



**BELARUS**  
**Ministry of Education**

*National Chemistry Olympiad*  
*Theoretical Examination Final. Theoretical round*  
*Mogilev, March 28-April 02, 2005*



### ***BELARUSIAN CHEMISTRY OLYMPIAD***

The Belarusian Chemistry Olympiad is an annual multilevel competition with more than three decades of tradition. The olympiads are organized and coordinated by faculty members of chemistry departments of major Belarusian universities with financial support from the Ministry of Education. Most participants are high school students of grades 9 through 11. It is not unusual, however, that exceptionally gifted students of the eighth grade compete in the National Final. To ensure that younger students are not discouraged by advanced topics while senior students are challenged to test the limits of their abilities, three different versions of the exam are administered at each level.

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

The National Final consists of a theoretical exam and a laboratory practical. Each five-hour theoretical exam includes a 10-item multiple choice test and a set of 5 problems. The laboratory practical involves 1-2 experimental problems and lasts 4 to 5 hours. The winners of the National Final attend a study camp at the Belarusian State University (Minsk) in preparation for the International Olympiad.

## PROBLEMS

### GRADE 9

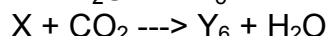
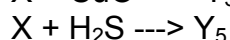
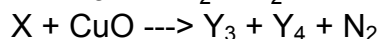
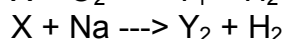
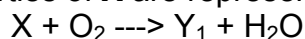
#### Problem 9-1

According to Henry's law, the mole fraction of a solute gas in an ideal liquid solution is directly proportional to the partial pressure of that gas above the solution. The solubility of nitrogen gas in water at 20° C and 500 kPa is 87 mg/L. Under the same conditions, the solubility of oxygen gas is 205 mg/L. Assume the solutions to be ideal.

- Calculate the mole fractions of  $N_2$  and  $O_2$  in water at 20° C if the partial pressure of each gas is 500 kPa.
- What is the mass fraction of nitrogen and oxygen in water kept in open air at 20° C for a long time? Indicate your reasoning and show all calculations.

#### Problem 9-2

A certain compound **X** is produced commercially on a large scale. Chemical properties of **X** are represented by the following equations:



At standard temperature and pressure (S.T.P.), 1 L of water dissolves up to 750 L of **X**. The concentration of  $H^+$  ions in the saturated solution is  $5.43 \cdot 10^{-13}$  mol/L. The density of this solution is 0.880 g/mL.

- Identify compound **X** and write its chemical formula. Give your reasoning.
- Write chemical equations for the reactions of **X** with  $O_2$ , Na, CuO,  $H_2S$ , and  $CO_2$ . Indicate conditions under which these reactions normally occur.
- Calculate the mass percent and molar concentration of **X** in its saturated solution at S.T.P.
- What is the pH of this solution ?
- What will be the pH of the saturated solution if it is diluted by an equal volume of water ?

#### Problem 9-3

Substances **A**, **B**, **C**, **D**, and **E** have the same density of  $1.72 \cdot 10^3$  g/m<sup>3</sup> at 30° C and 740 mm Hg. Substance **A** burns in **B** to produce substance **C**. Substance **D** reacts with bromine in  $CCl_4$  and can undergo explosive decomposition. Substance **E** contains no multiple bonds yet can be hydrogenated in the presence of a catalyst.

- What is the molecular mass of substances **A** - **E** ?
- Draw the structural formulas of substances **A** - **D**.
- Propose a structural formula for compound **E** knowing that **E** has the same qualitative composition as **A**.
- How would you prepare **B** in the chemical laboratory ?

#### Problem 9-4

A certain chemical element **X** forms several oxides, one of which is oxide **A**. When a sample of **A** is heated above 500° C for a long time, the mass percent of oxygen in the sample decreases by a factor of 1.520. The product of this reaction is a

dark-green solid which is used as an inorganic dye and as an abrasive. Reaction of compound **A** with a certain acid **B** produces salt **C**.

In industry, metal **X** is produced by the reduction of a certain mineral **D** with coke in an electric furnace. Metal **X** is widely used in the manufacture of alloyed steels and anticorrosive coatings.

The mass percent of oxygen in **B**, **C**, and **D** is given in the table below.

Compound	<b>B</b>	<b>C</b>	<b>D</b>
w(O), %	58.48	48.96	28.59

- Identify metal **X** and each of the lettered compounds **A**, **B**, **C**, **D**.
- The ground-state electron configuration of element **X** is slightly irregular. Explain.
- Write chemical equations to represent the transformations described in the problem statement.

### Problem 9-5

Hydrogen occurs in nature in the form of three isotopes: protium, deuterium, and tritium. Protium and deuterium are stable isotopes, while tritium is radioactive and undergoes beta-decay. Tritium is continuously produced in the upper atmosphere when neutrons (knocked out from atmospheric gases by cosmic rays) interact with nitrogen-14. In the laboratory, tritium was first produced by the bombardment of deuterated compounds with fast deuterium ions. Nowadays, tritium is made in nuclear reactors by neutron activation of lithium-6. The fusion reaction of tritium and deuterium to form helium-4 is used in the hydrogen bomb.

Particle	$A_r$
$^1\text{H}$	1.007825
$^2\text{H}$	2.01410178
$^3\text{H}$	3.01604927
$^4\text{He}$	4.00260324
$^6\text{Li}$	6.0151215
p	1.0072765
n	1.0086649
e	0.00054858

Chemical bond	Bond energy, kJ/mol
C–C	262
C–H	358
O=O	493
C=O	753
H–O	460

- Write equations for the nuclear reactions mentioned in the text.
- A 12.0 mg sample of lithium-6 was sealed in an evacuated 200 cm<sup>3</sup> vial, placed into a nuclear reactor channel, and irradiated with neutrons for a long time. What maximum possible pressure can build up in the vial at 400 K?
- How much energy is released when tritium and deuterium nuclei are fused to form 1 mol of helium?
- What volume of propane gas (S.T.P.) has to be burned to produce the same amount of energy as the nuclear fusion reaction in part c)?

