

## GRADE 9

### Problem 9-1

The first step in the commercial production of concentrated sulfuric acid involves roasting of a sulfide ore such as pyrite in oxygen-enriched air. The resulting sulfur dioxide is oxidized in the presence of a catalyst and the oxidation products are dissolved in dilute sulfuric acid. The residual gas is usually released into the atmosphere. The maximum allowable concentration of SO<sub>2</sub> in air is 0.050 mg/m<sup>3</sup>.

- a) Write a chemical equation representing the roasting of pyrite.
- b) Calculate the volume of sulfur dioxide (at 600 K and 108 kPa) generated by the oxidation of 100 metric tonnes of a pyrite ore that is 78% FeS<sub>2</sub>, assuming that 5.0% of the sulfur and 8.0% of the iron (by mass) remain unreacted.
- c) Calculate the volume (at 0 °C and 1 atm) of the oxygen-enriched air (60% O<sub>2</sub> by volume) required in part b) given that the residual gas is 6.0% O<sub>2</sub> by volume.
- d) Calculate the mass of sulfur dioxide released into the atmosphere per each 100 tonnes of the ore when the concentration of SO<sub>2</sub> in the residual gas exceeds the maximum allowable concentration by a factor of 5.

### Problem 9-2

The acidity of a solution is commonly reported in terms of the pH value which is defined as the negative decimal logarithm of the molar concentration of H<sup>+</sup> ions, that is,  $\text{pH} = -\log c(\text{H}^+)$ , where  $c(\text{H}^+)$  is expressed in mol/L. In some cases, calculation of the pH value should take into account the self-ionization of water,  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ . At a given temperature and pressure, the product of the molar concentrations of H<sup>+</sup> and OH<sup>-</sup> is a constant. This constant is called the ion product of water and is symbolized by  $K_w$ . The corresponding equation is  $K_w = c(\text{H}^+)c(\text{OH}^-)$ . At standard ambient temperature and pressure (i.e., 298.15 K and 100 kPa),  $K_w = 1.0 \times 10^{-14}$ . Use this value of  $K_w$  when answering the following questions.

- a) Calculate the pH of  $1.0 \times 10^{-1}$  M and  $1.0 \times 10^{-7}$  M aqueous NaOH.
- b) The concentration of OH<sup>-</sup> ions in a certain aqueous solution of NaOH is twice the analytical concentration of NaOH. Is this possible? Show your reasoning.
- c) Ammonia and urea are examples of weak bases. Weak bases partially dissociate in water according to the equation:  $\text{X} + \text{H}_2\text{O} \rightleftharpoons \text{HX}^+ + \text{OH}^-$ . The equilibrium constants for this dissociation are  $1.8 \times 10^{-5}$  for ammonia and  $1.5 \times 10^{-14}$  for urea. Calculate the pH values of 0.10 M aqueous NH<sub>3</sub> and 0.10 M aqueous urea.

### Problem 9-3

Complete combustion of one volume of a gas mixture consisting of pentane and an unknown hydrocarbon requires 6.5 volumes of oxygen gas (measured at the same temperature and pressure). The total mass of carbon atoms in the original mixture is 17/3 times greater than the total mass of all hydrogen atoms. Assume for simplicity that atomic masses have integer values.

- a) Draw all plausible structures for the compounds that may have been present in the original mixture. Name each compound. Show your reasoning.
- b) Narrow down the list drawn up in part a) given that the mixture does not react with aqueous bromine.
- c) Identify the hydrocarbons present in the original mixture given that its <sup>1</sup>H-NMR

spectrum contains just two peaks.

#### Problem 9-4

An acid halide is a compound that reacts with water to produce an acid and a hydrogen halide. An example of an acid halide is phosphoryl chloride  $\text{POCl}_3$ , a compound that is hydrolyzed by water to give hydrogen chloride and phosphoric acid. Acid halides are said to be mixed if they contain atoms of different halogens.

An unknown compound **A** is a mixed acid halide. The molecular formula of **A** is  $\text{SO}_x\text{ClX}_y$ , where  $x$  and  $y$  are both positive. When a sample of **A** is dissolved in aqueous barium hydroxide, a white precipitate is formed. When an identical sample of **A** is reacted with an excess of aqueous  $\text{AgNO}_3$ , another precipitate is formed whose mass is 1.419 times greater than that of the first precipitate.

- Determine the composition of **A** and write balanced chemical equations for the reactions of **A** with aqueous barium hydroxide and silver nitrate.
- What is the geometric structure of **A**?
- What is the geometric structure of other possible compounds of the general formula  $\text{SO}_x\text{ClX}_y$  ( $x > 0$ ,  $y > 0$ )?
- Propose a synthesis of **A** starting from commercial reagents.

#### Problem 9-5

Suppose you have at your disposal the following reagents: iron, aluminum, concentrated hydrochloric acid, concentrated nitric acid, potassium hydroxide, and water. The laboratory is also stocked with standard chemical equipment.

- How would you prepare 5 salts containing iron and 5 salts containing aluminum? Write balanced chemical equations for the preparation of these 10 salts and specify conditions under which these reactions occur.
- Give an example of a salt of iron in which iron is found in the highest possible oxidation state. Name this compound.

### GRADE 10

#### Problem 10-1

See Problem 9-1.

#### Problem 10-2

Albertus Magnus in his treatise *Libellus de Alchimia* laid down basic precepts of the alchemical art. The sixth precept is as follows: "All vessels in which medicines may be put, either waters or oils, whether over the fire or not, should be of glass or glazed. For, if acid waters are placed in a copper vessel, they will turn green; if placed in an iron or lead one, they will be blackened and corrupted; if placed in earthenware, the walls will be \_\_\_\_\_ and all will be lost".

