL glass flask is filled at STP with a mixture of gases **X**, **Y**, and **Z**, all of which are diatomic elemental substances. The initial volume ratio of **X**, **Y**, and **Z** is 5:3:1. When the mixture was heated, a violent exothermal reaction occurred in which all reactants were used up. After the flask was allowed to cool to its initial temperature, a colorless crystalline compound **A** was found on the walls inside the flask. Chemical analysis of **A** showed that it is a ternary compound in which the mass percentage of one of the elements is 36.0%.

1) *Identify the gases **X**, **Y** and **Z**, given that the density of the heaviest gas is no more than 25 times greater than the density of the lightest.*

2) *Determine the chemical composition of compound **A**.*

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

Problem 9-5

Normal growth and development of plants require the availability of various minerals among which the so-called macroelements—nitrogen, phosphorous, and potassium—are particularly important. These macroelements can be supplied in the form of "compound" or "NPK" fertilizers such as ammonium phosphate potassium nitrate, $NH_4H_2PO_4$ + $(NH_4)_2HPO_4$ + KNO_3. According to agroindustry standards, each 1.0 m^2 of freshly tilled soil should contain 5.0 g of nitrogen, 5.0 g of phosphorous, and 4.0 g of potassium.

1) *Calculate the mass percent composition of an ammonium phosphate potassium nitrate mixture that would be ideally suited to the above requirements.*

2) *A small farm ran out of the NPK fertilizer but has in stock other chemicals including KCl, $NaNO_3$, NH_4NO_3, $CaHPO_4 \cdot 2H_2O$, $Ca(H_2PO_4)_2 \cdot H_2O$. Which of these compounds and in what proportion should be combined to prepare enough NPK fertilizer to treat 30 ha? Assume that each of the listed ingredients contains 2% of impurities by mass. Find an optimal solution, that is, the composition that minimizes the total mass of the mixture and thus reduces transportation costs.*

3) *Write the chemical formulas and give the names of three mineral fertilizers that are produced in Belarus on an industrial scale.*

Grade 11

Problem 11-1

See Problem 9-5.

Problem 11-2

The ability of a metal to react with aqueous solutions of acids and salts can be determined based on the metal's position in the electrochemical series, i.e., a series in which chemical species are arranged according to the standard potentials of cell reactions $A^{n+} + ne^- \rightarrow A$ starting with the most negative value at the top and ending with the most positive at the bottom. The general rules are as follows: (i) only the metals that are placed above hydrogen dissolve in acids; (ii) a metal will displace any lower-placed metal from a solution of its salt. However, every rule has exceptions.

1) *Give three examples of a metal that is placed in the electrochemical series above hydrogen but does not dissolve in an aqueous solution of an acid. Explain why this occurs.*
2) *Give three examples of a metal that is placed below hydrogen but does dissolve in an aqueous solution of an acid. Write the balanced chemical equations for these reactions and indicate the condition under which they occur.*
3) *A 2.0 g sample of copper filings was added to a weighed amount of a heated aqueous solution of an unknown acid. After the metal was completely dissolved, a transparent blue solution was formed. The mass of the resulting solution was found to be equal to the mass of the initial solution of the acid. Explain these observations. Write the chemical equations and show details of your calculations. What is the smallest possible mass of the acid in the initial solution?*
4) *A 10.00 g plate of an unknown metal X was immersed in an aqueous solution containing 10.00 g of copper(II) chloride. After the reaction was complete, the plate was removed, dried, and weighed. Its mass was found to be 10.57 g. In a second experiment, a 10.00 g copper plate was immersed in an aqueous solution containing 10.00 g of the chloride of metal X. After a sufficiently long exposure, the mass of the plate decreased to 8.04 g. Identify the unknown metal X and write the chemical equations that represent the above transformations. Are the results of these experiments consistent with the positions of X and copper in the electrochemical series?*
5) *Quantitative description of oxidation-reduction reactions is based on the Nernst equation:*

$$E = E^0 - \frac{0.059}{z}\log\frac{[\text{Red}]}{[\text{Ox}]},$$

where E^0 is the standard electrode potential and z is the number of electrons transferred. What fraction of Mn(II) cations in a 1.00 mM solution of $MnSO_4$ will become oxidized after a long exposure to air at atmospheric pressure? Assume that the pH of the solution remains constant at 2.0.
The half-reactions are as follows:

$O_2 + 4H^+ + 4e^- = 2H_2O$	$E^0 = 1.23$ V;
$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	$E^0 = 1.23$ V.
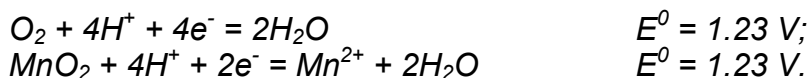
Problem 11-3

What do spoilage of food, radioactive decay, and bacterial growth have in com-

mon? It turns out that all these processes are described by the same equations:

$$\ln k = -\frac{E_a}{RT} + \ln A,$$ where k is the rate constant of the process, A and E_a are certain parameters, R is the universal gas constant, and T is the absolute temperature;

$$\ln N = \pm\frac{t \ln 2}{T_{1/2}} + \ln N_0,$$ where N is the number of objects at time t, N_0 is the initial number of objects at $t = 0$, and $T_{1/2}$ is a constant that has a dimension of time and shows how long it takes to double or halve (depending on the sign of the first term) the number of objects.

1) *Many food items have to be refrigerated to retard spoilage. The manufacturer's label on a certain food item states that it may be stored for one day at 0 °C or for one week at −5 °C. Assuming that the spoilage is entirely due to a chemical oxidation reaction, estimate the temperature at which this food item will remain safe for consumption for one month.*

2) *What are other ways of extending the shelf life of food products?*

3) *Suppose a terrorist got hold of a nuclear "suitcase" bomb. The bomb consists of two hemispheres of weapon-grade plutonium-239; each hemisphere has a radius of 42 mm. A nuclear explosion will occur if the hemispheres are merged but only if the amount of plutonium-239 in both halves exceeds the critical mass. How long would the world have to hold its breath before knowing that the danger has passed and the bomb is no longer capable of exploding? The density of ^{239}Pu is 19.8 g/cm³, the critical mass is 5.6 kg, the half-life of ^{239}Pu is 2.4×10^4 years.*

4) *Under favorable conditions, bacterial cells of Escherichia coli divide every 20 minutes. A cell of E. coli is placed on top of a nutrient-rich broth in a Petri dish with a diameter of 10 cm. Assuming that the cells are spread in a single layer, estimate how long it will take the colony to cover the entire surface of the dish. Take each cell to be a cylindrical rod 2.0 μm in length and 0.60 μm in diameter.*

Problem 11-4

Three vessels contain three isomeric hydrocarbons **A**, **B** and **C**. Each of these compounds has a density of 2.67 g/L at 100 °C and 101 kPa. One equivalent of each compound readily reacts with 1 equivalent of bromine. Complete combustion of a small sample taken from one of the vessels produces 1.540 g of water and 2.414 L of carbon dioxide (at 292 K and 103.1 kPa).