## GRADE 10

### Problem 10-1

2,3-Dihydroxybutanedioic acid occurs in the form of three stereoisomers (*D*-tartaric, *L*-tartaric, and meso-tartaric acids) and as a racemic mixture (uvic acid). *D*-tartaric acid is produced by fermentation of grape juice. In 1880, Kekule found that meso-tartaric acid can be prepared by treating one of the stereoisomers of butenedioic acid with dilute aqueous KMnO<sub>4</sub> in the cold.

- Draw the stereochemical formulas of *D*-tartaric, *L*-tartaric, and meso-tartaric acids. Assign configuration of each chiral center using the *R/S*-nomenclature.

- b) *What types of isomerism are exhibited by the three tartaric acids in relation to one another? Name these types for each acid pair.*
- c) *What product would be formed in Kekule's experiment if the other stereoisomer of butenedioic acid were used ?*
- d) *Show schematically the reactions occurring in Kekule's experiment.*

### Problem 10-2

In the early 18th century, miners in the Upper Saxony used a peculiar red ore for coloring glass. Although this substance superficially resembled the copper ore, the miners were unable to extract a workable metal from it, so they called it "the Devil's copper". In 1751, the Swedish mineralogist A. F. Cronstedt converted this ore into an oxide, reduced the oxide with hydrogen and obtained a previously unknown metal **X**. One of the oxides of this metal (oxide **A**) can be prepared by controlled heating of the metal's nitrate **B**. Oxide **A** corresponds to the hydroxide **C**, which is a common component of electrochemical cells. Results of a quantitative chemical analysis of Devils's copper and compounds **A**, **B**, **C** are summarized in the table below.

Compound	"Devil's copper"	<b>A</b>	<b>B</b>	<b>C</b>
w(O), %	–	29.02	52.54	43.75
w(X), %	43.93	70.98	32.13	53.50

- a) *Identify the unknown metal **X**. Write the chemical formulas of compounds **A**, **B**, and **C**.*
- b) *What substance is the principal ingredient of "Devil's copper"? Write the chemical equations for the extraction of metal **X** from this ore.*
- c) *Write chemical equations representing the preparation of compounds **A** and **B**.*
- d) *In the chemical laboratory, compound **C** can be prepared by acting with chlorine gas on an alkaline solution of **B**. Write the chemical equation for this process.*
- e) *What are the products of the reaction of **C** with sulfuric and hydrochloric acids ?*
- f) *What chemical reaction occurs in electrochemical cells based on compound **C** ?*

### Problem 10-3

Spectrophotometry is one of the most common analytical techniques. The method is based on the Beer-Bouguer-Lambert law:

$$A = \log \frac{I_0}{I} = \varepsilon cl,$$

where  $A$  is the absorbance (optical density),  $\varepsilon$  is molar absorptivity,  $c$  is the molar concentration of the absorbing solute, and  $l$  is the optical path length (the distance that the light travels through the material).

A 0.5000 g sample containing chromium was treated with aqueous  $\text{H}_2\text{SO}_4$ . Insoluble impurities were removed by filtration and the filtrate was neutralized with  $\text{NaOH}$  to an alkaline pH. Chlorine gas was bubbled vigorously through the neutralized solution. After the excess of chlorine was removed, the solution was placed into a volumetric flask, combined with 1 mL of a 0.5% solution of diphenylcarbazide, neutralized to a slightly acidic pH, and diluted with 0.10 N sulfuric acid to 50.00 mL. The optical density of the final solution was 0.272.

A similar experiment was carried out under the same conditions using a standard solution. A 5.00 mL aliquot of standard aqueous potassium bichromate with a

density of  $15.00 \text{ g/dm}^3$  was placed into a volumetric flask, combined with 1 mL of a 0.5% solution of diphenylcarbazide, and diluted to 50.00 mL with 0.10 N sulfuric acid. The optical density of the final solution was found to be 0.354.

- Write chemical equations for the reactions occurring in this experiment.*
- Calculate the mass percent of chromium in the assayed sample. Assume that all other components of the solution have zero absorbance.*

#### **Problem 10-4**

[see Problem 9-5]

#### **Problem 10-5**

A certain fragrant compound **F** with a rose scent is found in high-quality cognacs and brandies where it contributes to the odor bouquet. Complete combustion of a 1.439 g sample of **F** in oxygen produces  $2.320 \text{ dm}^3$  (at 328 K and 110.7 kPa) of carbon dioxide and 1.061 g of  $\text{H}_2\text{O}$ . Oxidation of **F** with potassium permanganate under harsh conditions yields acid **X** which has the same molecular mass as compound **F**. Under mild conditions, oxidation of **F** produces acid **Y** which is a homolog of **X**. The most intense peak of compound **F** occurs at  $m/Z=122$ .

- Draw the structural formulas of compounds **F**, **X**, and **Y**. Explain how you arrived at the structure of **F**.*
- Show schematically the chemical reactions described in the problem statement.*
- Propose a synthesis of compound **F** starting from benzene.*

### **GRADE 11**

#### **Problem 11-1**

Nitric acid and its salts are extensively used in chemical industry.