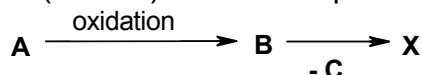
- Write chemical equations to represent the reactions that occur when "acid waters" are placed in a copper, iron, or lead vessel. Comment on your answers.
- What happens if "acid waters" are placed in earthenware? (Fill in the blank).
- Albertus Magnus also recommended glazing earthenware before use: "Dilute the liquor from beer or wine fermentation with water in the proportion of ten to one, then add as much minium as you wish, mix well, and smear the vessel with a brush or with the hand, and let dry: then place it in the furnace... Fire slowly at first for the space of an hour, then increase the fire until you see the minium flow like wax, then permit the furnace to cool, open it and take out the well-glazed

vessel." Write chemical equations for the reactions that occur in the above process given that minium, or red lead, is a binary compound.

d) What is the function of the glaze coating?

### Problem 10-3

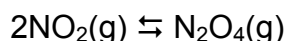
In living organisms, amino acids are sometimes interconverted into one another. For example, a certain standard amino acid **A** (29.74% C, 5.82% H and 26.47% S by mass) is converted to amino acid **X** (taurine) in a two-step reaction:



- Determine the molecular formula of **A** and draw its structure given that **A** readily undergoes oxidative dimerization.
- Identify the other lettered compounds given that: **C** is a triatomic gas; the number of carbon atoms in **A** and **B** is the same; **X** is 38.35% oxygen by mass.
- Which amino acid has a higher isoelectric point, **A** and **X**?
- How many distinct dipeptides can one prepare from amino acids **A** and **X**? Draw structural formulas for all possible products.
- Draw a Fischer projection for the naturally occurring form of amino acid **A**.

### Problem 10-4

Nitrogen dioxide is usually found in equilibrium with its dimer:

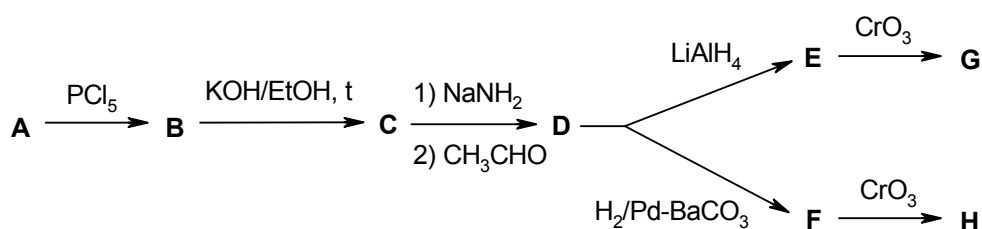


At 25.0 °C and 1.00 atm, the equilibrium mixture has a density of 3.16 g/L.

- Determine the mole fractions of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in the equilibrium mixture under the stated conditions.
- Write down an equilibrium-constant expression for the dimerization of  $\text{NO}_2$  in terms of partial pressures. What are the units of the equilibrium constant?
- Calculate the equilibrium constant for a  $\text{NO}_2/\text{N}_2\text{O}_4$  mixture at 25.0 °C.
- When a 1.206 g sample of anhydrous nitrate of a certain divalent *d*-metal is heated in air, a mixture of gases is produced whose volume is 239 mL at 25 °C and 1.0 atm. Identify the *d*-metal and write a chemical equation to represent the thermal decomposition of the nitrate.

### Problem 10-5

Vapors of certain ketone **A** have a density of 4.09 g/L at 25 °C. The  $^1\text{H-NMR}$  spectrum of **A** reveals that this compounds contains only two types of hydrogen atoms. Compound **A** has been used as the starting material in the following reaction sequence:



Compounds **E** and **F**, as well as **G** and **H**, are related to each other as stereoisomers.

- Identify compounds **A** through **H** and draw their structural formulas.
- Comments on the regioselectivity of the transformations of **D** into **E** and **F**.
- Propose a synthesis of compound **A** starting from acetone and using any inorganic reagents.

## GRADE 11

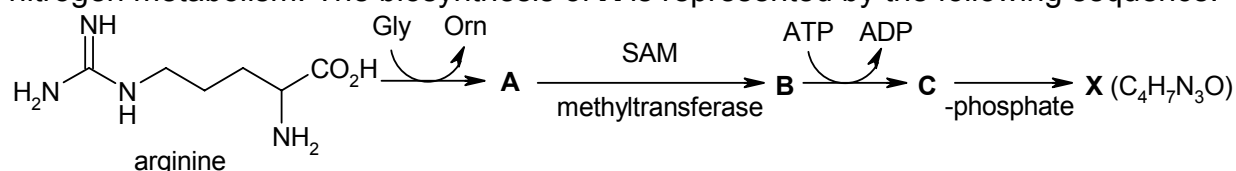
### Problem 11-1

See Problem 9-1.

### Problem 11-2

Two renowned 19th-century German scientists whose first names are Justus and Friedrich maintained extensive correspondence in which they often discussed their experiments. In one letter, Justus proudly wrote to Friedrich, “*I have processed an old horse in effort to isolate enough **X** to complete my investigation. In total, I have used 102 chickens and about 300 pounds of horse meat...*” In response, Friedrich wrote, “*...I vividly imagine those fetid extracts in your laboratory and the soup reeking of horse...*”

Compound **X** contains a five-member carbon ring and is an important product of nitrogen metabolism. The biosynthesis of **X** is represented by the following sequence:



Compound **X** is excreted in urine. The amount of **X** present in the body is proportional to the mass of muscle tissue.

