BELARUSIAN CHEMISTRY OLYMPIAD

The annual Belarusian High-School Chemistry Olympiad is a multilevel competition with more than three decades of history. The olympiads are coordinated by faculty members of chemistry departments of major Belarusian universities with financial support from the Ministry of Education. Most participants are high school students of grades 9 through 11. It is not unusual, however, that exceptionally gifted students of even lower grades make their way to the National Final. To ensure that ninth-graders are not overwhelmed by advanced topics while senior students have a chance to test the limits of their abilities, three different versions of the exam are administered at each level.

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

The National Final consists of a theoretical exam and a laboratory practical. Each five-hour theoretical exam includes a 10-item multiple choice test and 6 problems. The laboratory practical involves 1-2 experimental problems and lasts 4 to 5 hours. The top-scoring students from the national competition spend several days in a study camp held at the Belarusian State University in Minsk as part of the preparation for the International Olympiad.

GRADE 9

Problem 9-1.

A 1.000 g sample of the nitrate of a certain metal was thermally decomposed at 220 C to give 0.4858 g of a solid residue.
   a) What substances are produced when nitrates undergo thermal decomposition? Write the corresponding chemical equations.
   b) What nitrate was used in the experiment? Write the equation for this reaction.

Problem 9-2.

Crystals of $FeCl_3*6H_2O$ can be prepared by the following method. Metallic iron is dissolved in 25% hydrochloric acid. The solute is oxidized by bubbling chlorine gas until the solution gives a negative reaction with $K_3[Fe(CN)_6]$. The solution is evaporated at 95 C until its density equals exactly 1.695 g/cm^3 and then cooled to 4 C. The resulting precipitate is separated by suction on a porous filter and placed into a tightly sealed container.
   a) Write equations for the reactions involved in the preparation of $FeCl_3*6H_2O$.
   b) How many grams of iron and milliliters of hydrochloric acid with a concentration of 36% (by weight) and a density of 1.18 g/cm^3 are needed for the preparation of 1.00 kg of the target compound? Assume a total actual yield of 65%.
   c) When a 2.752 g sample of the prepared $FeCl_3*6H_2O$ is heated in air at 350 C, a solid residue in the amount of 0.8977 g is produced. What is the qualitative and quantitative composition of this residue?

Problem 9-3.

A face-centered cubic (fcc) lattice is the densest of the three types of cubic packing of spheres. The unit cell of an fcc lattice is a cube in which spheres occupy the corners and the centers of the faces.

In ionic compounds, the spheres (ions) differ in size. Usually, anions are larger than cations, so an fcc structure of ionic compounds can be described as cubic close packing of anions, with cations occupying voids (holes) between the negative ions.

Consider an fcc packing of anions. Such a structure is unstable, but may become stable if some of the holes (tetrahedral or octahedral) are occupied by cations.
   a) Why is the cubic close-packed arrangement of anions unstable?
   b) How many tetrahedral and octahedral holes per unit cell are there in an fcc lattice?
   c) Which holes and how many of them are occupied by cations in an fcc structure of an ionic compound of the AB type (A is the cation, B the anion)? Give your reasoning.
   d) One of the uranium oxides crystallizes in an fcc structure in which 25% of the tetrahedral holes are occupied by uranium ions. What is the oxidation number of uranium atoms in this oxide?
   e) Assuming that the radius of the oxygen anion is 140 pm, calculate the density of the uranium oxide characterized in part (d).

Problem 9-4.

A mixture of propane and chlorine gases was exposed to UV light under room conditions. After the reaction was complete, the mixture was found to have a density of 1.762 relative to nitrogen gas.
   a) Provide a reaction scheme for this process.
   b) Assuming that the reaction produced only mono-substituted derivatives, calculate the mass percent of elemental chlorine in the final mixture.

c) What is the molar ratio between the monochloropropanes in the final mixture? Give your reasoning.
d) Compare the composition of mixtures obtained by monochlorination and monobromination of 2-methyl propane.

Problem 9-5.
A certain compound **A** can be prepared by treating benzene with oleum, fusing the product with sodium hydroxide and decomposing the melt with aqueous carbon dioxide. Catalytic hydrogenation of **A** produces compound **B**. Dehydration of **B** yields hydrocarbon **C**. Destructive ozonolysis of **C** gives a carboxylic acid **D**.
a) Identify the lettered compounds.
b) Write the chemical reactions for the indicated transformations.
c) What is the principal commercial application of acid **D**?
d) In air, compound **C** turns into an explosive compound **E** whose composition is 20.03% oxygen (by weight). Write the structural formula for compound **E**.