- What naturally occurring substances are involved in the industrial manufacture of nitric acid? Write the chemical equations representing the industrial synthesis of  $\text{HNO}_3$ .*
- One of the steps of this process is the reaction of nitric oxide (NO) with oxygen. What is special about the structure of the NO molecule? What is unusual about the thermochemistry of the reaction of NO and  $\text{O}_2$ ?*
- Let the volume percent of NO in a mixture of gases be  $a$ . In what volume ratio should this mixture be combined with air in order to achieve the maximum rate of oxidation? Assume that the other components of the mixture are inert. Show your calculations.*
- The rate of oxidation is greatest at the start of the reaction. What mole fraction of  $\text{O}_2$  should be maintained in the reaction mixture in order for the reaction rate to be always at a maximum? Show your calculations.*

#### **Problem 11-2**

When an unknown metal **X** is treated with a certain liquid **A**, only gas **B** and compound **C** are produced. When **C** is reacted with aqueous NaOH, compound **D** is formed. When **C** reacts with  $\text{H}_2\text{O}_2$  in a strongly alkaline (NaOH) solution, compound **E** is formed. The same reaction of **C** with  $\text{H}_2\text{O}_2$  in a neutral solution yields compound **F**, in an acidic solution - compound **G**, in a strongly acidic solution - compound **H**. Results of

an elemental analysis of compounds **B - H** are as follows:

Compound	w(O), %	w(X), %	Appearance of the solution
<b>B</b>	53.32	-	-
<b>C</b>	55.19	35.14	colorless
<b>D</b>	34.80	27.70	colorless
<b>E</b>	51.63	20,55	violet
<b>F</b>	44.46	23.59	yellow
<b>G</b>	59.65	31.65	red
<b>H</b>	58.65	26.68	blue

- Identify metal **X** and compounds **A** through **H**. Write their chemical formulas.
- Write the chemical equations for the reactions occurring in this experiment.
- What is the chemical structure of compounds **E**, **F**, and **G** in the solid state? Explain.
- The reaction of **X** with **A** is usually slow. It can be accelerated by adding certain compounds to the reaction mixture. What are these compound? Explain briefly how they work.

### Problem 11-3

Enzyme-catalyzed biochemical reactions are amazingly stereospecific: they can produce only one enantiomer even from a completely achiral substrate. For example, the hydration of trans-butenedioic (fumaric) acid catalyzed by the enzyme fumarase results exclusively in (S)-malic acid.

- The hydration of fumaric acid is a step in the citric acid cycle which plays a pivotal role in cellular energy production. Write the chemical equation for this reaction.
- Draw the stereochemical formulas for the stereoisomers of malic acid and assign the (R) or (S) configuration to each stereocenter.
- In the presence of heavy water, the fumarase-catalyzed hydration of fumaric acid produces exclusively (2S,3R)-3-monodeuteromalic acid. Draw the stereochemical formula of this compound.
- Does the fumarase-catalyzed hydration involve syn- or anti- addition of the water molecule? Give your reasoning and show schematically the reactions.
- What do think will happen if cis-butenedioic (maleic) acid is treated with water in the presence of fumarase? Give your reasoning.

### Problem 11-4

The enthalpy of formation of an aqueous solution ( $\Delta H$ ) of a given substance (regardless of whether the substance reacts with water or not) is defined as the amount of heat absorbed or released (under constant pressure) when the substance is dissolved in water to produce a solution with the given molar concentration.

Experiments show that, at 298 K, the enthalpy of formation of 1 mol of aqueous  $\text{SO}_3(\text{l})$  can be calculated by the following empirical equation:

$$\Delta H = -159x + 60x^2 + 251x^3 - 151x^4,$$

where  $x$  is the mole fraction of the solute.

- How many liters of water are needed to prepare a 45% (by mass) solution of sulfuric acid from 50 kg of 35% (by mass) oleum ?
- If the initial and final temperature of this solution is 298 K, what is the enthalpy of the dilution ?



**Problem 11-5**

A 13.96 g sample of a mixture containing Ba metal and BaO was treated with 100.0 mL of water. The resulting gas was collected above water and found to have a volume of 2.290 dm<sup>3</sup> at 304 K and 98.3 kPa. The precipitate was separated from the solution by filtration. A 25.00 mL aliquot of the filtrate was placed into a volumetric flask, 15.00 mL of 0.0200 M HNO<sub>3</sub> was added, and the mixture was diluted with water to 100.0 mL. The pH of the final solution was 1.38.

- a) *Calculate the mass percent and molar concentration of nitric acid in 0.0200 M HNO<sub>3</sub> if this solution has a density of 1.035 g/mL.*
- b) *Calculate the percent of Ba metal in the initial sample. The pressure of water vapor at 304 K is 33.7 mm Hg.*
- c) *What is the mass of the filtered precipitated if the density of the filtrate is 1.140 g/mL ?*
- d) *How many milliliters (mL) of 0.200 M aqueous KOH are needed to completely dissolve this precipitate ?*

## SOLUTIONS

### GRADE 9

#### Problem 9-1

a) At 20° C and 500 kPa, 1 L of water contains  $\frac{1000}{18} = 55.56$  mol of H<sub>2</sub>O.

This amount dissolves  $\frac{0.087}{28} = 3.11 \cdot 10^{-3}$  mol of N<sub>2</sub>.

The mole fraction of N<sub>2</sub> in the solution is  $\frac{3.11 \cdot 10^{-3}}{3.11 \cdot 10^{-3} + 55.56} = 5.60 \cdot 10^{-5}$ .

Similarly, the mole fraction of O<sub>2</sub> is  $\frac{0.205}{\frac{32}{0.205} + 55.56} = 11.5 \cdot 10^{-5}$ .

b) We assume that air is 21% oxygen and 79% nitrogen by volume and that the atmospheric pressure is 101.3 kPa.

The partial pressure of O<sub>2</sub> in air above the solution is  $101.3 \cdot 0.21 = 21.3$  kPa.

The partial pressure of nitrogen is  $101.3 \cdot 0.79 = 80.0$  kPa.

By Henry's law, the mole fraction of N<sub>2</sub> is  $5.60 \cdot 10^{-5} \cdot \frac{80}{500} = 8.96 \cdot 10^{-6}$ .

The mole fraction of O<sub>2</sub> is  $11.5 \cdot 10^{-5} \cdot \frac{21.3}{500} = 4.9 \cdot 10^{-6}$ .

1 mol of this solution contains  $8.96 \cdot 10^{-6}$  mol of N<sub>2</sub> and  $(1 - 8.96 \cdot 10^{-6}) \approx 1$  mol of H<sub>2</sub>O.