Vigorous oxidation of each of the three hydrocarbons with potassium permanganate gives only one organic product. Specifically, compound **A** gives an optically active methyldicarboxylic acid; compound **B** yields a keto acid which gives a negative iodoform test; compound **C** gives rise to a dicarboxylic acid in which the COOH groups have the maximum possible separation.

1) *Determine the molecular formula of the isomeric hydrocarbons **A**, **B** and **C**. What subclass of hydrocarbons do they represent? Draw the formulas of all stable structural isomers of **A**, **B**, and **C** that belong to the same subclass. Mark the structures that exist as geometric isomers.*

2) *What is the mass of the hydrocarbon sample used in the above experiment?*

3) *Deduce the structures of compound **A**, **B** and **C** and give the IUPAC names of their oxidation products.*

Problem 11-5

A gaseous mixture of ammonia and carbon dioxide was bubbled through 200 mL

of water at 20 °C, causing the gases to be completely absorbed. The resulting transparent solution was transferred to a volumetric flask which was then filled with distilled water to the 500 mL mark. A 10.00 mL sample of the prepared solution was treated with an excess of baryta water, which gave 29.6 mg of a white precipitate.

1) *What is the volume of the initial gaseous mixture at 20 °C and 105 kPa, given that the number of molecules of one ingredient is 2.5 times greater than the number of molecules of the other?*
2) *What is the density of the initial gaseous mixture at STP?*
3) *Calculate the mass percentage of the salt in the solution obtained by dissolving the initial gaseous mixture in water.*
4) *A gaseous mixture of the same qualitative composition as the one described above is used for the commercial production of a white crystalline compound **X** which is 7.74% hydrogen by mass. When **X** is heated in an autoclave at 100 atm and 150 °C, a certain compound **Y** is formed. Give the chemical structures of **X** and **Y** and write the chemical reactions to represent their preparation.*
5) *What is the density of the stoichiometric mixture of gases used for the preparation of compound **X**?*

SOLUTIONS

Grade 9

Problem 9-1

1) The molecular formula of cubane is C_8H_8. The three stable isomers of cubane are:
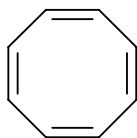
cyclooctatetraene   styrene   4-octen-2,6-diyne
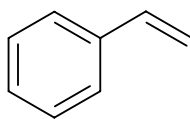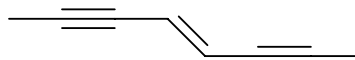
2) The general formula of chloro-substituted cubanes is $C_8H_{8-x}Cl_x$.
   Their molar mass is $M(C_8H_{8-x}Cl_x) = (104 + 34.5x)$ g/mol.
   According to the problem statement, M does not exceed

   $$\frac{\rho RT}{p} = \frac{6.0 \times 8.314 \times (273 + 200)}{100} = 236 \text{ g/mol, from which we find that } x \leq 3.$$

   There are 7 chloro-substituted cubanes that meet these requirements:
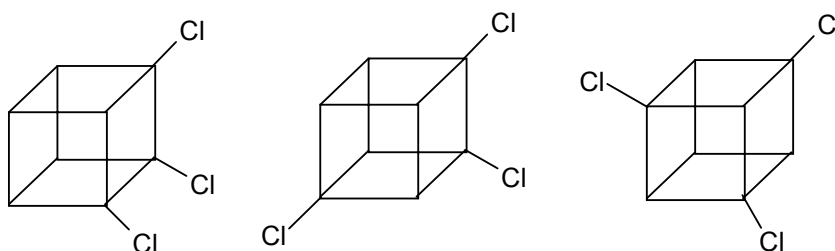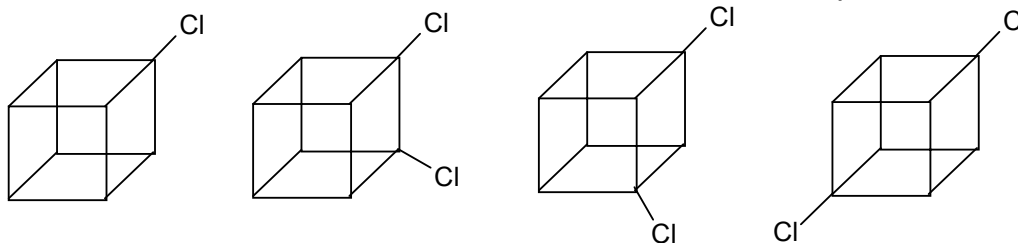
3) The molar mass of compound **X** does not exceed $6 \times 29 = 174$ g/mol, which means that the molar mass of the substituents is no more than 70 g/mol. The fact that there are only two combustion products (whose total mass is substantially greater than the mass of the sample) suggests that these are CO_2 and water. This allows us to conclude that the molecular formula of **X** is $C_xH_yO_z$, where $x \geq 8$, y is even, and $z \geq 0$. The chemical equation representing the combustion reaction is

   $$C_xH_yO_z + \frac{2x + \frac{y}{2} - z}{2} O_2 \rightarrow xCO_2 + \frac{y}{2} H_2O.$$
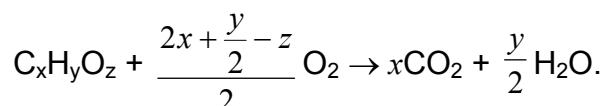
   Based on the stoichiometry of this reaction, the ratio of the combined masses of the products to the initial mass of the sample of **X** is

   $$\frac{544}{150} = \frac{44.0x + (18.0)\frac{y}{2}}{12.0x + 1.0y + 16.0z}, \text{ from which we obtain the equation } 16z = 0.132x + 1.48y.$$