Problem 9-6.
An ancient treatise of the alchemist named Merichlundius Glucopotamus (the younger) contains the following passage: Make this substance thus. Take eleven ounces of bone meal made from a black poodle which was slain during a full moon, and mix with seven ounces of oil of vitriol. To which mixture add three parts of sand and grind the whole finely in a mortar. Into the powder thus obtained pour a viscous fluid, called water glass, mix thoroughly, and you will obtain a thick slurry which is good for... (here the writing is illegible). Now if you start with twice as much oil of vitriol as at first and add eleven ounces of ground up chalk ere you pour in water glass, you will find a different composition. The second is suited for the same purpose as the first but is easier to scrape off because... (illegible).
a) Write the chemical formulas for all the compounds mentioned in the above passage. Give their modern chemical names.
b) Write equations for the chemical reactions involved in the preparation of the two compositions. What observable changes in physical properties of the substances accompany these reactions? Explain.
c) Why is water glass viscous?
d) What was the alchemist likely to do with the prepared compositions? What applications could these compositions find today?
e) What differences in structure and properties between the first and second compositions would you expect? Give your reasoning.

GRADE 10
Problem 10-1.
[see Problem 11-3]

Problem 10-2.
[see Problem 9-5]

Problem 10-3.
The label on a bottle of Fairy(R) dishwashing liquid provides the following consumer information:
FAIRY Plus. Juicy Lemon
Thick, full-bodied formula fights grease even in cold water... A delicate scent inspired by nature will make washing dishes a pleasure. Does not irritate skin.

...Ingredients: anionic surfactants 5-15%, nonionic surfactants <5%, stabilizing agents.

The extent to which a dishwashing detergent irritates skin is largely determined by its pH value. In aqueous solution, most surfactants are (weakly) basic.

a) Formation of what type of colloidal dispersions explains the cleansing action of surfactants? Elaborate.

b) What is the principal difference between anionic and nonionic surfactants? Give one example of each type of surfactants. Which surfactants are less likely to irritate skin and eyes? Why?

c) Assuming that the statements about the detergent's performance are correct, what substances must be missing from the list of ingredients? What is their role? Explain.

Problem 10-4.

[see Problem 9-2]

Problem 10-5.

[see Problem 11-5]

Problem 10-6.

[see Problem 11-6]

GRADE 11

Problem 11-1.

Complete combustion of 25.0 L (30 C, 100.8 kPa) of a methane-ethane mixture (40% ethane by mass) in oxygen produces 1055 kJ of heat. Combustion of an equal amount of methane alone produces only 882 kJ of heat.

a) Estimate the specific heat of combustion of higher alkanes (in kJ/mol). Explain each step in your reasoning.

b) Estimate the specific heat of combustion of gasoline (in kJ/kg) assuming that gasoline has a density of 0.75 g/cm^3 and consists of isomeric octanes.

c) What volume of gasoline must be burnt to accelerate a 2.00 ton car from 0 to 100 km/h, assuming a 50% efficiency? Explain each step in your calculations.

Problem 11-2.

The drug called thalidomide first appeared in Europe in the late 1950's. It was used as a sleeping pill and a treatment for morning sickness during pregnancy. Tragically, pregnant women who took the drug gave birth to severely deformed babies. In 1961, scientists discovered that only one of the two enantiomeric compounds present in the medicine actually prevented sickness, while the other was responsible for disfiguring genetic disorders. Shown below is a simplified synthetic route leading to thalidomide
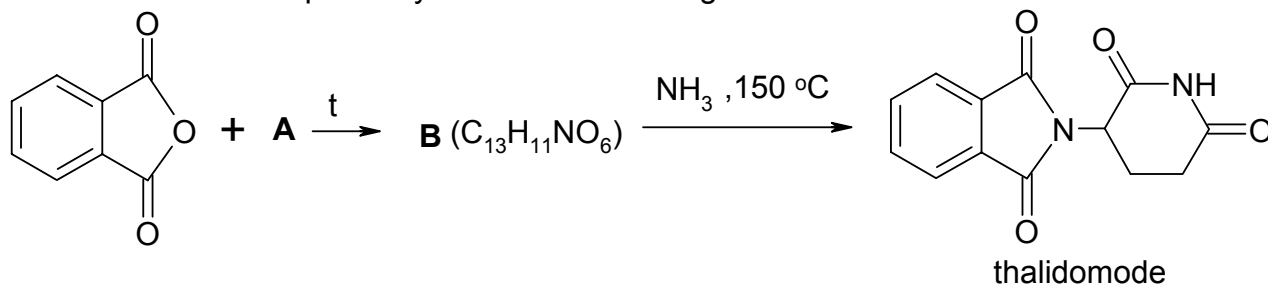
thalidomode

Reagent **A** is a naturally occurring amino acid which contains 9.52% nitrogen by weight.

a) Give the structural formula and a name for reagent **A**.

b) Draw the structural formulas for the intermediate product **B**.

c) Which atom in the thalidomide molecule is the stereocenter?
d) Draw the stereochemical formula for the R-isomer of thalidomide.