The mass fraction of N<sub>2</sub> is therefore  $\frac{8.96 \cdot 10^{-6} \cdot 28}{8.96 \cdot 10^{-6} \cdot 28 + 1 \cdot 18} = 1.39 \cdot 10^{-5}$ .

Similarly, the mass fraction of O<sub>2</sub> is  $\frac{4.9 \cdot 10^{-6} \cdot 32}{4.9 \cdot 10^{-6} \cdot 32 + 1 \cdot 18} = 8.71 \cdot 10^{-6}$ .

#### Problem 9-2

a) **X** is ammonia NH<sub>3</sub>.

b)  $4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$

$2\text{NH}_3 + 2\text{Na} \rightarrow 2\text{NaNH}_2 + \text{H}_2$

$2\text{NH}_3 + 3\text{CuO} \rightarrow 3\text{Cu} + 3\text{H}_2\text{O} + \text{N}_2$

$\text{NH}_3 + \text{H}_2\text{S} \rightarrow \text{NH}_4\text{HS}$  (or  $(\text{NH}_4)_2\text{S}$ )

$2\text{NH}_3 + \text{CO}_2 \rightarrow \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O}$

c) 1 L or 1000 g of water dissolves 750 L or  $\frac{750}{22.4} = 33.48$  mol of NH<sub>3</sub>.

This means that the saturated solution contains  $33.48 \cdot 17 = 569$  g of NH<sub>3</sub> per 1000 g

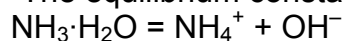
of H<sub>2</sub>O. Thus, the mass percent of NH<sub>3</sub> is  $\frac{569}{569 + 1000} = 0.363 = 36.3\%$

The volume of the solution is  $\frac{1569}{0.88} = 1783 \text{ cm}^3 = 1.783 \text{ dm}^3$ .

The molar concentration of NH<sub>3</sub> in the solution is  $\frac{33.48}{1.783} = 18.78 \text{ mol/dm}^3$ .

d)  $\text{pH} = -\log[\text{H}^+] = -\log(5.43 \cdot 10^{-13}) = 12.26$ .

e) The equilibrium constant for the reversible reaction:



$$\text{is given by } K_b(\text{NH}_3 \cdot \text{H}_2\text{O}) = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_3 \cdot \text{H}_2\text{O}]}$$

In order to calculate the pH of the diluted solution, we need to know the dissociation constant of  $\text{NH}_3 \cdot \text{H}_2\text{O}$ .

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1 \cdot 10^{-14}}{5.43 \cdot 10^{-13}} = 1.84 \cdot 10^{-2} \text{ mol/dm}^3$$

$$[\text{NH}_3 \cdot \text{H}_2\text{O}] = 18.78 - 1.84 \cdot 10^{-2} = 18.76 \text{ mol/dm}^3$$

$$K_b(\text{NH}_3 \cdot \text{H}_2\text{O}) = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_3 \cdot \text{H}_2\text{O}]} = \frac{(1.84 \cdot 10^{-2})^2}{18.76} = 1.81 \cdot 10^{-5}$$

After the dilution, the concentration of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  becomes  $\frac{18.78}{2} = 9.39 \text{ mol/dm}^3$ .

Substitution of  $[\text{NH}_4^+] = [\text{OH}^-]$  and  $[\text{NH}_3 \cdot \text{H}_2\text{O}] = (9.39 - [\text{OH}^-])$  into the expression for the dissociation constant gives:

$$K_b(\text{NH}_3 \cdot \text{H}_2\text{O}) = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_3 \cdot \text{H}_2\text{O}]} = \frac{[\text{OH}^-] \cdot [\text{OH}^-]}{9.39 - [\text{OH}^-]} = 1.81 \cdot 10^{-5}$$

The solution of this equation is  $[\text{OH}^-] = 0.0130$ .

Thus,  $\text{pOH} = -\log[\text{OH}^-] = -\log(0.0130) = 1.88$ .

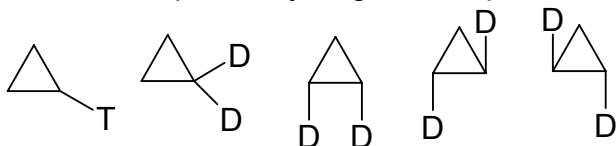
$\text{pH} = 14 - \text{pOH} = 14 - 1.88 = 12.32$ .

### Problem 9-3

- a) The pressure at which the density was measured is  $101.325 \cdot \frac{740}{760} = 98.66 \text{ kPa}$ , the temperature is  $273 + 30 = 303 \text{ K}$ .

The molar mass of compounds A-E is  $\frac{1.72 \cdot 8.314 \cdot 303}{98.66} = 44 \text{ g/mol}$ .

- b) A -  $\text{C}_3\text{H}_8$   
 B -  $\text{N}_2\text{O}$   
 C -  $\text{CO}_2$   
 D -  $\text{CH}\equiv\text{CF}$ .
- c) Compound E is a hydrocarbon with no multiple bonds. Since E can be hydrogenated, it is not a saturated hydrocarbon. Therefore, it must contain a ring of three carbon atoms. However, cyclopropane has only 6 hydrogen atoms ( $M=42 \text{ g/mol}$ ). All these clues can be made to agree by assuming that the molecule contains heavier isotopes of hydrogen. The possible structures are:

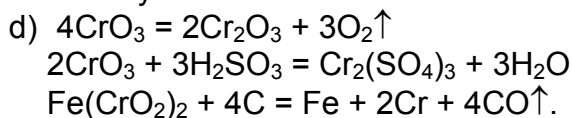


- d)  $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$ .