   The latter equation tells us unambiguously that $z > 0$, so **X** contains oxygen. On the other hand, z cannot be greater than 1 because for $z > 1$ the molar mass would be out of the range of possible values. Further analysis of this equation ($16 = 0.132x + 1.48y$) shows that it has the following solution in integers: $x = 9$, $y = 10$. Thus, **X** = $C_9H_{10}O$. The chemical composition of the substituent(s) is CH_2O. There are 5 isomeric deriva-

tives of cubane that meet all of the above requirements:
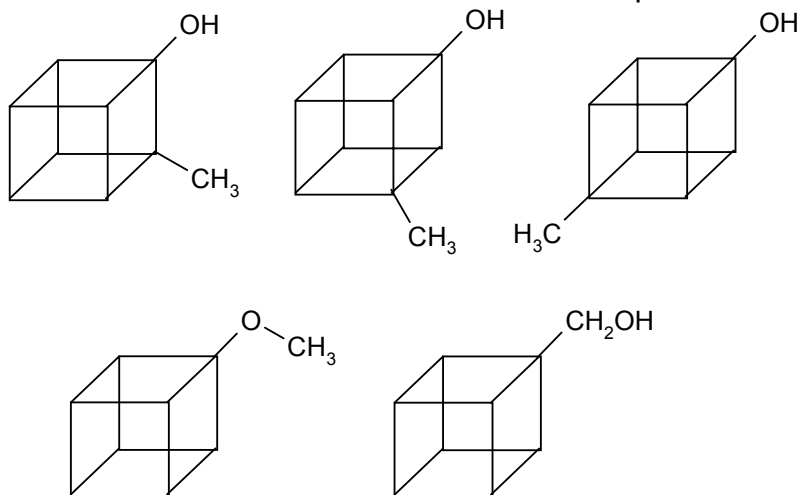
Problem 9-2

1) $M(Fe)$ = 55.9 g/mol.
   $M(H_2SO_4)$ = 98.1 g/mol.
   Thus, the amount of iron in the sample is

   $n(Fe) = \dfrac{40}{55.9}$ = 0.716 mol;

   The sulfuric acid solution has a mass of 415 × 1.10 = 456 g and contains

   456 × 0.15 = 68.5 g or $\dfrac{68.5}{98.1}$ = 0.698 mol of H_2SO_4.

   The reaction of iron and sulfuric acid is
   $Fe + H_2SO_4 = FeSO_4 + H_2\uparrow$.
   The percentage of sulfur in the final product is different from the percentage of sulfur in $FeSO_4$. Therefore, the precipitate is a crystalline hydrate, $FeSO_4 \cdot xH_2O$. We have
   $M(FeSO_4)$ = 152 g/mol
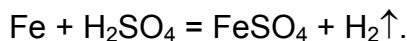
   $M(FeSO_4 \cdot xH_2O) = \dfrac{32.07}{0.1154}$ = 278 g/mol, which gives x=7.

   Thus, the blue crystals are iron(II) sulfate heptahydrate, $FeSO_4 \cdot 7H_2O$.

2) 60% sulfuric acid passivates iron, so it cannot be used in place of the 15% solution. In principle, iron does dissolve in 60% H_2SO_4 if the mixture is heated long enough, but in that case the reaction product is different:
   $2Fe + 6H_2SO_4 = Fe_2(SO_4)_3 + 3SO_2\uparrow + 6H_2O$.
   A few drops of sulfuric acid are added to prevent hydrolysis of iron(II):
   $Fe^{2+} + H_2O \leftrightarrows FeOH^+ + H^+$.
   The saturation of the filtered solution with hydrogen sulfide serves two purposes: to prevent oxidation of Fe^{2+} and to remove impurities. This works because iron(II) sulfide (FeS) does not precipitate from an acidic solution whereas sulfides of other metals that can be present in commercial-grade iron as impurities (e.g., tin) are not soluble even in the presence of an acid:
   $Sn^{2+} + H_2S = SnS + 2H^+$
   Carbon dioxide gas creates an inert atmosphere which prevents Fe(II) ions from being oxidized. In open air, Fe^{2+} would readily oxidize to Fe^{3+}, and the higher the pH value of the solution, the faster the oxidation:
   $4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O$.
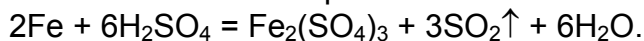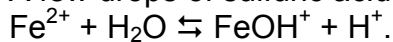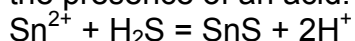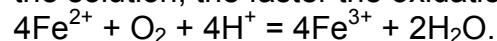
3) Filter paper is a porous material which absorbs the residual solvent. Drying the product in an oven is not a good idea because at elevated temperatures iron(II) is readily oxidized by oxygen to iron(III).

4) We will ignore the presence of impurities in the initial sample. The amount of iron and, hence, the amounts of $FeSO_4$ and H_2 gas are all $n=0.698$ mol. Therefore, the mass of the solution obtained by dissolving the sample in H_2SO_4 is

$(0.698 \times 55.9 + 456 - 0.698 \times 2.0) = 494$ g.

This solution contains $0.698 \times 152 = 106$ g of $FeSO_4$.

The mass of the evaporated solution is $\dfrac{494}{2} = 247$ g. The mass of water in this solution is $247 - 106 = 141$ g. Suppose that the amount of $FeSO_4 \cdot 7H_2O$ is y mol. Then we have $\dfrac{106-152y}{141-126y} = \dfrac{100-78}{78}$, which gives $y = 0.569$ mol.

Thus, the theoretical yield of $FeSO_4 \cdot 7H_2O$ is $0.569 \times 278 = 158$ g.

The actual yields is $\dfrac{140}{158} = 0.886$ or 89 %.

5) The mixture of sulfuric and nitric acids is a very strong oxidizing agent which oxidizes the iron of the sample to Fe^{3+}. Nitric acid is volatile and so it is eliminated during the evaporation. Thus, the final product is iron(III) sulfate or one of its crystalline hydrates. We have

$M(Fe_2(SO_4)_3) = 400$ g/mol.

$M(Fe_2(SO_4)_3 \cdot zH_2O) = \dfrac{32.07 \times 3}{0.1712} = 562$ g/mol, which gives $z = 9$.

Thus, the yellowish crystals are $Fe_2(SO_4)_3 \cdot 9H_2O$.

The equation for the reaction is:

$2FeSO_4 + H_2SO_4 + 2HNO_3 = Fe_2(SO_4)_3 + 2NO_2 + 2H_2O$.
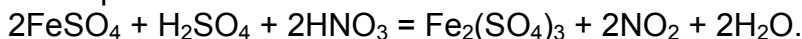
Problem 9-3

1) Suppose the formula of the unknown hydrocarbon is C_nH_{2m}. The combustion is described by the equation

$C_nH_{2m} + \dfrac{2n+m}{2} O_2 \rightarrow nCO_2 + mH_2O$.
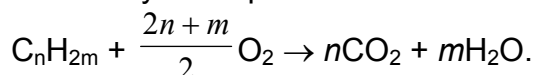
At 99 °C and 101 Pa, all reactants and products of this reaction are gases. By Avogadro's law we have the following equation for relative volumes:

$1 + \dfrac{2n+m}{2} = n + m$. Solution of this equation gives $m = 2$. Therefore, the molecular formula of the unknown hydrocarbon may be one of the following: CH_4, C_2H_4, C_3H_4, C_4H_4. The corresponding possible structures are shown below.
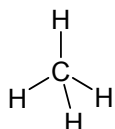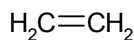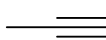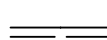

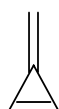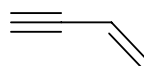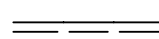methane   ethene   propyne   propadiene   cyclopropene

methylenecyclopropene   cyclobutadiene   1-buten-3-yne   butatriene

(Cyclopropene and cyclobutadiene are unstable and may be excluded).