Problem 11-3.

A 1.538 g sample of a certain organic compound **X** was dissolved in water and diluted to 250.0 mL in a graduated flask. Titration of a 25.00 mL aliquot of the prepared solution required 23.83 mL of a standardized 0.1024 M KOH solution.

If heated, compound **X** breaks down. One of the volatile products of the thermal decomposition of **X** gives a positive test with an ammoniacal solution of Ag_2O. The only products of combustion of **X** in excess oxygen are carbon dioxide and water.
a) Identify compound **X**.
b) Calculate the molar concentration of **X** in the prepared solution.
c) Write equations for the reactions occurring in the experiment.
d) How would you synthesize **X** starting with inorganic reagents?

Problem 11-4.

Elements **A** and **B** belong to the same group of the periodic table. Atomic weights of **A** and **B** form the ratio 1:1.649. Compounds in which elements **A** and **B** occur are of vital importance in organic nature.

The elements **A** and **B** exist in the form of elemental substances **C** and **D**, respectively. **C** does not react with water under room conditions, whereas **D** reacts vigorously. The oxides of these elements, **E** and **F**, can be obtained by thermal decomposition of a certain mineral **G**.
a) Identify compounds **A** through **G**.
b) Suggest a way to accelerate the reaction of **C** with water under room conditions. Give your reasoning.
c) What is the role played by elements **A** and **B** in organic nature?

Problem 11-5.

A solution of acetic acid with a density of 1.00 g/cm^3 was used in the following experiments. In the first experiment, an excess of calcium metal was added to a 1.00 mL sample of the solution. The reaction produced 684 mL of gas measured at 20.0 C and 98.0 kPa. In the second experiment, 100.0 mL of the same solution were reacted with an excess of magnesium metal. The volume of gas collected within one minute after the start of the reaction was 17.85 mL, as measured at 22 C and 103 kPa.
a) Write net ionic equations for the reactions involved in the experiments.
b) Calculate the molar concentration of acetic acid in the solution.
c) Assuming that the degree of dissociation of acetic acid in the initial solution is 0.916%, estimate the volume of gas (at S.T.P.) that will evolve within the second minute of the second experiment.

Problem 11-6.

In the wake of the discovery of high-temperature superconductivity, chemists faced the challenge of manufacturing materials that would remain superconducting even at temperatures close to normal.

One class of promising candidates for high-T superconductors includes ceramic compositions based on yttrium, barium, and copper. The general molecular formula of such compounds can be written as $YBa_2Cu_3O_x$. The value of x varies from 6 to 7 depending on the ratio between the reactants and the conditions under which the sample was prepared.
a) Write the chemical formula for the barium-yttrium-copper ceramic in which all copper atoms are in the oxidation state +2.

b) What is the oxidation number of copper in $YBa_2Cu_3O_7$?

The value of x in a certain barium-yttrium-copper ceramic was determined from the results of two experiments. In the first experiment, a 1.686 g sample was dissolved in a hot dilute acid.

c) Which of the following acids is best suited for this purpose: sulfuric, hydrochloric, phosphoric or nitric? Explain.

d) Assuming that the composition of the sample is $YBa_2Cu_3O_7$, write the net ionic equation for the reaction with the dilute acid.

The resulting solution was boiled, cooled, transferred to a graduated flask and diluted to 500.0 mL. A 25.00 mL aliquot of the prepared solution was combined with an excess of aqueous potassium iodide and titrated with sodium thiosulfate. The titration required 12.30 mL of a 0.03095 M thiosulfate solution.

e) Why is it necessary to boil the solution before adding potassium iodide?

f) Write equations for the reactions with potassium iodide and sodium thiosulfate.

In the second experiment, a 0.1054 g sample of the ceramic was dissolved in dilute acid containing an excess of iodide ions and titrated with 19.28 mL of 0.03095 M sodium thiosulfate.

g) Write the equation for the reaction of $YBa_2Cu_3O_7$ with the acid in the presence of iodide ions. Explain why one should use an excess of iodide ions.

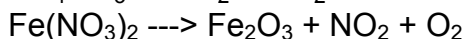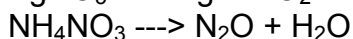h) Based on the results of the above experiments, determine the molecular formula of the ceramic sample.
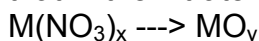
KEY SOLUTIONS