- Draw structural formulas for compounds **A** through **X** and for each of the following amino acids: Gly (glycine), Orn (ornithine or 2,5-diaminopentanoic acid), and SAM (S-adenosyl methionine). *Hint*: SAM acts as a methylating agent on the nitrogen nearest to the carboxylic group.
- Estimate the total mass of compound **X** obtained by Justus assuming that the concentration of its precursor **C** in the muscle tissue is 20 mmol/dm<sup>3</sup> and that the total amount of **X** does not exceed 2% of the amount of **C**. Assume that 1 pound is equal to 0.4 kg.
- What is the common name of compound **X**?
- Justus and Friedrich are also known as proponents of the theory of “compound radicals”. Based on their experiments with bitter almond oil, they concluded that a certain group of atoms is transferred unchanged from one compound to another. Using the contemporary chemical notation, they represented bitter almond oil as (14C + 10H + 2O) + 2H. Mild oxidation of the oil yielded a compound which they represented by the formula (14C + 10H + 2O) + O, while the oxidation in the presence of chlorine gave (14C + 10H + 2O) + 2H → (14C + 10H + 2O) + 2Cl. Identify the radical discovered by Justus and Friedrich. Draw structural formulas for the compounds involved in the above transformations.
- What are the last names of Justus and Friedrich?

### Problem 11-3

The Dumas method is a classic technique for determining the vapor density of a volatile compound. In this method, a liquid sample is allowed to vaporize into a glass

bulb that is kept at a constant temperature. The bulb is then sealed, cooled to room temperature, and weighed. The mass of the sample is found as the difference of mass measurements. Knowing the mass of the sample allows one to determine the vapor density at a given temperature and pressure.

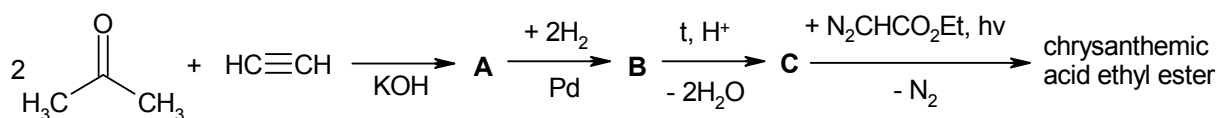
In a study of the dimerization of vaporized acetic acid by the Dumas method, the mass of the substance contained in a 20.00 mL bulb at 160 °C and 1 atm was found to be 40.7 mg. In a second experiment conducted at 200 °C and 1 atm, it was 33.4 mg.

- Calculate the equilibrium constants (in terms of mole fractions) for the molecular dimerization of vaporized acetic acid at 160 °C and at 200 °C.
- What is the mole fraction of the dimer in the vapor at 160 °C and 200 °C?
- Calculate the enthalpy of dimerization of vaporized acetic acid using the equation  $\ln K = \text{const} - \Delta H/RT$ .
- Draw a structure for the acetic acid dimer and rationalize the value of the enthalpy of dimerization obtained in part c).
- Which solvent, water or benzene, would favor dimerization of acetic acid in solution? Give your reasoning.
- Ionization constants of most carboxylic acids in aqueous solutions are similar. Which of the two solvents, pyridine or propionic acid, would you use for titrating a mixture of HCOOH and CH<sub>3</sub>COOH? Give your reasoning.

#### Problem 11-4

Chrysanthemic acid is a commercially significant derivative of cyclopropyl carboxylic acid. Chrysanthemic acid esters, called pyrethrins, occur naturally in certain parts of the plant pyrethrum. Pyrethrins have potent insecticidal activity but are generally harmless to humans and mammals.

An elemental analysis of chrysanthemic acid is 71.39% carbon and 9.59% hydrogen by mass. Titration of a 123.5 mg sample of the acid requires 16.85 mL of 0.0436 M NaOH. Chrysanthemic acid is produced commercially in the form of its ethyl ester starting from acetone and acetylene:



- Elucidate the molecular formula of chrysanthemic acid.
- Identify compounds **A**, **B**, and **C** in the above reaction sequence. Draw structural formulas for these compounds and provide their names.
- Draw the stereoisomers of chrysanthemic acid and indicate their stereochemical relation to one another.

#### Problem 11-5

An unknown acid **A** can be prepared by nitration of phenol under appropriate conditions. **A** is a yellowish crystalline compound that is less than 40% carbon by mass. Titration of a 229 mg sample of **A** requires 19.52 mL of 0.05124 M KOH.

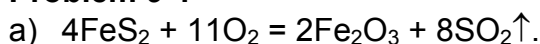
- Determine the molecular formula of acid **A** and draw its structure.
- What is the IUPAC name of compound **A**? What is its common name?
- Compound **A** is partially soluble in water. In solution, it behaves as a weak acid,

- although a stronger one than phenol. Account for these properties of **A**.
- d) Compound **A** explodes violently under certain conditions. Write a chemical equation to represent this reaction.

## SOLUTIONS

### GRADE 9

#### Problem 9-1



b)  $M(\text{FeS}_2) = 120 \text{ g/mol}$ .

The amount of  $\text{FeS}_2$  contained in 100 metric tonnes of the pyrite ore is

$$100 \text{ t} \times 0.78 = 78 \text{ t} = 78 \cdot 10^6 \text{ g, or } \frac{78 \cdot 10^6}{120} = 65 \times 10^4 \text{ mol.}$$

Since 8% of the iron and 5% of the sulfur remain unreacted, the amounts of sulfur and iron that have been oxidized are:

$$65 \times 10^4 (1.0 - 0.08) = 59.8 \times 10^4 \text{ mol of Fe;}$$

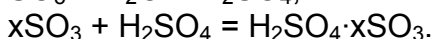
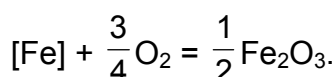
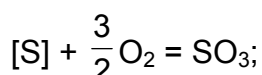
$$2 \times 65 \times 10^4 (1.0 - 0.05) = 123.5 \times 10^4 \text{ mol of S.}$$

The amount of  $\text{SO}_2$  produced by the oxidation of the ore is  $123.5 \times 10^4$  mol.