2) We have

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

$M(C_nH_{2m})$ = (12.0n + 2.0m) g/mol.

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

Referring to the equation for the combustion reaction in part 1 we see that if the amount of the unknown hydrocarbon in the sample is 1 mol, then

$$4.43 = \frac{44.0n + 18.0m}{12.0n + 2.0m}, \text{ which gives } m = n.$$

Therefore, the formula of the unknown hydrocarbon is C_xH_{2x}. This can be either an alkene or a cycloalkane.

3) Suppose the amount of the hydrocarbon in the sample is 1 mol. Then we have the equation

$$4.26 = \frac{44.0n + 18.0m}{12.0n + 2.0m}, \text{ from which we find that } 4m = 3n.$$

The general empirical formula of the hydrocarbon is $C_{2y}H_{3y}$. The simplest possible compound of this composition is C_4H_6, e.g., 1,3-butadiene. This compound can be prepared from inorganic reagents as follows:
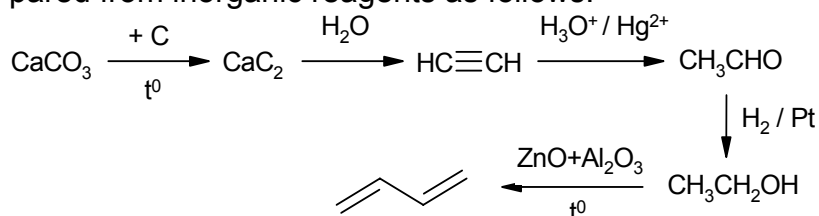
4) For a compound of the general formula C_nH_{2m} the ratio of the combined masses of the products to the mass of the initial hydrocarbon is given by

$$\frac{44.0n + 18.0m}{12.0n + 2.0m} = \frac{44.0 + 18.0 \times \dfrac{m}{n}}{12.0 + 2.0 \times \dfrac{m}{n}}.$$

The value of this fraction increases with the ratio $\dfrac{m}{n}$. The latter achieves a maximum value of 2 for methane (CH_4). Thus, the maximum possible products-to-sample mass ratio is (44.0+18.0×2)/(12.0+2.0×2)=5.00.

5) Complete hydrogenation of an alkene C_nH_{2m} produces an alkane of the general formula C_nH_{2n+2}. The equation for this reaction is

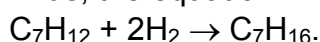$$C_nH_{2m} + \frac{2n + 2 - 2m}{2} H_2 \rightarrow C_nH_{2n+2}.$$
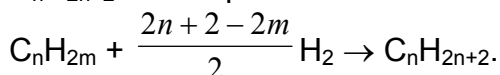
Therefore, we can write

$$1.042 = \frac{M(C_nH_{2n+2})}{M(C_nH_{2m})} = \frac{14.03n + 2.02}{12.01n + 2.02m}.$$

This gives $2.105m = 1.516n + 2.02$ which can be simplified to $m = 0.720n + 0.96$.

The simplest integer solution of this equation is $n = 7$ and $m = 6$.

Thus, the equation in question is

$C_7H_{12} + 2H_2 \rightarrow C_7H_{16}$.

Problem 9-4

1) The only diatomic elemental substances that exist as gases at STP are H_2, N_2, O_2, F_2, and Cl_2. However, nitrogen gas is essentially inert, while oxygen gas does not combine with halogens directly under the specified conditions. This suggests that N_2 and O_2 cannot be present in the mixture simultaneously. Therefore, one of the gases in the
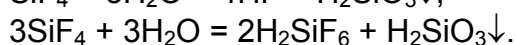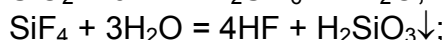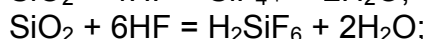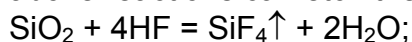
mixture must be H_2. But then the molar mass of the heaviest gas does not exceed $2 \times 25 = 50$ g/mol, which allows us to rule out Cl_2. We conclude that the initial mixture of gases consisted of H_2, O_2, and F_2.

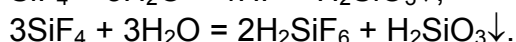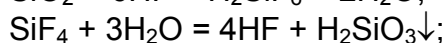The vigorous reactions mentioned in the problem statement are

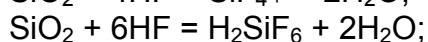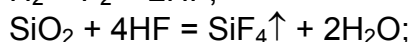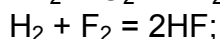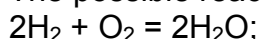$2H_2 + O_2 = 2H_2O$;

$H_2 + F_2 = 2HF$.
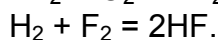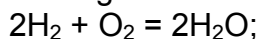
The fact that the reactants were used up completely suggests that the gas with the largest volume is hydrogen. The 5:3:1 volume ratio of **X**, **Y**, and **Z** is possible only under the assumption that **X** = H_2, **Y** = F_2, and **Z** = O_2.

2) Hydrogen, oxygen and fluorine do not form any binary or ternary compounds that are crystalline at STP. However, aqueous hydrogen fluoride which is produced by the above reactions can etch the glass walls of the flask (made mainly of SiO_2):

$SiO_2 + 4HF = SiF_4\uparrow + 2H_2O$;

$SiO_2 + 6HF = H_2SiF_6 + 2H_2O$;

$SiF_4 + 3H_2O = 4HF + H_2SiO_3\downarrow$;

$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3\downarrow$.

Therefore, compound **A** contains hydrogen, silicon, and either oxygen or fluorine. In any case, the hydrogen content cannot be as high as 36%, so this value must be the percentage of Si, O, or F. By trial and error we find that **A** is H_2SiO_3 (the mass percentage of Si is 36.0%).

3) The possible reactions are as follows:

$2H_2 + O_2 = 2H_2O$;

$H_2 + F_2 = 2HF$;

$SiO_2 + 4HF = SiF_4\uparrow + 2H_2O$;

$SiO_2 + 6HF = H_2SiF_6 + 2H_2O$;

$SiF_4 + 3H_2O = 4HF + H_2SiO_3\downarrow$;

$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3\downarrow$.

Problem 9-5

1) We have

$M(NH_4H_2PO_4) = 115$ g/mol.

$M((NH_4)_2HPO_4) = 132$ g/mol.

$M(KNO_3) = 101$ g/mol.