SOLUTIONS

GRADE 9

Problem 9-1.
a) When heated, nitrates can produce nitrites, free metals, oxides of metals in various oxidation states, oxygen, water, and nitrogen oxides:
$NaNO_3 \longrightarrow NaNO_2 + O_2$
$Mg(NO_3)_2 \longrightarrow MgO + NO_2 + O_2$
$AgNO_3 \longrightarrow Ag + NO_2 + O_2$
$NH_4NO_3 \longrightarrow N_2O + H_2O$
$Fe(NO_3)_2 \longrightarrow Fe_2O_3 + NO_2 + O_2$
b) The solid residue is an oxide. The oxidation number of the metal may or may not have changed during the decomposition. A quick calculation rules out the latter possibility. Most likely, the oxidation state of the metal in the oxide is higher than that in the nitrate due to oxidation.
$M(NO_3)_x \longrightarrow MO_y$
Assuming x=y, we obtain $A_r(M)=27.48*x$.
For x=2, $A_r(M)=54.96$. Hence, the metal is Mn, and the nitrate is $Mn(NO_3)_2$.
The equation for the reaction is: $Mn(NO_3)_2 \longrightarrow MnO_2 + 2NO_2$.
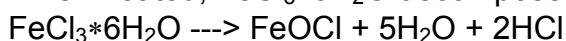
Problem 9-2.
a) The reactions:
$Fe + 2HCl \longrightarrow FeCl_2 + H_2$
$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$
$3FeCl_2 + 2K_3[Fe(CN)_6] \longrightarrow Fe_3[Fe(CN)_6]_2 + 6KCl$
$FeCl_3 + 6H_2O \longrightarrow FeCl_3*6H_2O$
b) $\dfrac{1000}{270}$ =3.704 mol $FeCl_3*6H_2O$.
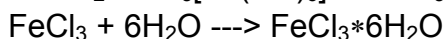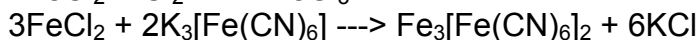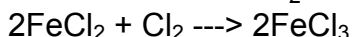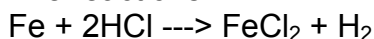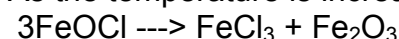
This requires $\dfrac{3.704*55.85}{0.65}$ = 318 g of Fe

and $\dfrac{3.704*2*36.5}{0.36*1.18*0.65}$ = 978 mL of 36% HCl.
c) When heated, $FeCl_3*6H_2O$ decomposes according to the equation
$FeCl_3*6H_2O \longrightarrow FeOCl + 5H_2O + 2HCl$
As the temperature is increased, FeOCl decomposes further:
$3FeOCl \longrightarrow FeCl_3 + Fe_2O_3$
Volatile $FeCl_3$ escapes.

The amount of $FeCl_3*6H_2O$ in the sample is $\dfrac{2.752}{270.3}$ = 10.18 mmol.

This corresponds to 10.18 mmol or 107.3*0.01018 = 1.092 g of FeOCl.
Since the actual mass of the residue was smaller, we conclude that FeOCl must have partially turned into Fe_2O_3.

The loss of $FeCl_3$ by evaporation is $\dfrac{1.092-0.8977}{162.2}$ = 1.20 mmol.

Thus, the final residue contains (0.01018-3*0.00120)=6.58 mmol of FeOCl and 1.20 mmol of Fe_2O_3.

Problem 9-3.
a) Because of a strong repulsion between like charges.

b) 4 octahedral and 8 tetrahedral holes.
c) The 8 corners and the centers of the 6 faces of the cube are occupied by anions.

This gives a total of $8*\dfrac{1}{8} + 6*\dfrac{1}{2}$ = 4 anions per unit cell.

Since the formula of the compound is AB, the number of cations per unit cell must also equal 4.
The cations can occupy either all octahedral or half of the tetrahedral holes.
d) Since a quarter of tetrahedral holes are occupied by uranium atoms, there must be 2 such atoms per unit cell.
Therefore, the formula of the oxide is UO_2.
The oxidation state of the U atom in this oxide is +4.
e) The diagonal of the cube is 4r, where r is the radius of an oxygen anion. Each edge of the cube has a length of $r\sqrt{8}$, so the volume of a unit cell is $(r\sqrt{8})^3$.

Each UO_2 formula unit has a mass of $\dfrac{M(UO_2)}{N_A}$ g.

Since there are 2 formula units per unit cell, the density of UO_2 is

$$\frac{m}{V} = \frac{\dfrac{M(UO_2)}{N_A}*2}{(r\sqrt{8})^3} = \frac{270*2}{6.02*10^{23}*(140*10^{-10}*\sqrt{8})^3} = 14.25 \text{ g/cm}^3.$$

Problem 9-4.