The volume of this amount of sulfur dioxide at 600 K and 108 kPa is

$$\frac{nRT}{p} = \frac{(123.5 \times 10^4)(8.314)(600)}{108} = 57.0 \times 10^6 \text{ L} = 57.0 \times 10^3 \text{ m}^3.$$

- c) The reactions are:



We know from part b) that the 100 tonne batch of the ore contains  $59.8 \times 10^4$  mol of Fe and  $123.5 \times 10^4$  mol of S. According to the chemical equations, oxidation of these amounts of sulfur and iron requires

$$\left(\frac{3}{4} \cdot 59.8 \times 10^4 + \frac{3}{2} \times 123.5 \times 10^4\right) = 230 \times 10^4 \text{ mol of O}_2.$$

Let the volume of oxygen-enriched air required for the roasting of 100 tonnes of the ore be  $x$  L. The amount of  $\text{N}_2$  in the initial gas mixture ( $0.4x$ ) does not change in the course of the reaction, whereas the amount of  $\text{O}_2$  decreases. The residual gas is 94.0%  $\text{N}_2$  by volume, while the remaining 6.0% is  $\text{O}_2$ . The total volume of

the residual gas is  $\frac{0.4x}{0.940} = 0.4255x$  L, of which  $0.4x$  L is  $\text{N}_2$  and the rest is oxygen.

The volume of  $\text{O}_2$  in the residual gas is, therefore,  $0.4255x - 0.4x = 0.0255x$  liters.

The volume of the oxygen gas reacted with pyrite is  $0.6x - 0.0255x = 0.5745x$ .

On the other hand, we know that the volume of  $\text{O}_2$  required for the roasting is  $(22.4 \text{ L/mol})(230 \times 10^4 \text{ mol}) = 5.152 \times 10^7 \text{ L of O}_2$ .

Thus, we have the equation  $5.152 \times 10^7 = 0.5745x$ , whose solution is

$$x = \frac{5.152 \times 10^7}{0.5745} = 8.97 \times 10^7 \text{ L} = 89.7 \times 10^3 \text{ m}^3 \text{ of oxygen-enriched air.}$$

- d) The volume of the residual gas released into the atmosphere is

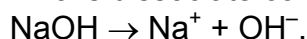
$$42.55 \times \frac{230 \times 10^4}{2.564} = 38.17 \times 10^6 \text{ L} = 38.17 \times 10^3 \text{ m}^3.$$

The concentration of SO<sub>2</sub> in this mixture is  $0.050 \times 5 = 0.25 \text{ mg/m}^3$ .

Thus, the mass of SO<sub>2</sub> released into the atmosphere per 100 tonnes of the ore is  $(38.17 \times 10^3)(0.25) = 9.54 \times 10^3 \text{ mg} = 9.54 \text{ g}$ .

### Problem 9-2

- a) Alkalis dissociate completely in water:



Unless the solution is extremely dilute, the total concentration of hydroxide ions will be essentially the same as the analytical concentration of NaOH. By taking the logarithm of both sides of the equation  $[\text{H}^+][\text{OH}^-] = 10 \times 10^{-14}$  we obtain

$$\text{pH} = -\log[\text{H}^+] = -\log \frac{1.0 \times 10^{-14}}{[\text{OH}^-]} = 14 + \log[\text{OH}^-].$$

The pH value of 0.10 M NaOH is 13.00.

If the NaOH solution is extremely dilute, we must allow for the self-ionization of water. The charge balance condition is

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] \quad \text{or} \quad 1.0 \times 10^{-7} + [\text{H}^+] = [\text{OH}^-].$$

Substitution of this result into the definition of the ion product of water yields

$$[\text{H}^+](1.0 \times 10^{-7} + [\text{H}^+]) = 1.0 \times 10^{-14}.$$

Solving this equation for [H] we obtain  $[\text{H}^+] = 6.2 \times 10^{-8} \text{ M}$ , or  $\text{pH} = 7.21$ .

- b) Yes, this is possible. Let this analytical concentration of NaOH in the solution be  $c$  mol/L. Then, according to the problem statement,  $[\text{OH}^-] = 2c$ . The charge balance condition and the ionic product condition give us two more equations,  $[\text{H}^+] + c = 2c$  and  $[\text{H}^+](2c) = K_w = 1.0 \times 10^{-14}$ .

Simultaneous solution of these equations yields  $c = 7.1 \times 10^{-8} \text{ M}$ .

- c) The dissociation of ammonia in water is represented by the following equation:  
 $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ ,

$$\text{The equilibrium constant is } K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

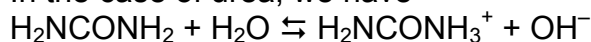
Let the equilibrium concentration of hydroxide ions in 0.1 M ammonia be  $x$  mol/L.

$$\text{We have } 1.8 \times 10^{-5} = \frac{x \cdot x}{0.10 - x}.$$

The root of this equation is  $x = 1.3 \times 10^{-3}$ .

Thus,  $[\text{OH}^-] = 1.3 \times 10^{-3} \text{ mol/L}$  and  $\text{pH} = 11.12$ .

In the case of urea, we have



$$\text{and } K = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = 1.5 \times 10^{-14}, \text{ where B stands for urea.}$$

Let the equilibrium concentration of hydroxide ions in a 0.1 M solution of urea be  $x$  mol/L. Using the above dissociation-constant expression, we write

$$1.5 \times 10^{-14} = \frac{x \cdot x}{0.10 - x}, \text{ from which } x = 3.9 \times 10^{-8}.$$