The required amount of potassium per 1.0 m^2 is $\dfrac{4.0}{39} = 0.103$ mol

or $0.103 \times 101 = 10.4$ g of KNO_3. The required amounts of N and P per 1.0 m^2 are $\dfrac{5.0}{14} = 0.357$ mol and $\dfrac{5.0}{31} = 0.161$ mol, respectively.

However, 0.103 mol of N is already available in the form of KNO_3, which means that the remaining (0.357 – 0.103) = 0.254 mol of N should come from the two ammonia phosphates. Suppose that the required amounts of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ are x mol and y mol, respectively. Then we have the system of simultaneous equations:

$x + y = 0.161$;

$x + 2y = 0.254$.

The solution is $x = 0.068$ mol, $y = 0.093$ mol.

Therefore, the required masses of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ per square meter are $0.068 \times 115 = 7.82$ g and $0.093 \times 132 = 12.3$ g, respectively.

Thus, the composition of the "ideal" NPK fertilizer is:

$w(NH_4H_2PO_4) = \dfrac{7.82}{10.4 + 12.3 + 7.82} = 0.256$ or 26%;

$$w((NH_4)_2HPO_4) = \frac{12.3}{10.4+12.3+7.82} = 0.403 \text{ or } 40\%;$$

$$w(KNO_3) = \frac{10.4}{10.4+12.3+7.82} = 0.341 \text{ or } 34\%.$$

2) 1 ha = 10000 m^2.

The total area of the field is 3×10^5 m^2. Therefore, the required amounts of N, P, and K are, respectively, 1500 kg, 1500 kg, and 1200 kg.

$M(NH_4NO_3)$ = 80 g/mol.

$M(NaNO_3)$ = 85 g/mol.

$M(KCl)$ = 74.5 g/mol.

$M(Ca(H_2PO_4)_2 \cdot H_2O)$ = 252 g/mol.

$M(CaHPO_4 \cdot 2H_2O)$ = 172 g/mol.

The only compound that supplies potassium is KCl. The required amount of KCl is

$$1.2 \times \frac{74.5}{39} \times \frac{1}{1-0.02} = 2300 \text{ kg.}$$

In the case of nitrogen and phosphorous, the farmer has a choice. To minimize transportation costs, however, it is advantageous to use those ingredients that have the highest nitrogen and phosphorous content, that is, ammonia nitrate and calcium dihydrogen phosphate. The required amounts are

$$1.5 \times \frac{80}{2 \times 14} \times \frac{1}{1-0.02} = 4400 \text{ kg of } NH_4NO_3 \text{ and}$$

$$1.5 \times \frac{252}{2 \times 31} \times \frac{1}{1-0.02} = 6200 \text{ kg of } Ca(H_2PO_4)_2 \cdot H_2O.$$

3) Potassium chloride, KCl (produced in Soligorsk); calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$ (Gomel); carbamide (urea), NH_2CONH_2 (Grodno).
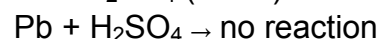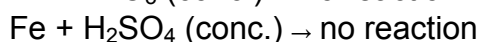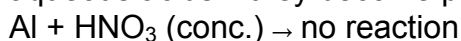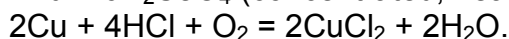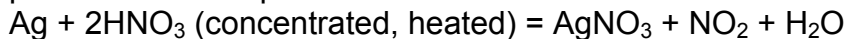
Grade 11

Problem 11-1

See Problem 9-5.

Problem 11-2

1) Metals that are placed in the electrochemical series above hydrogen will *not* dissolve in aqueous acids if they become passivated. Examples:

Al + HNO$_3$ (conc.) → no reaction

Fe + H$_2$SO$_4$ (conc.) → no reaction

Pb + H$_2$SO$_4$ → no reaction

2) Metals that are placed in the electrochemical series below hydrogen *can* dissolve in aqueous acids if the solution contains species that are stronger oxidizing agent than protons H$^+$. Examples:

Ag + 2HNO$_3$ (concentrated, heated) = AgNO$_3$ + NO$_2$ + H$_2$O

2Au + 6H$_2$SeO$_4$ (concentrated, heated) = Au$_2$(SeO$_4$)$_3$ + 3SeO$_2$ + 6H$_2$O

2Cu + 4HCl + O$_2$ = 2CuCl$_2$ + 2H$_2$O.

3) The fact that the blue solution is transparent indicates that the copper was dissolved completely. The equality of the masses of the initial and final solutions means that one of the reaction products is a gas (with a mass of 2 g). We have

$M(Cu)$ = 63.5 g/mol and

$n(Cu) = \dfrac{2.0}{63.5}$ = 0.0315 mol. Each copper atom donates two electrons to the oxidizing agent. If the reduction half-reaction involves *x* electrons per gas molecule, then the mo-
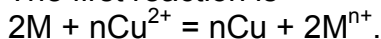
lar mass of the gas is

$$\frac{2.0}{(0.0315)(2)} x = 32x \text{ g/mol}.$$

The compound that meets all these requirements is sulfur dioxide ($x=2$). The reaction is $Cu + 2H_2SO_4 = CuSO_4 + SO_2\uparrow + 2H_2O$.
$M(H_2SO_4) = 98.1$ g/mol.
The minimum required amount of sulfuric acid is $2 \times 0.0315 \times 98.1 = 6.2$ g.

4) The first reaction is
$2M + nCu^{2+} = nCu + 2M^{n+}$.
Since the mass of the plate has increased, one equivalent of metal **X** has a lower mass than one equivalent of copper. We have: $M(CuCl_2) = 134.5$ g/mol.

The initial amount of $CuCl_2$ is $\frac{10}{134.5} = 0.0743$ mol (while metal **X** is in excess).

Let the molar mass of **X** be A g/mol. Then $10.57 - 10 = 63.5 \times 0.0743 - A \times 0.0743 \times \frac{2}{n}$,

which gives $A = 27.9n$ g/mol. For $n = 2$, $A = 55.8$ g/mol, which suggests that **X** = Fe. The reaction is:
$Fe + CuCl_2 = Cu + FeCl_2$. (1)
Now let us analyze the second experiment. There are two stable chlorides of iron: $M(FeCl_2) = 126.8$ g/mol, $M(FeCl_3) = 162.2$ g/mol.

Thus, the solution could have contained either $\frac{10}{126.8} = 0.0789$ mol of $FeCl_2$

or $\frac{10}{162.2} = 0.0617$ mol of $FeCl_3$.