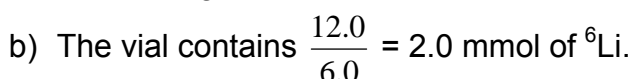
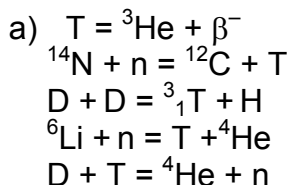
### Problem 9-4

- a) X is chromium Cr.  
 b) A -  $\text{CrO}_3$   
 Б -  $\text{H}_2\text{SO}_3$   
 B -  $\text{Cr}_2(\text{SO}_4)_3$   
 Г -  $\text{Fe}(\text{CrO}_2)_2$
- c) The electron configuration of the Cr atom is not  $3d^4 4s^2$ , as one might expect, but

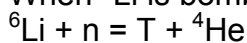
$3d^5 4s^1$ . The reason for this irregularity is that the half-filled shell ( $3d^5$ ) has a greater stability than  $3d^4$ .



### Problem 9-5



When  ${}^6\text{Li}$  is bombarded with neutrons, the following reaction occurs:



This gives 1 mmol of  $\text{T}_2$  and 2.0 mmol of He, a total of 3 mmol of gases. The

maximum pressure in the vial is  $\frac{0.0030 \cdot 8.314 \cdot 400}{0.200} = 49.9$  kPa.

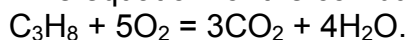
c) The mass defect per 1 mol of helium-4 is:

$$(3.1604927 + 2.01410178) - (4.00260324 + 1.0086649) = 0.01888291 \text{ g.}$$

This corresponds to a release of:

$$0.01888291 \cdot 10^{-3} \cdot (3 \cdot 10^8)^2 = 1.69946 \cdot 10^{12} = 1.69946 \cdot 10^6 \text{ MJ of energy.}$$

d) The equation for the combustion of propane is



We can estimate the heat of this reaction using the standard values of bond energies:

$$\begin{aligned} Q &= [6E(\text{C}=\text{O}) + 8E(\text{H}-\text{O})] - [2E(\text{C}-\text{C}) + 8E(\text{C}-\text{H}) + 5E(\text{O}=\text{O})] = \\ &= (6 \cdot 753 + 8 \cdot 460) - (2 \cdot 262 + 8 \cdot 358 + 5 \cdot 493) = 2345 \text{ kJ.} \end{aligned}$$

The amount of propane gas needed to produce that much heat is

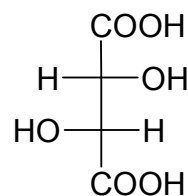
$$\frac{1.69946 \cdot 10^9}{2345} = 724.7 \cdot 10^3 \text{ mol.}$$

The volume of the gas is  $22.4 \cdot 724.7 \cdot 10^3 = 1.62 \times 10^7$  L.

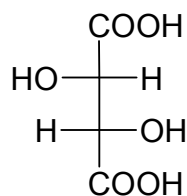
## GRADE 10

### Problem 10-1

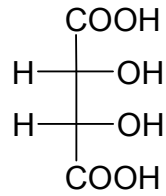
a)



D-tartaric  
(R, R)  
(I)



L-tartaric  
(S, S)  
(II)



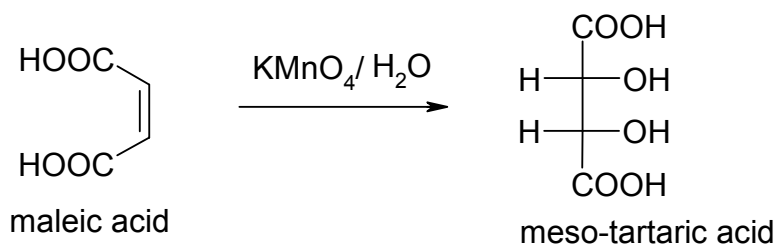
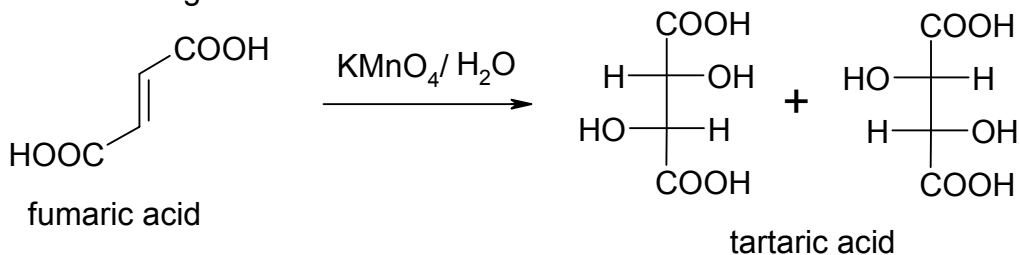
meso-tartaric  
(R, S)  
(III)

b) I and II is a pair of enantiomers.

I and III, II and III are pairs of diastereomers.

c) Cis- and trans-isomers of butenedioic acid are maleic and fumaric acids,

respectively. Oxidation of fumaric acid gives uvic acid. Oxidation of maleic acid under similar conditions gives meso-tartaric acid.



### Problem 10-2

- Metal X is nickel (Ni).
- A -  $\text{Ni}_2\text{O}_3$   
B -  $\text{Ni}(\text{NO}_3)_2$   
B -  $\text{Ni}(\text{OH})_3$ .
- The principal ingredient of "Devil's copper" is NiAs.  
 $4\text{NiAs} + 5\text{O}_2 = 4\text{NiO} + 2\text{As}_2\text{O}_3$   
 $\text{NiO} + \text{H}_2 = \text{Ni} + \text{H}_2\text{O}$
- $4\text{Ni}(\text{NO}_3)_2 = 2\text{Ni}_2\text{O}_3 + 8\text{NO}_2 + \text{O}_2$   
 $2\text{Ni}(\text{NO}_3)_2 + \text{Cl}_2 + 6\text{NaOH} = 2\text{Ni}(\text{OH})_3 \downarrow + 2\text{NaCl} + 4\text{NaNO}_3$
- The  $\text{Ni}^{3+}$  ion is a very strong oxidizing agent.  
 $4\text{Ni}(\text{OH})_3 + 4\text{H}_2\text{SO}_4 = 4\text{NiSO}_4 + \text{O}_2 \uparrow + 10\text{H}_2\text{O}$   
 $2\text{Ni}(\text{OH})_3 + 6\text{HCl} = 2\text{NiCl}_2 + \text{Cl}_2 \uparrow + 6\text{H}_2\text{O}$
- Positive plates (anodes) of alkaline batteries are made of nickel(III) hydroxide. The reaction is:  
 $\text{Fe} + 2\text{Ni}(\text{OH})_3 = \text{Fe}(\text{OH})_2 + 2\text{Ni}(\text{OH})_2$ .