a) $CH_3\text{-}CH_2\text{-}CH_3 + Cl_2 \text{ ---> } ClCH_2\text{-}CH_2\text{-}CH_3 + CH_3\text{-}CHCl\text{-}CH_3 + HCl$
b) Let us assume that each mole of the initial mixture of propane and chlorine gases contains x mol of Cl_2 and (1-x) mol of propane.
Since the final mixture contains only monochloropropanes, we conclude that propane was in excess.
The final mixture contains (1-x)-x=(1-2x) mol of propane, x mol of monochloropropanes and x mol of HCl.
The total amount of gases in the final mixture is (1-2x) + x + x = 1 mol.
Since $M(C_3H_8)$ = 44.1 g/mol, $M(C_3H_7Cl)$ = 78.5 g/mol, and $M(HCl)$=36.5 g/mol, the molar mass of the final mixture is

$$\frac{(1-2x)*44.1 + x*78.5 + x*36.5}{1} = 28*1.762$$

By solving this equation we obtain x = 0.198 mol.
Therefore, the mass fraction of chlorine gas in the initial mixture is

$$\frac{0.198*70.9}{0.198*70.9 + 0.802*44.1} = 0.491 \text{ or } 49.1\%$$

c) Primary hydrogen atoms react with chlorine at a relatively slow rate but there are 6 of them. Secondary atoms react faster, but there are only 2 such atoms.
As a trade-off, the amounts of 1- and 2-chloropropanes are roughly equal (55% and 45%, respectively, according to experiment).
d) Bromium is much more regioselective though less reactive than chlorine. That is why bromination is usually carried out at a higher temperature. Bromination of 2-methyl propane yields almost exclusively 2-bromo-methyl propane (99%). In the reaction with chlorine, tertiary hydrogens are much more likely to be displaced than primary atoms. Experiment shows that the final mixture will contain 37% of 2-chloro-2-methyl propane and 63% of 1-chloro-2-methyl propane.
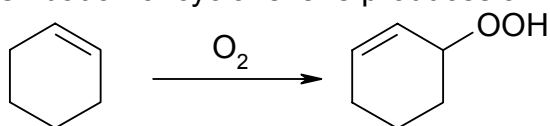
Problem 9-5.

a) A - phenol,
   B - cyclohexanol,
   C - cyclohexane,
   D - adipic acid

b)
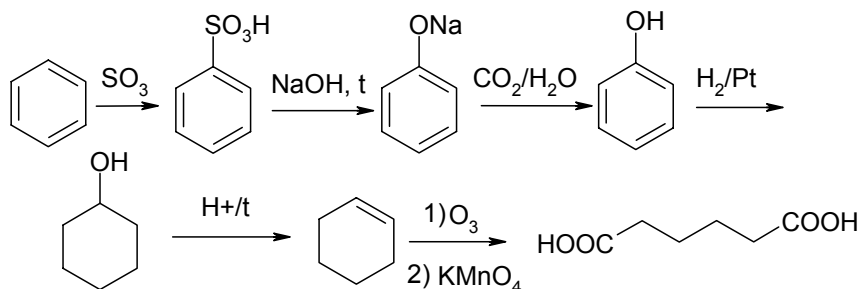
c) Adipic acids is used for production of polyamides.
d) Oxidation of cyclohexene produces an organic peroxide:

   Most organic peroxides are highly explosive.

Problem 9-6.

a) Bones consist mainly of $Ca_3(PO_4)_2$ or $Ca_5(PO_4)_3(OH)$. Oil of vitriol is H_2SO_4, chalk is $CaCO_3$, sand is mostly SiO_2. Water glass is a concentrated solution of sodium silicate which for simplicity can be represented by the formula Na_2SiO_3.

b) Before writing down the equations we need to perform some calculations.
   The molar ratio of H_2SO_4 to $Ca_3(PO_4)_2$ is 7*310 to 11*98 or approximately 2:1.
   Hence, the reaction is
   $2H_2SO_4 + Ca_3(PO_4)_2 = Ca(H_2PO_4)_2 + 2CaSO_4$
   SiO_2 does not react with the resulting mixture and is merely a filler. When water glass is added to the mixture, the reaction is
   $3Ca(H_2PO_4)_2 + 3Na_2SiO_3 = 2Ca_3(PO_4)_2\downarrow + 3H_2SiO_3\downarrow + 2Na_3PO_4$
   The water present in water glass binds with the products to yield crystallohydrates $CaSO_4*2H_2O$ and $Na_3PO_4*12H_2O$. In practice, this means that the composition will set like cement.

c) Water glass is viscous because silicate anions exist in solution in the form of long chains of anions of polisilicic acid $(H_2SiO_3)_n$. Aqueous sodium silicate is not a true solution but a colloidal system.

d) Both plaster-like compositions can be used as quick-setting inorganic putties. One may expect them to be resistant to heat (because there are no organic ingredients) and highly adhesive to glass. The putties may have been used by alchemists for sealing retorts and other laboratory equipment. Even now they are occasionally used for the same purposes. The compositions may be also applied as glues for glass, concrete and like materials.

e) If the mixture contains extra 11 parts of H_2SO_4 and an equal amount of $CaCO_3$ (note that the number of moles of these compounds must be approximately equal since they have almost identical molecular weights), then the following reaction will also occur:
   $H_2SO_4 + CaCO_3 = CaSO_4 + H_2O + CO_2\uparrow$
   Some of the resulting CO_2 reacts with water glass:
   $CO_2 + H_2O + Na_2SiO_3 = H_2SiO_3\downarrow + Na_2CO_3$
   and some is given off as gas.