Thus,  $[\text{OH}^-] = 3.9 \times 10^{-8}$  mol/L and  $\text{pH} = 6.6$ . This result is physically nonsensical because it implies that a solution of a weak base is acidic. The error has crept in when we did not account for the self-ionization of water. The correct concentration of hydroxide ions can be obtained by solving the following system of equations:

$$[\text{BH}^+][\text{OH}^-] = 1.5 \times 10^{-14}[\text{B}]; \quad (1)$$

$$[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}; \quad (2)$$

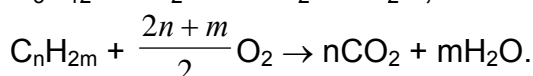
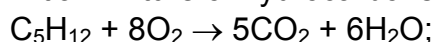
$$[\text{H}^+] + [\text{BH}^+] = [\text{OH}^-] \text{ (charge balance)}; \quad (3)$$

$$[\text{BH}^+] + [\text{B}] = 0.10 \text{ (material balance)}. \quad (4)$$

The simplest way of solving this system of equations is to express  $[\text{H}^+]$  and  $[\text{BH}^+]$  in terms of  $[\text{OH}^-]$  from Eqs. (1), (2), (4) and substitute the resulting expressions into Eq. (3). This gives  $[\text{OH}^-] = 1.1 \times 10^{-7}$  mol/L and  $\text{pH} = 14 + \log(1.1 \times 10^{-7}) = 7.03$ .

### Problem 9-3

- a) Let the molecular formula of the unknown hydrocarbon be  $\text{C}_n\text{H}_{2m}$ . Combustion of the initial mixture of hydrocarbons is represented by the following equations:



$$M(\text{C}_5\text{H}_{12}) = 72 \text{ g/mol}; \quad M(\text{C}_n\text{H}_{2m}) = (12n + 2m) \text{ g/mol}; \quad M(\text{CO}_2) = 44 \text{ g/mol}.$$

Suppose the mole ratio of pentane to the unknown hydrocarbon in the initial mixture is  $1 : x$ . Given that the volume of  $\text{O}_2$  is 6.5 times greater than the volume of the initial

hydrocarbon mixture, we write  $\frac{8 + x \cdot \frac{2n+m}{2}}{1+x} = 6.5$ .

From the mass ratio of carbon atoms to hydrogen atoms we find the mass fraction of carbon in the mixture,  $\frac{17}{17+3} = 0.85$ .

On the other hand, based on the molecular formulas of pentane and the unknown hydrocarbon, we can write:  $0.85 = \frac{12 \cdot (5 + x \cdot n)}{72 + x \cdot (12 \cdot n + 2 \cdot m)}$ .

Combining these two equations and eliminating  $x$  we obtain:  $m = 2n - 4$ .

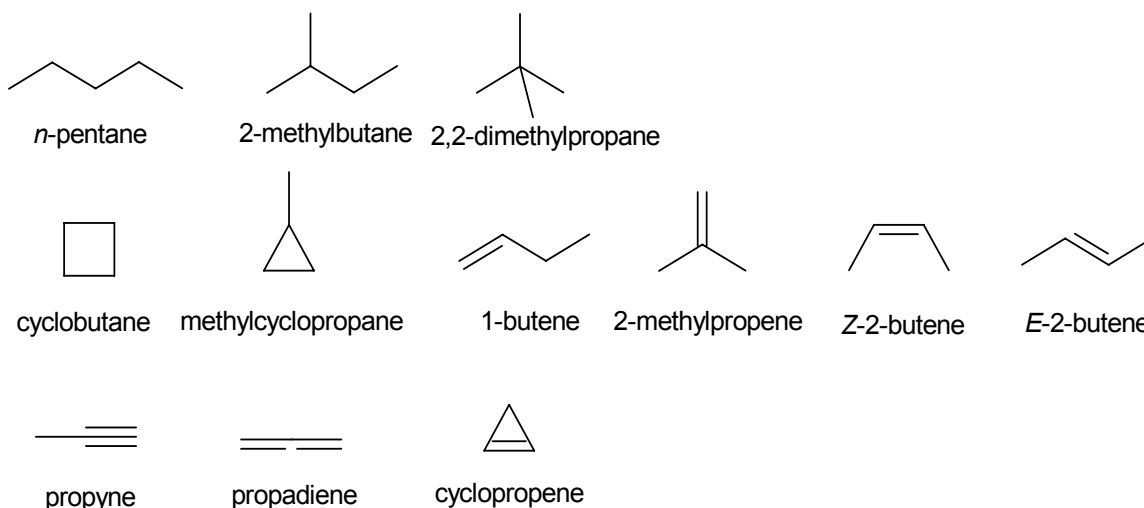
Since the unknown compound is a hydrocarbon, it contains at least two hydrogen atoms ( $m=1$ ), which requires that  $n \geq 3$ . On the other hand,  $2m$  cannot exceed the number of H atoms in the corresponding alkane ( $2n+2$ ), which means that  $m \leq n+1$ .

The equation  $m = 2n - 4$  together with the inequality  $m \leq n + 1$  imply that  $n \leq 5$ .

Thus, the molecular formula of the unknown hydrocarbon is  $\text{C}_3\text{H}_4$ ,  $\text{C}_4\text{H}_8$ , or  $\text{C}_5\text{H}_{12}$ .

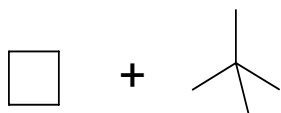
The formula  $\text{C}_5\text{H}_{12}$  can be ruled out immediately because it is inconsistent with the known ratio of masses of carbon to hydrogen. The hydrocarbons that could have been present in the initial mixture are as follows:





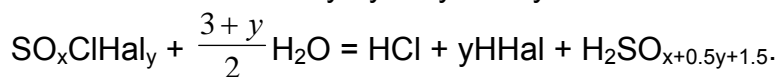
Cyclopropene is unstable and, therefore, can be also ruled out.