However, neither of these assumptions is consistent with the numerical data (the decrease of the plate mass from 10.00 g to 8.04 g). We do not know whether iron is deposited on the surface of the copper plate but it is certain that some part of the plate is dissolved. Assuming that the mass reduction is due entirely to the transfer of copper into solution, we obtain the amount of oxidized copper:
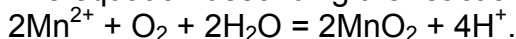
$\frac{10 - 8.04}{63.5} = 0.0309$ mol, which is exactly half the amount of $FeCl_2$. This suggests that

the reaction that took place in the second experiment is
$Cu + 2FeCl_3 = CuCl_2 + 2FeCl_2$. (2)
Both reactions (1) and (2) are consistent with the electrochemical series. In the former case, Fe displaces Cu because copper is placed lower than iron. In the latter case, we need to compare the standard reduction potentials of the half-cells Cu^{2+}/Cu and Fe^{3+}/Fe^{2+} (rather than Fe^{2+}/Fe). The standard potential of the Fe^{3+}/Fe^{2+} half-reaction is higher, which means that Cu should dissolve in aqueous solutions of Fe^{3+} to give Fe^{2+}.

5) The equation describing the reaction in question is
$2Mn^{2+} + O_2 + 2H_2O = 2MnO_2 + 4H^+$.
Because the standard reduction potentials of the two half-reactions are equal, the direction of this reaction will strongly depend on external conditions. Using the Nernst

equation we can write $E = (E^0_{O2} - E^0_{Mn}) - \frac{0.059}{4} \log \frac{[H^+]^4}{[Mn^{2+}]^2 \cdot p(O_2)}$.

At equilibrium, $E = 0$, which gives $E^0_{O2} = E^0_{Mn} \Rightarrow \frac{[H^+]^4}{[Mn^{2+}]^2 \cdot p(O_2)} = 1$.

At standard atmospheric pressure, $p(O_2) = 0.21$ bar. Given also that pH = 2.0, we ob-

tain $[Mn^{2+}] = \sqrt{\dfrac{[H^+]^4}{p(O_2)}}$ = 2.2 × 10^{-4} M.

The fraction of Mn^{2+} ions that will undergo oxidation to MnO$_2$ is therefore

$\dfrac{1.00 - 0.22}{1.00}$ = 0.78 or 78%.

Problem 11-3

1) We will assume that a food item becomes spoiled when the fraction of its oxidized form exceeds a certain *small* threshold. In that case, the concentration of the reactant is essentially constant, so the storage time is inversely proportional to the oxidation rate,

that is, $\dfrac{t_1}{t_2} = \dfrac{k_2}{k_1}$. Using the Arrhenius equation $k = A\exp\left(-\dfrac{E_a}{RT}\right)$ we can write

$\ln\dfrac{t_2}{t_1} = \ln\dfrac{k_1}{k_2} = \dfrac{E_a}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$. This allows us to estimate the activation energy:

$E_a = \ln\dfrac{t_1}{t_2} \cdot \dfrac{RT_1T_2}{T_1 - T_2}$ = $\ln\dfrac{7}{1} \cdot \dfrac{8.314 \times 268 \times 273}{5} \times 10^{-3}$ = 237 kJ/mol.

The temperature required to preserve the item for 1 month (i.e., 30.5 days on average) is determined by the equation

$\ln\dfrac{30.5}{1} = \dfrac{2.37 \times 10^5}{8.314}\left(\dfrac{1}{T_2} - \dfrac{1}{273}\right)$, which gives T_2 = 264.4 K or –8.7 °C.

2) Vacuum packing, sterilization (pasteurization), addition of preservatives.

3) The combined volume of the two plutonium hemispheres is $\dfrac{4\pi(4.2)^3}{3}$ = 310 cm^3. Initially, the hemispheres contain 19.8(310 × 10^{-3})= 6.14 kg of ^{239}Pu, but this amount decreases over time due to nuclear fission. The time t it takes the mass of ^{239}Pu to drop below the critical value (5.6 kg) can be found from the equation $m = m_0(1/2)^{t/\tau}$.

This gives $t = \tau_{1/2} \cdot \dfrac{\ln\dfrac{m_0}{m}}{\ln 2} = (2.4 \times 10^4)\dfrac{\ln\dfrac{6.14}{5.6}}{\ln 2}$ = 3200 years, which is a very long time.

The moral of the story is: Never let a nuclear bomb get into the hands of terrorists!

4) Cell division is described by the same equation as nuclear fission except that the rate of change of the number of objects N has an opposite sign. Instead of exponential decay we now have exponential growth: $N = N_0 \times 2^{t/\tau}$.

The total surface area of the Petri dish is $\dfrac{\pi d^2}{4} = \dfrac{3.142(0.10)^2}{4}$ = 7.85 × 10^{-3} m^2.
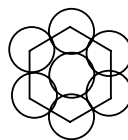
If the cells fill the surface by lying horizontally next to one another, then the area occupied by each cell is (2.0 × 10^{-6})(0.6 × 10^{-6}) = 1.2 × 10^{-12} m^2.

The entire surface will be covered by $\dfrac{7.85 \times 10^{-3}}{1.2 \times 10^{-12}}$ = 6.54 × 10^9 cells in

$t = 20 \cdot \dfrac{\ln(6.54 \times 10^9)}{\ln 2}$ = 652 min or 11 hrs.

If the bacteria stay vertically and are packed side-by-side as closely as possible, then some part of the surface will remain uncovered. Assuming the hexagonal close packing
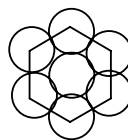
shown schematically in the following diagram , we find that the area occupied

by each cell is $\dfrac{6 \times 0.5 \times \sin 60° \times (0.6 \times 10^{-6})^2}{3}$ = 3.12 × 10^{-13} m^2. The entire surface will be

covered by $\dfrac{7.85 \times 10^{-3}}{3.12 \times 10^{-13}}$ =2.52 × 10^{10} cells in $t = 20 \cdot \dfrac{\ln(2.52 \times 10^{10})}{\ln 2}$ = 691 min or 11.5 hrs.

Problem 11-4

1) Suppose the composition of the isomers **A**, **B**, **C** is C_nH_{2m}. Combustion of any of these hydrocarbons is described by the chemical equation:

C_nH_{2m} + $\dfrac{2n + m}{2}$ O$_2$ → nCO$_2$ + mH$_2$O.
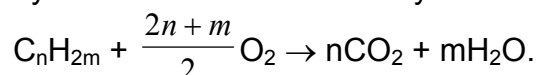
The molar mass of C_nH_{2m} is $M = \dfrac{\rho RT}{p} = \dfrac{2.67 \times 8.314 \times (273 + 100)}{101}$ = 82.0 g/mol.

Thus, we have an equation in integers: $12n + 2m = 82$ (1)

Recall that $M(H_2O)$ = 18.02 g/mol. The combustion gave

$\dfrac{1.540}{18.02}$ = 0.08546 mol of H$_2$O and $\dfrac{2.414 \times 103.1}{8.314 \times 292}$ = 0.1025 mol of CO$_2$.