### Problem 10-3

- $\text{Cr} + \text{H}_2\text{SO}_4 = \text{CrSO}_4 + \text{H}_2 \uparrow$   
 $\text{CrSO}_4 + 8\text{NaOH} + 2\text{Cl}_2 = \text{Na}_2\text{CrO}_4 + 4\text{NaCl} + \text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O}$   
 $2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}$ .
- The concentration of chromium in the standard solution is  $0.5303 \text{ g/dm}^3$ .  
 The concentration of chromium in the solution under investigation is then  $0.4074 \text{ g/dm}^3$ .

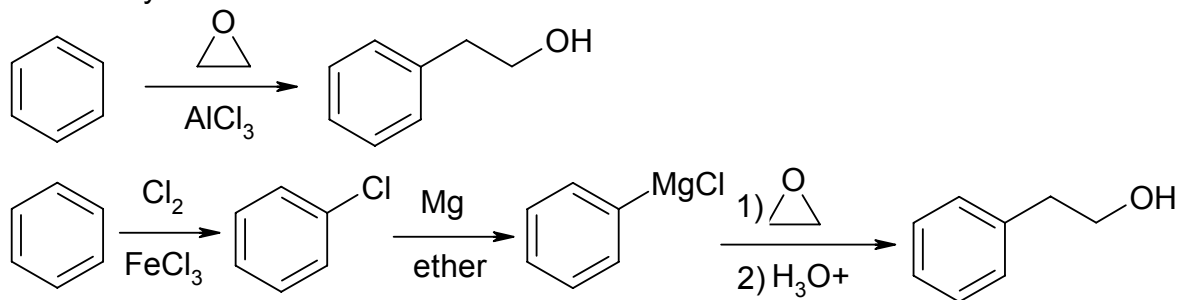
$$\text{The mass percent of Cr in the sample is } \frac{50.00 \cdot 0.4074}{1000 \cdot 0.5000} = 0.0407 = 4.07\%$$

### Problem 10-4

[see Problem 9-5]

**Problem 10-5**

- a) The molecular formula of compound F is  $C_8H_{10}O$ .  
 X = PhCOOH (benzoic acid)  
 Y = PhCH<sub>2</sub>COOH (phenylacetic acid)  
 F is 2-phenylethanol, PhCH<sub>2</sub>CH<sub>2</sub>OH
- b)  $2C_8H_{10}O + 20O_2 \rightarrow 16CO_2 + 10H_2O$   
 $C_6H_5CH_2CH_2OH + [O] \rightarrow C_6H_5CH_2CHO + H_2O$   
 $C_6H_5CH_2CHO + [O] \rightarrow C_6H_5CH_2COOH$
- c) Possible synthetic routes:

**GRADE 11****Problem 11-1**

- a) Air ( $N_2$  and  $O_2$ ), water, methane.  
 $CH_4 = C + 2H_2$   
 $N_2 + 3H_2 = 2NH_3$   
 $4NH_3 + 5O_2 = 4NO + 6H_2O$   
 $2NO + O_2 = 2NO_2$   
 $3NO_2 + H_2O = 2HNO_3 + NO\uparrow$ .
- b) The NO molecule is a radical. The  $O_2$  molecule is also a radical (in fact, a biradical). The reaction between two radicals has a negligible activation barrier.
- c)  $2NO + O_2 = 2NO_2$ .  
 The rate of oxidation is given by the equation  $v = k \cdot [NO]^2 \cdot [O_2]$ .  
 We assume that air is 21% oxygen and 79% nitrogen by volume.  
 Let x be the volume of air that should be added to 1 L of the mixture to achieve the maximum oxidation rate.

$$\text{In the reaction mixture, } [NO] = \frac{a}{1+x} \text{ and } [O_2] = \frac{x}{4.76 \cdot (1+x)}.$$

$$\text{The rate of oxidation is } v = k \cdot \left(\frac{a}{1+x}\right)^2 \cdot \left(\frac{x}{4.76 \cdot (1+x)}\right) = k \cdot \frac{a^2}{4.76} \cdot \frac{x}{(1+x)^3}.$$

At the maximum v, the derivative of v with respect to x is zero:

$$\frac{dv}{dx} = \frac{ka^2}{4.76} \cdot \frac{1-2x}{(1+x)^4} = 0.$$

The solution of this equation is  $x = 0.5$ .

Thus, the initial oxidation rate reaches a maximum if the mixture is combined with air in the ratio 2 : 1.

- d) In order to maintain the maximum possible rate of oxidation, the volume concentration of oxygen in the reaction mixture should be kept at:

$$[O_2] = \frac{x}{4.76 \cdot (1+x)} = \frac{0.5}{4.76 \cdot (1+0.5)} = 0.0700 \text{ or } 7.00\% \text{ by volume.}$$

**Problem 11-2**

a) X is vanadium (V).