- b) The fact that the mixture does not react with aqueous bromine suggests that the unknown hydrocarbon contains neither multiple bonds nor a 3-member carbon ring. This leaves only one possibility: the unknown hydrocarbon is cyclobutane.
- c) The fact that the proton NMR spectrum of the mixture consists of two peaks suggests that each hydrocarbon contains only equivalent hydrogen atoms. This is possible only if the other compound (a pentane isomer) is neopentane:



#### Problem 9-4

- a) Acid halides are readily hydrolyzed by water:



In the first experiment, the precipitate contains barium sulfate or barium sulfite. In the second experiment, the precipitate contains AgCl and an unknown silver halide. The unknown halogen cannot be fluorine because the mass of the Ag-containing precipitate is greater than the mass of the Ba-containing precipitate, which is impossible considering that AgF is readily soluble in water. Therefore, Hal=Br or I. Since the number of moles of the first precipitate is equal to the number of moles of the second precipitate, we write

$$\frac{m(\text{precipitate 2})}{M(\text{AgCl}) + y \cdot M(\text{AgHal})} = \frac{m(\text{precipitate 1})}{M(\text{BaSO}_{\frac{2x+y+3}{2}})}$$

This gives:

$$1.419 = \frac{m(\text{precipitate 2})}{m(\text{precipitate 1})} = \frac{143.3 + y(107.9 + M(\text{Hal}))}{137.3 + 32.1 + 16(x + 0.5y + 1.5)}$$

and

$$M(\text{Hal}) = \frac{131.1 + 22.7x - 96.5y}{y} \text{ g/mol.}$$

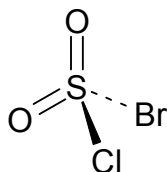
By analyzing all possible oxidation states of the atoms in  $\text{SO}_x\text{ClHal}_y$ , we conclude that  $x$  is either 1 or 2, while  $y$  is either 1 or 3. By trial and error we find that  $x = 2$  and  $y = 1$ , so  $M(\text{Hal}) = 79.9 \text{ g/mol}$ . Hence, Hal=Br and **A** is  $\text{SO}_2\text{ClBr}$ .

The equations for the formation of the precipitates are as follows:

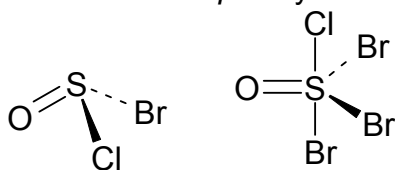




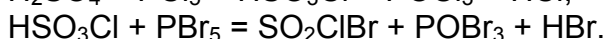
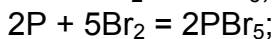
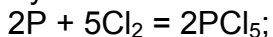
- b) The sulfur atom in  $\text{SO}_2\text{ClBr}$  forms  $sp^3$ -hybrid orbitals, so the molecule is tetrahedral:



- c) The other compounds that have the general formula  $\text{SO}_x\text{ClBr}_y$  with  $x > 0$  and  $y > 0$  are  $\text{SOClBr}$  and  $\text{SOClBr}_3$ . The  $\text{SOClBr}$  molecule is pyramidal (because the S atom forms  $sp^3$ -hybrid orbitals), whereas  $\text{SOClBr}_3$  has a trigonal pyramidal geometry (the S atom forms  $sp^3d$ -hybrid orbitals):

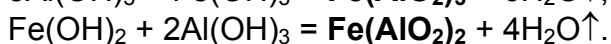
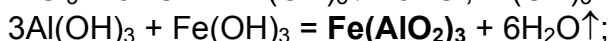
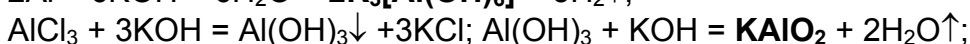
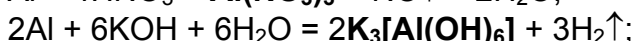
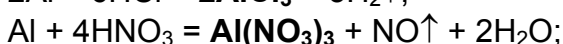
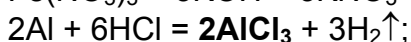
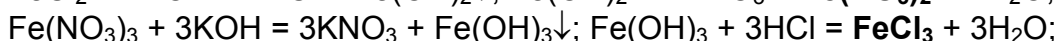
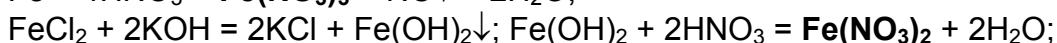


- d) Synthesis of **A**:



### Problem 9-5

- a) An acceptable answer is below (the target compounds are in bold):



- b) The highest possible oxidation state of iron is +6. It occurs in ferrates, salts of ferric acid  $\text{H}_2\text{FeO}_4$  (which is not known to exist in the free state). An example is potassium ferrate(VI),  $\text{K}_2\text{FeO}_4$ .

## GRADE 10

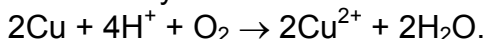
### Problem 10-1

See Problem 9-1.

### Problem 10-2

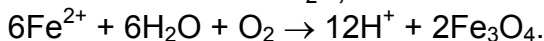
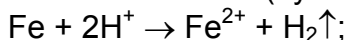
- a) In the presence of an acid, metals are oxidized by air oxygen. This process is better known as corrosion. When speaking of "corruption" of the vessels, Albertus Magnus

almost certainly refers to corrosion. In the case of copper, this process can be represented by the reaction

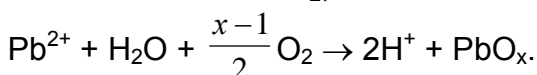
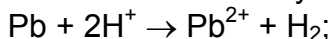


The expression “acid waters” refers to vinegar, so the green substance is malachite or copper acetate:  $\text{Cu}(\text{OH})_2 \cdot x\text{CuCO}_3$  or  $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot y\text{H}_2\text{O}$ .