Using this information we obtain $\dfrac{n}{m} = \dfrac{0.1025}{0.08546} = \dfrac{6}{5}$ (2)

The simultaneous solution of eqs. (1) and (2) is n=6, m=5. Thus, the molecular formula of the isomers is C_6H_{10}. Since 1 mol of **A**, **B**, or **C** reacts with only 1 mol of Br$_2$, we conclude that each of these compounds contains a cycle and a double C=C bond. The 27 possible structure are shown below (compounds that exist as optical isomers are marked with an asterisk).

(*)   (*)   (*)   (*)   (*)
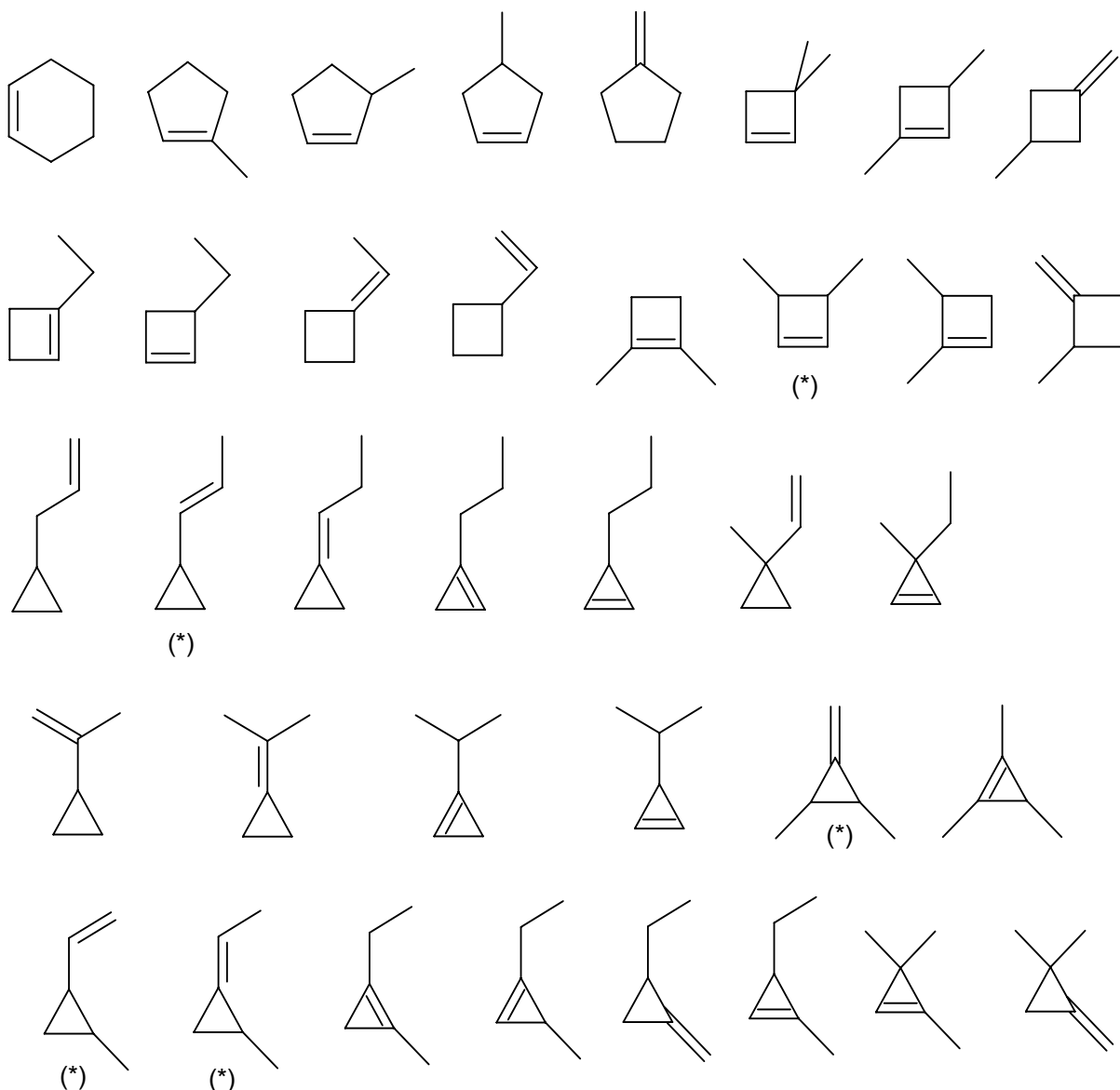
*Remark:* Substituted cyclopropenes are unstable and may be omitted from the list.

2) The combustion produced 0.1025 mol of CO_2. The molar mass of the hydrocarbon is 82.0 g/mol. Therefore, the mass of the initial sample is $82.0 \times \dfrac{0.1025}{6}$ = 1.40 g.

3) Vigorous oxidation of alkenes with potassium permanganate breaks the double carbon-carbon bond and produces carbonyl compounds. Example:

$$\text{KMnO}_4$$

+ CH_3COOH
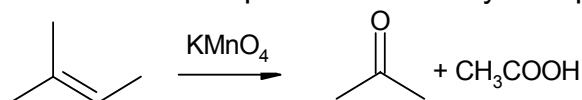
The fact that each of the hydrocarbons **A**, **B**, and **C** yields only one oxidation product suggests that these compounds are cycloalkenes with an endocyclic C=C bond. Compound **C** can be identified from the fact that the two COOH groups in its oxidation product are as far apart as possible. This leaves only one possibility, namely, that **C** is cyclohexene:

[O]

HO_2C CO_2H

C
cyclohexene

hexanedioic (adipic) acid

– 16 –
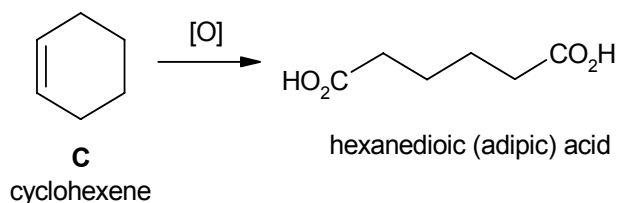
The methyl-substituted dicarboxylic acid is formed by oxidation of methyl cyclopentene. The requirement that this acid be optically active is satisfied by only one structure:
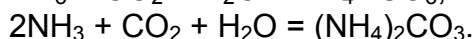