A = liquid  $\text{N}_2\text{O}_4$

B = NO

C =  $\text{VO}_2\text{NO}_3$

D =  $\text{Na}_3\text{VO}_4$

E =  $\text{Na}_3\text{VO}_8$

F =  $\text{Na}_3\text{VO}_6$

G =  $\text{VNO}_6$

H =  $\text{VO}(\text{NO}_3)_2$

b)  $\text{V} + 2\text{N}_2\text{O}_4 = \text{VO}_2\text{NO}_3 + 3\text{NO}$

$\text{VO}_2\text{NO}_3 + 4\text{NaOH} = \text{NaNO}_3 + \text{Na}_3\text{VO}_4 + 2\text{H}_2\text{O}$

$\text{VO}_2\text{NO}_3 + 4\text{NaOH} + 2\text{H}_2\text{O}_2 = \text{Na}_3[\text{VO}_2(\text{O}_2)_2] + 4\text{H}_2\text{O} + \text{NaNO}_3$

$\text{VO}_2\text{NO}_3 + 4\text{NaOH} + 4\text{H}_2\text{O}_2 = \text{Na}_3[\text{V}(\text{O}_2)_4] + 6\text{H}_2\text{O} + \text{NaNO}_3$

$\text{VO}_2\text{NO}_3 + \text{H}_2\text{O}_2 = \text{VO}(\text{O}_2)\text{NO}_3 + \text{H}_2\text{O}$

$2\text{VO}_2\text{NO}_3 + \text{H}_2\text{O}_2 + 2\text{HNO}_3 = 2\text{VO}(\text{NO}_3)_2 + \text{O}_2\uparrow + 2\text{H}_2\text{O}$ .

c) Anions of E and F and cations of G contain one or more superoxide groups ( $\text{O}_2^{2-}$ ) in place of the oxygen ions ( $\text{O}^{2-}$ ).

To emphasize this, the chemical formulas of E, F, and G can be rewritten as  $\text{Na}_3[\text{V}(\text{O}_2)_4]$ ,  $\text{Na}_3[\text{VO}_2(\text{O}_2)_2]$ , and  $\text{VO}(\text{O}_2)\text{NO}_3$ , respectively.

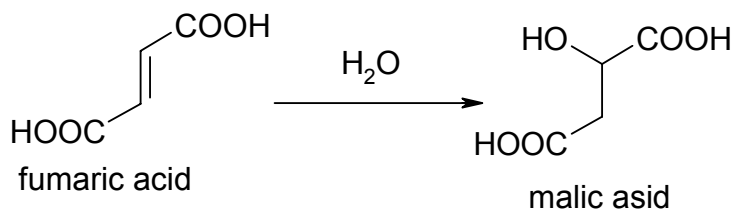
d) The reaction of X and A can be accelerated by adding acetonitrile or ethyl acetate.

These compounds increase the degree of self-ionization:

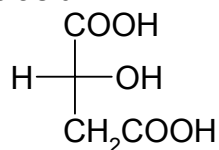
$\text{N}_2\text{O}_4 = \text{NO}^+ + \text{NO}_3^-$ .

**Problem 11-3**

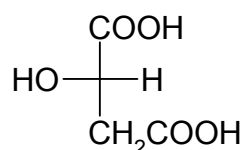
a)



b) Malic acid:

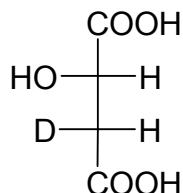


(R)-malic acid

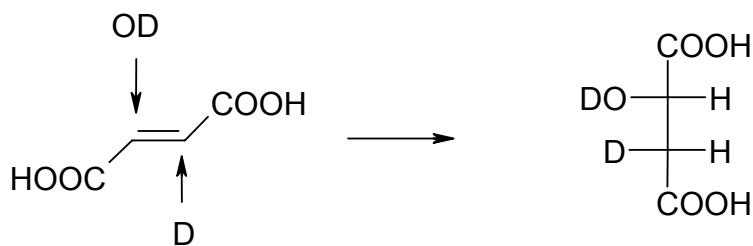


(S)-malic acid

c) The stereochemical formula of (S,R)-3-monodeuteromalic acid:

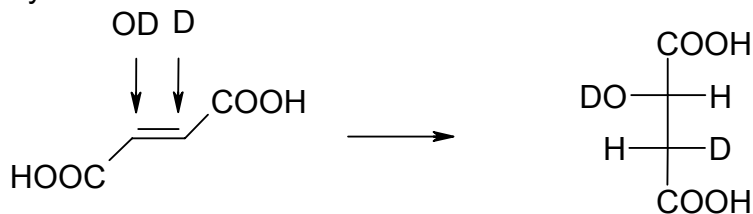


d) Anti-addition:



erythro-

Syn-addition results in a different diastereomer:



threo-

- e) Enzymes are very substrate-specific. Therefore, addition of water to maleic acid in the presence of fumarase would be much slower.

#### Problem 11-4

- a) Let  $x$  be the number of moles of water needed to dilute the oleum.

The initial solution contains  $0.35 \cdot 50000 = 17500$  g or  $\frac{17500}{80} = 218.75$  mol of  $\text{SO}_3$  and  $(50000 - 17500) = 32500$  g of  $\text{H}_2\text{SO}_4$ .

We have the equation  $w(\text{H}_2\text{SO}_4) = \frac{34500 + 193.75 \cdot 98}{50000 + x \cdot 18} = 0.45$ .

The solution is  $x = 3881.2$  mol, i.e.  $3881.2 \cdot 18 = 69681$  g or 69.68 L of water.

- b) The mole fraction of  $\text{SO}_3$  in 35% oleum is  $x_1 = \frac{\frac{35}{80} + \frac{65}{98}}{\frac{35}{80} + \frac{65}{98} + \frac{65}{98}} = 0.624$

The mole fraction of  $\text{SO}_3$  in a 45% solution of  $\text{H}_2\text{SO}_4$  is  $x_2 = \frac{\frac{45}{98}}{\frac{55}{18} + \frac{45}{98} + \frac{45}{98}} = 0.116$ .