Iron corrodes relatively fast in the presence of an acid. The black substance could have been one of (hydrated) iron oxides:



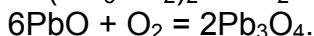
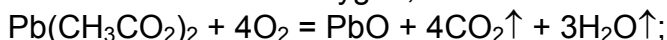
Oxidation is also responsible for the “corruption” of lead. Compared with iron, lead corrodes more slowly. The reactions are



- b) Earthenware is porous, so its walls will be *penetrated* (this is the missing word) by “acid waters”.
- c) The chemical formula of minium (red lead) is  $\text{Pb}_3\text{O}_4$ . When minium is mixed with the “liquor from beer or wine fermentation” (i.e., vinegar), lead acetate (“white lead”) is formed:



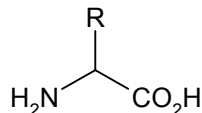
When heated in the furnace, lead acetate decomposes to give lead(II) oxide. When the latter reacts with oxygen, red lead is recovered in the form of a glaze coating:



- d) To prevent the loss of liquid through porous walls. The minium glaze can also act as a chemically inert protective coating.

### Problem 10-3

- a) Standard amino acids have the general formula

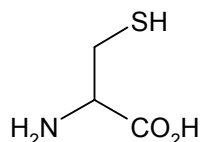


The element not mentioned in the elemental analysis of **A** must be oxygen. Then

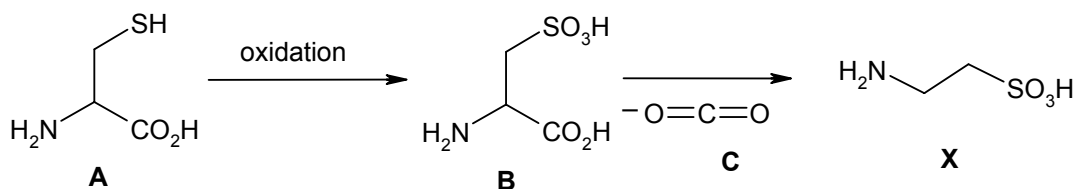
$$\text{C} : \text{H} : \text{S} : \text{N} : \text{O} = \frac{29.74}{12.01} : \frac{5.82}{1.01} : \frac{26.47}{32.07} : \frac{w}{14.01} : \frac{37.97 - w}{16.00}$$

$$= 2.48 : 5.76 : 0.825 : \frac{w}{14.01} : \frac{37.97 - w}{16.00} = 3 : 7 : 1 : 0.0865w : (2.88 - 0.0758w).$$

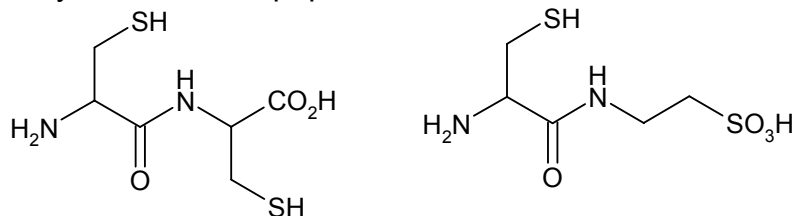
All the numbers in this ratio become integers if  $w = 11.86\%$ . Thus, the molecular formula of **A** is  $\text{C}_3\text{H}_7\text{NO}_2\text{S}$ . Amino acid **A** is cysteine:



- b) Since the number of carbon atoms in **A** and **B** is the same, oxidation of **A** does not involve dimerization. Furthermore, the oxidized functional group is not  $\text{NH}_2$  because otherwise compound **B** would no longer be an amino acid. This suggests that **B** is a sulfonic acid which yields **X** by decarboxylation (**C** is  $\text{CO}_2$ ):

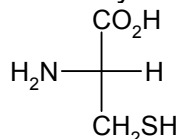


- c) Sulfonic acids are stronger than carboxylic acids. Therefore, the isoelectric point of taurine occurs at a lower pH than that of cysteine:  $pI(\mathbf{X}) < pI(\mathbf{A})$ .
- d) Only two distinct dipeptides can be obtained from taurine and cysteine:



The molecules that are formed by condensation via the  $\text{SO}_3\text{H}$  and  $\text{NH}_2$  groups are not peptides (they are sulfamides).

- e) Naturally occurring cysteine has the L-configuration:



### Problem 10-4

- a) The average molecular mass of the gas mixture is found from the vapor density:

$$M = \frac{\rho \cdot R \cdot T}{p} = \frac{3.16 \times 8.314 \times 298}{101.3} = 77.3 \text{ g/mol};$$

$$M(\text{NO}_2) = 46.0 \text{ g/mol}, M(\text{N}_2\text{O}_4) = 92.0 \text{ g/mol}.$$

The chemical reaction is:  $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ .

Let the mole fraction of the dimer in the equilibrium mixture be  $x$ . We have  $92.0x + 46.0(1 - x) = 77.3$ , which gives  $x = 0.680$ .

Thus,  $x(\text{NO}_2) = 0.320$ ,  $x(\text{N}_2\text{O}_4) = 0.680$ .

- b) The equilibrium-constant expression is

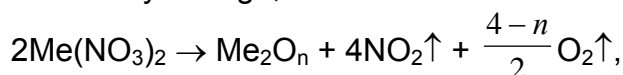
$$K_p = \frac{p(\text{N}_2\text{O}_4)}{p^2(\text{NO}_2)}, \text{ where } p \text{ is the partial pressure.}$$

- c)  $K_p = \frac{p(\text{N}_2\text{O}_4)}{p^2(\text{NO}_2)} = \frac{1}{p} \cdot \frac{x(\text{N}_2\text{O}_4)}{x^2(\text{NO}_2)} = \frac{1}{p} \cdot \frac{(1 - x(\text{NO}_2))}{x^2(\text{NO}_2)}$ , where  $x$  is the mole fraction.

Using the mole fractions of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  obtained in part a) we obtain

$$K_p = \frac{1}{p} \cdot \frac{(1 - x(\text{NO}_2))}{x^2(\text{NO}_2)} = \frac{1}{1} \cdot \frac{1 - 0.320}{(0.320)^2} = 6.64 \text{ atm}^{-1}.$$

- d) Nitrites of  $d$ -metals are unstable. Therefore, the product of the thermal decomposition of the nitrate is either the free metal or an oxide. Since the oxidation state of the metal may change, we write



where  $n$  is the oxidation number of the unknown metal in the product ( $n \geq 0$ ).