Bubbles of CO_2 springing up throughout the setting composition will create a porous structure. The second composition differs from the first by a much higher porosity.

GRADE 10

Problem 10-1.
[see 11-3]

Problem 10-2.
[see 9-5]

Problem 10-3.
a) Surfactants are molecules that have a long non-polar chain ("tail") and a polar fragment ("head"). In water solutions, surfactants tend to aggregate to form hollow, colloid-size particles called micelles. The hydrophobic tails of the surfactant molecules point inward to the center of the micelle, and the hydrophilic heads point outward so they interact with water molecules. In the presence of a surfactant, oil and grease become encapsulated inside the micelles and are washed away with the rinse water. The rinse water is a colloidal dispersion rather than a true solution because the solute is present not in the form of individual molecules but as supramolecular aggregates (each micelle can contain one or more grease molecules). If there is not enough detergent, grease will form isolated droplets. The resulting colloidal dispersion is called emulsion.
b) Anionic surfactants are anions; nonionic surfactants are neutral molecules. Examples: $CH_3(CH_2)_{16}COO^-$ is an anionic surfactant, $CH_3(CH_2)_{16}CH_2(OCH_2CH_2)_4OH$ is nonionic. Human skin's pH value is close to neutral (somewhere from 5 to 5.5). Nonionic surfactants do not hydrolize in solution and therefore are less likely to irritate skin than anionic surfactants which have considerably higher pH values.
c) The "delicate scent inspired by nature" cannot come from non-volatile surfactants. This means that the detergent contains a fragrance. If the claim "does not irritate skin" is to be believed, the detergent should have a pH value in the range 5 to 5.5 (see above). Usually, this is achieved by adding citric or some other weak acid. Moreover, anyone who has ever seen this detergent knows that it comes in several flavors ("Lemon", "Wild berry", etc.) which have different colors. This means that the liquid contains a coloring agent. Taking a formal approach, we might also expect water to be listed as an ingredient. Finally, it is very likely that the detergent contains a thickening agent. This can be an inorganic salt or a water-soluble polymer. Such agents make the product thicker and thereby improve its appearance.

Problem 10-4.
[see 9-2]

Problem 10-5.
[see 11-5]

Problem 10-6.
[see 11-6]

GRADE 11

Problem 11-1.

a) The initial mixture contains $\dfrac{100.8 * 25.0}{8.31 * (273 + 30)}$ = 1.00 mol of gases.

In 100 g of such a mixture, there are 40 g or $\dfrac{40}{30}$ = 1.33 mol of ethane, 60 g

or $\dfrac{60}{16}$ = 3.75 mol of methane, or 1.33+3.75=5.08 mol of gases in total. Proportion-

ally, 1 mol of the mixture contains $\dfrac{1 * 3.75}{5.08}$ = 0.262 mol of ethane and

1*3.75/5.08=0.738 mol of methane.

The equations for the combustion of ethane and methane:

CH_4 + $2O_2$ ---> CO_2 + $2H_2O$

$2C_2H_6$ + $7O_2$ ---> $4CO_2$ + $6H_2O$
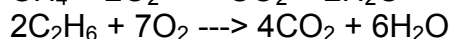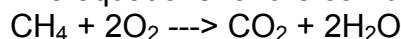
1 mol of ethane produces 882 kJ of heat. Let the specific heat of combustion of eth-
ane be x kJ/mol. Then we can write

882*0.738 + x*0.262 = 1055

By solving this equation we obtain x=1542 kJ/mol.

Comparing the structure of ethane and methane we see that the heat of combustion
of the CH_2 unit is 1542-882=660 kJ/mol.

The general formula of alkanes is C_nH_{2n+2} or, equivalently, $[CH_4 + (n-1)CH_2]$.

Thus, 1 mol of C_nH_{2n+2} will produce 882 + (n-1)*660 = 222 + 660*n kJ of heat.

The molar mass of C_nH_{2n+2} is (14n+2) g/mol.

Combustion of 1 kg of an alkane produces $\dfrac{222 + 660n}{14n + 2}$ kJ of heat.

As n increases indefinitely, the value of the fraction approaches $\dfrac{660n}{14n}$ = 47.

Thus, the specific heat of combustion of higher alkanes is 47 MJ/mol.

b) The heat of combustion of gasoline is $\dfrac{222 + 660 * 8}{14 * 8 + 2}$ = 48.2 MJ/kg.