The enthalpy of formation of 35% oleum is:

$$\Delta H_1 = -159 \cdot 0.624 + 60 \cdot (0.624)^2 + 251 \cdot (0.624)^3 - 151 \cdot (0.624)^4 = -37.76 \text{ kJ/mol.}$$

The enthalpy of formation of a 45% solution of  $\text{H}_2\text{SO}_4$  is:

$$\Delta H_2 = -159 \cdot 0.116 + 60 \cdot (0.116)^2 + 251 \cdot (0.116)^3 - 151 \cdot (0.116)^4 = -17.27 \text{ kJ/mol.}$$

The enthalpy of the dilution process is:

$$\begin{aligned} \Delta H &= (-17.27) \cdot \left( \frac{17500}{80} + \frac{32500}{80} + \frac{32500}{98} + 3881.2 \right) - (-37.76) \cdot \left( \frac{17500}{80} + \frac{32500}{98} + \frac{32500}{98} \right) \\ &= -48955.8 \text{ kJ} = -48.96 \text{ MJ.} \end{aligned}$$

#### Problem 11-5

- a) 1 mol of the solution contains 0.0200 mol or  $0.0200 \cdot 63 = 1.26$  g of  $\text{HNO}_3$  and 0.980 mol or  $0.980 \cdot 18 = 17.64$  g of  $\text{H}_2\text{O}$ .

The mass fraction of  $\text{HNO}_3$  in this solution is  $\frac{1.26}{1.26 + 17.64} = 0.0667$  or 6.67%.

The mass of the solution is  $(1.26 + 17.64) = 18.90$  g



and its volume is  $\frac{18.90}{1.035} = 18.26$  mL.

The molar concentration of  $\text{HNO}_3$  is  $\frac{0.0200}{0.01826} = 1.095$  mol/L.

- b) The water vapor pressure is  $101325 \cdot \frac{33.7}{760} = 4493$  Pa = 4.49 kPa.

The pressure of  $\text{H}_2$  is  $(98.3 - 4.49) = 93.81$  kPa.

The amount of hydrogen gas released is  $\frac{PV}{RT} = \frac{93.81 \cdot 2.290}{8.314 \cdot 304} = 0.0850$  mol.

The initial sample contained 0.0850 mol or  $0.0850 \cdot 137 = 11.65$  g of Ba.

The mass percent of Ba in the sample is  $\frac{11.65}{13.96} = 0.835 = 83.5\%$ .

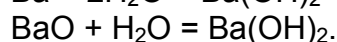
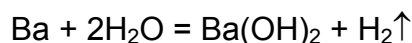
- c) The concentration of  $\text{H}^+$  ions in the final solution is  $10^{-1.38} = 0.0417$  mol/L.  
100.0 mL of this solution contains  $41.7 \cdot 0.100 = 4.17$  mmol of  $\text{HNO}_3$ .  
The amount of  $\text{HNO}_3$  added to the sample is  $15.00 \cdot 1.095 = 16.43$  mmol.  
Of these,  $(16.43 - 4.17) = 12.26$  mmol reacted with  $\text{Ba}(\text{OH})_2$ .

Therefore, the 25.00 mL aliquot of the filtrate contained  $\frac{12.26}{2} = 6.13$  mmol of

$\text{Ba}(\text{OH})_2$ . The molar concentration of  $\text{Ba}(\text{OH})_2$  in this aliquot is

$\frac{6.13}{0.025} = 245.2$  mmol/L, and the mass percent is  $\frac{6.13 \cdot 171}{25 \cdot 1.140 \cdot 1000} = 0.0378 = 3.78\%$ .

The initial Ba/BaO sample contained  $\frac{13.96 - 11.65}{153} = 0.0150$  mol of BaO.



The reaction of the sample with water produced  $(0.0850 + 0.0150) = 0.100$  mol of  $\text{Ba}(\text{OH})_2$  and 0.0850 mol of hydrogen gas.

The precipitate is  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .

The mass of the solution before the precipitation of barium hydroxide is  $(100.0 + 13.96 - 0.0850 \cdot 2) = 113.8$  g.

Let  $x$  be the number of moles of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  in the precipitate.

Then the mass of the filtrate is  $(113.8 - x \cdot 315.5)$  g.

The filtrate contains  $(0.100 - x)$  mol or  $(0.100 - x) \cdot 171$  g of  $\text{Ba}(\text{OH})_2$ .

The mass fraction of  $\text{Ba}(\text{OH})_2$  in the filtrate is 0.0378.

$$\frac{(0.100 - x) \cdot 171}{(113.8 - x \cdot 315.5)} = 0.0378.$$

Solving this equation we obtain  $x = 0.0805$  mol.

Thus, the mass of the precipitate is  $0.0805 \cdot 315.5 = 25.40$  g.

- d) The filtrate is a saturated solution of  $\text{Ba}(\text{OH})_2$  in which  $[\text{Ba}^{2+}] = 0.2452$  mol/L and  $[\text{OH}^-] = 0.2452 \cdot 2 = 0.4904$  mol/L.

The solubility product is  $K_{\text{sp}}(\text{Ba}(\text{OH})_2) = c(\text{Ba}^{2+}) \cdot c^2(\text{OH}^-) = 0.2452 \cdot (0.4904)^2 = 5.90 \cdot 10^{-2}$ .

Suppose that 1 L of 0.200 M KOH dissolves  $y$  mol of  $\text{Ba}(\text{OH})_2$ .

In the resulting solution,  $[\text{Ba}^{2+}] = y$  mol/L,  $[\text{OH}^-] = (0.200 + 2y)$  mol/L.

Using the value of  $K_{\text{sp}}(\text{Ba}(\text{OH})_2)$ , we have the equation

$$5.90 \cdot 10^{-2} = c(\text{Ba}^{2+}) \cdot c^2(\text{OH}^-) = y \cdot (0.200 + y \cdot 2)^2,$$

whose solution is  $y = 0.1835$  mol/L.

In order to dissolve 0.0805 mol of  $\text{Ba}(\text{OH})_2$  one needs  $\frac{0.0805}{0.1835} = 0.439$  L or 439 mL of 0.200 M KOH.