A

(3S)-3-methylcyclopentene   (2S)-2-methylpentandioic acid

A

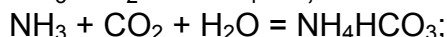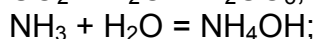(3R)-3-methylcyclopentene   (2R)-2-methylpentanedioic acid
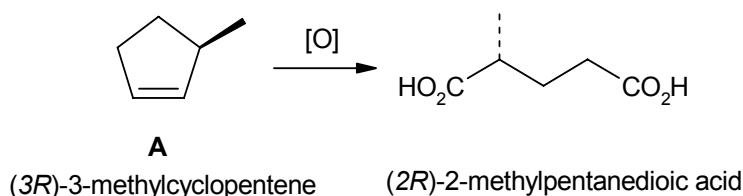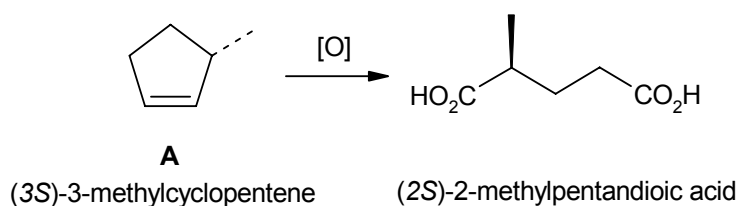
Keto acids can be formed only from cycloalkenes containing an alkyl substituent at the endocyclic double bond. On the other hand, compounds that give a positive iodoform test contain a CH_3CO- fragment. This allows us to conclude that **B** is an ethyl-substituted cycloalkene. Since cyclopropenes are unstable, this leaves only one possibility: ethyl cyclobutene.


B

1-ethylcyclobutene   4-oxohexanoic acid
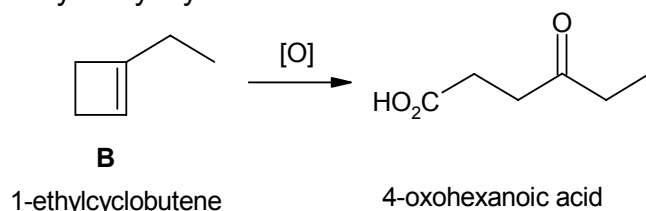
Problem 11-5

1) Depending on the ratio of ammonia and carbon dioxide in the initial mixture, the following processes can take place in solution:

$CO_2 + H_2O = H_2CO_3$;

$NH_3 + H_2O = NH_4OH$;

$NH_3 + CO_2 + H_2O = NH_4HCO_3$;

$2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3$.

Regardless of which ammonium salt is actually produced, the precipitate observed in the reaction with baryta water is barium carbonate:

$Ba^{2+} + CO_3^{2-} = BaCO_3\downarrow$,

or

$Ba^{2+} + HCO_3^- + OH^- = BaCO_3\downarrow + H_2O$.
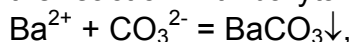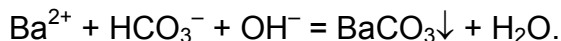
$M(BaCO_3) = 197$ g/mol.

The amount of $BaCO_3$ is $\dfrac{29.6}{197} = 0.150$ mmol, which means that the initial mixture con-

tained $0.150 \times \dfrac{500}{10.0} = 7.50$ mmol of CO_2.

The problem has two alternative solutions:

a)   The initial mixture has an excess of CO_2. Then the amount of ammonia is

$\dfrac{7.50}{2.5} = 3.00$ mmol. The volume of the initial mixture can be found from the ideal gas

equation of state: $V = \dfrac{nRT}{P} = \dfrac{(7.50 + 3.00)(8.314)(273 + 20)}{105} = 244$ mL.

b)   The initial mixture has an excess of NH_3. Then the amount of ammonia is

$2.5 \times 7.5 = 18.75$ mmol. The volume of the initial mixture of gases is

$$V = \frac{(7.50 + 18.75)(8.314)(273 + 20)}{105} = 609 \text{ mL}.$$

2) As implied in part 1, there are two alternative solutions to this problem. The density of the initial gaseous mixture at STP can be found from the relation $\rho = \dfrac{M}{V_m}$, where M is the average molar mass of the mixture.

$M(NH_3) = 17.0$ g/mol.
$M(CO_2) = 44.0$ g/mol.

a) CO_2 is in excess. Then $M = \dfrac{44.0 \times 2.5 + 17.0 \times 1}{2.5 + 1} = 36.3$ g/mol

and so $\rho = \dfrac{M}{V_m} = \dfrac{36.3}{22.4} = 1.62$ g/L.

b) NH_3 is in excess. Then $M = \dfrac{17.0 \times 2.5 + 44.0 \times 1}{2.5 + 1} = 24.7$ g/mol

and so $\rho = \dfrac{M}{V_m} = \dfrac{36.3}{22.4} = 1.10$ g/L.

3) As above, there are two alternative solutions.
a) If the carbon dioxide gas is in excess, then the salt is ammonium bicarbonate:
$M(NH_4HCO_3) = 79$ g/mol.
The mass of the salt is $79 \times 3.0 \times 10^{-3} = 0.24$ g.
The mass of the solution is $(200 + 36.3 \times 10.5 \times 10^{-3}) = 200.4$ g, so the mass percentage of the salt is $\dfrac{0.24}{200.4} = 0.00120$ or 0.12%.
b) If the ammonia gas is in excess, then the salt is ammonium carbonate:
$M((NH_4)_2CO_3) = 96$ g/mol.
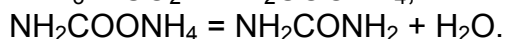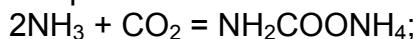The mass of the salt is $96 \times 7.5 \times 10^{-3} = 0.72$ g.
The total mass of the solution is $(200 + 24.7 \times 26.25 \times 10^{-3}) = 200.6$ g, so the mass percentage of the salt is $\dfrac{0.72}{200.6} = 0.00359$ or 0.36%.

4) Compound **X** can contain atoms H, C, N, O. Suppose that the number of hydrogen atoms is x. Then the molar mass of **X** is $M = \dfrac{1.008}{0.0774} x = 13.0x$ g/mol. Based on the de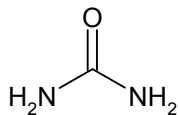scription of the synthesis of **X**, this compound is ammonium carbamate, NH_2COONH_4. When heated, ammonium carbamate loses a water molecule to give carbamide (urea), compound **Y**:
$2NH_3 + CO_2 = NH_2COONH_4$;
$NH_2COONH_4 = NH_2CONH_2 + H_2O$.
The structural formulas of **X** and **Y** are below:
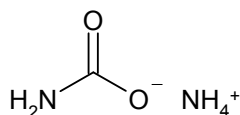
X   **Y**

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5) The stoichiometric volume ratio of NH_3 and CO_2 in the synthesis of urea is 2:1. The average molar mass of this mixture is $M = \dfrac{44.0 \times 1 + 17.0 \times 2}{1 + 2}$ = 26.0 g/mol, so its density is

$\rho = \dfrac{M}{V_m} = \dfrac{26.0}{22.4}$ = 1.16 g/L.

Translated by **V.Staroverov**