In terms of volume, this is equal to 48.2*0.75=36.0 MJ/dm^3.

c) The kinetic energy of a car with a mass of m = 2000 kg moving at a speed

of v = 100 km/h is $\dfrac{mV^2}{2}$ = $\dfrac{2000 * (\dfrac{100 * 10^3}{60 * 60})^2}{2}$ = 772 kJ

Assuming a 50% efficiency and using the above estimate of the heat of combustion

of gasoline (36.0 kJ/ml), the acceleration requires $\dfrac{772}{0.50 * 36.0}$ = 42.9 mL of gasoline.
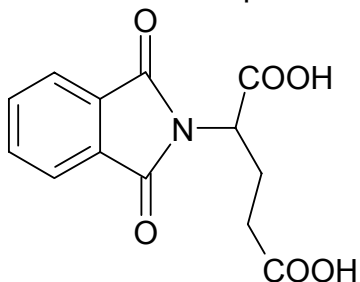
Problem 11-2.

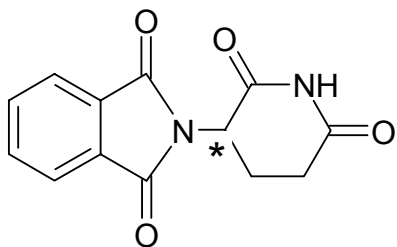a) Since the amino acid A contains only one nitrogen atom, its molecular mass is

$\dfrac{14.01}{0.0952}$ = 147.2 g/mol.

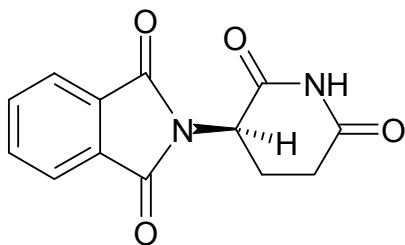This is glutamic acid, HOOC-CH_2-CH_2-CH(NH_2)-COOH.

b) The intermediate product B has the following structure:

c) The stereocenter in the thalidomide molecules is marked with an asterisk:

d)

Problem 11-3.

a) Compound X is composed of carbon, hydrogen, and oxygen atoms. Most likely, X is a carboxylic acid, since it can be titrated with an alkali.

The titration required $23.83*0.1024=2.440$ mmol of KOH.

The 25.00 mL aliquot contained 0.1538 g of X, hence the molecular mass of X is $0.1538*n/0.00244=63.03*n$, where n is the number of carboxyl groups in the acid.

The best guess is n = 2, since dicarboxylic acids, when heated, break down into CO_2 and the corresponding monocarboxylic acid.

The fact that at least one product of the decomposition of X is a reducing agent suggests that we are dealing with oxalic acid (it breaks down into CO_2 and formic acid)

The molecular mass of oxalic acid is only 90.04, which is $63.03*2-90.04 = 36.02$ a.m.u. less than one would expect based on the results of the titration.

We conclude that X is the dihydrate of oxalic acid, $(COOH)_2*2H_2O$.

b) The amount of acid in the solution is $\dfrac{1.538}{126.07}$ = 0.0122 mol.

The molar concentration is, therefore, $\dfrac{0.0122}{0.250}$ = 0.0488 mol/dm^3

c) $(COOH)_2*2H_2O$ ---> CO_2 + $2H_2O$ + HCOOH

   HCOOH + Ag_2O ---> 2Ag + CO_2 + H_2O

d) Oxalic acid can be prepared in various ways. For instance,

   4KCN + $2CuSO_4$ ---> $2K_2SO_4$ + 2CuCN + $(CN)_2$

   $(CN)_2$ + $4H_2O$ ---> $(COONH_4)_2$

   $(COONH_4)_2$ + H_2SO_4 ---> $(NH_4)_2SO_4$ + $(COOH)_2$

Problem 11-4.

a) A - Mg,
    B - Ca,
    C - Mg metal,
    D - Ca metal,
    E - MgO,
    F - CaO,
    G - $MgCO_3*CaCO_3$ (dolomite).
b) Here are several ways to accelerate the reaction of Mg with water. This can be achieved by reducing the size of metal particles (that is, by increasing the surface area) or by adding NH_4Cl to the water (NH_4Cl helps dissolve the insoluble film of magnesium hydroxide).
c) Magnesium is found in chlorophyll molecules. Calcium is one of the principal components of backbones in all vertebrates.

Problem 11-5.
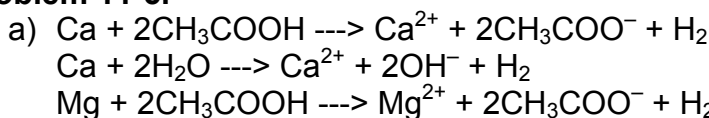
a) $Ca + 2CH_3COOH ---> Ca^{2+} + 2CH_3COO^- + H_2$
   $Ca + 2H_2O ---> Ca^{2+} + 2OH^- + H_2$
   $Mg + 2CH_3COOH ---> Mg^{2+} + 2CH_3COO^- + H_2$
b) Let the molar concentration of acetic acid be x mol/L.
   The initial solution contains x mmol of the acid and $(1 - x*60*10^{-3})$ g
   or $\dfrac{1-0.060*x}{18}$ mol of water.
   According to the equations in part (a), the reaction of this solution with excess cal-
   cium produces $(\dfrac{x*10^{-3}}{2} + \dfrac{1-0.060*x}{2*18})$ mol of H_2.

   The actual amount of H_2 was $\dfrac{0.684*98.0}{8.31*(273+20)}$ = 0.02753 mol.

   Solving the equation $(\dfrac{x*10^{-3}}{2} + \dfrac{1-0.060*x}{2*18})$ = 0.02753,
   we obtain x = 0.2124 mol/L.
c) The amount of hydrogen gas released within the first minute of the second experi-
   ment is $\dfrac{0.01785*103.0}{8.31*(273+22)}$ = 0.750 mmol.

   Within that time the reaction consumed 1.50 mmol of CH_3COOH and produced 1.50 mmol of acetate ions.
   The initial solution contains 0.100*0.2124=21.24 mol of CH_3COOH.
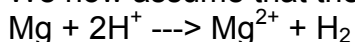   A minute later, the remaining amount of CH_3COOH is 21.24 - 1.50 = 19.74 mmol.
   At that point, the solution contains both acetic acid and acetate ions and, therefore, is a buffer.

   For CH_3COOH, $K_a = \dfrac{a^2C}{1-a} = \dfrac{(0.00916)^2*0.2124}{1-0.00916}$ = 1.80*10^{-5}
   The concentration of H^+ ions in the initial solution is 0.2124*0.00916 = 1.93 mmol/L. The concentration of H^+ ions in the reaction mixture by the end of the first
   minute is $1.80*10^{-5}*\dfrac{19.74}{1.50}$ = 0.237 mmol/L.
   We now assume that the rate of the reaction
   $Mg + 2H^+ ---> Mg^{2+} + H_2$
   is proportional to $[H^+]^2$.

As the concentration of H^+ decreases by a factor of $\dfrac{1.93}{0.237}$ = 8.14, the rate of the reaction decreases by a factor of $(8.14)^2$ = 66.26.

The volume of hydrogen gas produced in the course of the reaction should decrease proportionally.

Thus, the volume of H_2 released within the second minute is $\dfrac{0.75*22.4}{66.26}$ =0.253 mL.

Problem 11-6.

a) $YBa_2Cu_3O_{6.50}$

b) Each formula unit contains three copper atoms, two of which are in the +2 state and one in the +3 state.

c) Nitric acid is suited best.

   Sulfuric acid would produce insoluble $BaSO_4$, hydrochloric acid could give off chlorine gas, and phosphoric acid would react slowly.

d) The reaction is:

   $4YBa_2Cu_3O_7 + 52H^+$ ---> $4Y^{3+} + 8Ba^{2+} + 12Cu^{2+} + O_2 + 26H_2O$

e) The solution must be boiled to remove traces of molecular oxygen which can oxidize iodide ions. Besides oxygen, the reaction mixture may contain hydrogen peroxide which is also eliminated by boiling.

f) The reactions are:

   $2Cu^{2+} + 4I^-$ ---> $2CuI + I_2$

   $I_2 + 2Na_2S_2O_3$ ---> $2NaI + Na_2S_4O_6$

g) The reactions in the presence of iodide ions are:

   $YBa_2Cu_3O_7 + 14H^+ + 7I^-$---> $Y^{3+} + 2Ba^{2+} + 7H_2O + 3CuI + 2I_2$

   $2Cu^{3+} + 6I^-$ ---> $2CuI + 2I_2$

   If there are not enough iodide ions, Cu^{3+} ions will oxidize water and the analysis will yield incorrect results.

h) In the first experiment, titration required 12.30*0.03095 = 0.3807 mmol of $Na_2S_2O_3$. The sample contained 0.3807*20 = 7.614 mmol of Cu (the total of Cu^{2+} and Cu^{3+}).

   In the second experiment, titration required 19.28*0.03095 = 0.5967 mmol of $Na_2S_2O_3$.

   If the second sample had the same mass as the first, the last value would have been 0.5967*1.686/0.1054 = 9.545 mmol.

   The equation in part (d) indicates that out of the 7.614 mmol of Cu, (9.454 - 7.614) = 1.931 mmol was Cu^{3+}, and (7.614 - 1.931) = 5.683 mmol was Cu^{2+}. This corresponds to 0.760 mol of Cu^{3+} and 2.240 mol of Cu^{2+} for every 3.0 mol of copper atoms.

   Therefore, the composition of the ceramic was $YBa_2Cu_3O_{6.88}$.