We have  $M(\text{Me}(\text{NO}_3)_2) = (M(\text{Me}) + 124) \text{ g/mol}$ .

The gas mixture contains a total of  $\frac{p \cdot V}{R \cdot T} = \frac{101.3 \times 0.239}{8.314 \times 298} = 9.77 \times 10^{-3} \text{ mol}$

of  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ , and  $\text{O}_2$ .

Using the equilibrium constant  $K_p = \frac{p(N_2O_4)}{p^2(NO_2)} = \frac{1}{p} \cdot \frac{x(N_2O_4)}{x^2(NO_2)} = 6.64 \text{ atm}^{-1}$ ,

we find that, at  $p = 1 \text{ atm}$ ,  $x(N_2O_4) = K_p \cdot x^2(NO_2) = 6.64x^2(NO_2)$ .

Also,  $x(N_2O_4) + x(NO_2) + x(O_2) = 1$ .

Based on the stoichiometry of the decomposition reaction, the amounts of  $O_2$  and

$NO_2$  before the dimerization form the ratio:  $\frac{n(NO_2)}{n(O_2)} = \frac{8}{4-n}$ .

Let the mole fraction of  $NO_2$  in the equilibrium mixture (after the partial dimerization

of  $NO_2$ ) be  $x$ . Then we write  $\frac{8}{4-n} = \frac{x+2 \cdot K_p \cdot x^2}{1-x-K_p \cdot x^2}$

Solving the quadratic equation we obtain

$$x = \frac{n-12 + \sqrt{(12-n)^2 + 64 \cdot K_p \cdot (8-n)}}{4 \cdot K_p \cdot (8-n)} \quad (1)$$

The amount of the nitrate is half the amount of  $NO_2$  before dimerization, i.e.,

$$n(\text{Me}(\text{NO}_3)_2) = \frac{9.77 \times 10^{-3}}{2} \cdot (x + 2 \cdot K_p \cdot x^2) \text{ mol.}$$

$$\text{Hence, } M(\text{Me}) = \frac{1.206}{n(\text{Me}(\text{NO}_3)_2)} - 124 = \left[ \frac{247}{(x + 2 \cdot K_p \cdot x^2)} - 124 \right] \text{ g/mol.} \quad (2)$$

e) Solution of the simultaneous equations (1) and (2) is cumbersome. We proceed by analyzing four special cases:

(i) Suppose that  $n = 2$ . Eq. (1) gives  $x = 0.260$ ; Eq. (2) yields  $M(\text{Me}) = 89 \text{ g/mol}$ .

There are no metals with  $M=89 \text{ g/mol}$  that form a nitrate in the +2 oxidation state.

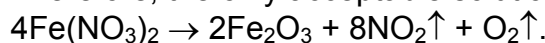
(ii) Suppose that the metal oxide is unstable, that is,  $\text{Me}(\text{NO}_3)_2 \rightarrow \text{Me}$ , and  $n = 0$ .

Then Eqs. (1) and (2) give  $x = 0.224$  and  $M(\text{Me}) = 153 \text{ g/mol}$ . There is no metal with this atomic mass.

(iii) Suppose that  $n = 3$ , that is,  $\text{Me}(\text{NO}_3)_2 \rightarrow \text{Me}_2\text{O}_3$ . In this case,  $x = 0.286$  and  $M(\text{Me}) = 56 \text{ g/mol}$ . The metal  $\text{Me}$  is iron, and the nitrate is  $\text{Fe}(\text{NO}_3)_2$ .

(iv) If  $n=4$ , then  $x = 0.320$  and  $M(\text{Me}) = 23 \text{ g/mol}$ . There is no metal with this atomic mass that forms a nitrate of the formula  $\text{Me}(\text{NO}_2)_2$ .

Therefore, the only acceptable solution is  $\text{Me} = \text{Fe}$ . The reaction is



Note: Ignoring the dimerization of  $NO_2$  does not lead to any other solutions.

### Problem 10-5

a) The molar mass of the unknown ketone can be found from the density of its vapor:

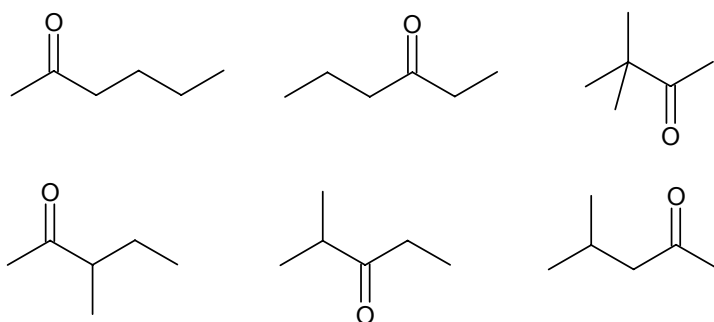
$$p \cdot V = n \cdot R \cdot T, \text{ hence } \rho = \frac{m}{V} = \frac{p \cdot m}{n \cdot R \cdot T} = \frac{p \cdot M}{R \cdot T}, \text{ which gives } M = \frac{\rho \cdot R \cdot T}{p}.$$

$$M(\mathbf{A}) = \frac{4.09 \times 8.314 \times 298}{101.3} = 100 \text{ g/mol.}$$

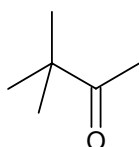
Let us assume first that the molecule of  $\mathbf{A}$  contains only one oxygen atom. If the numbers of C and H atoms are  $x$  and  $y$ , respectively, then  $12x + y + 16 = 100$ .

This equation has only one solution in integers:  $x = 6$  and  $y = 12$ .

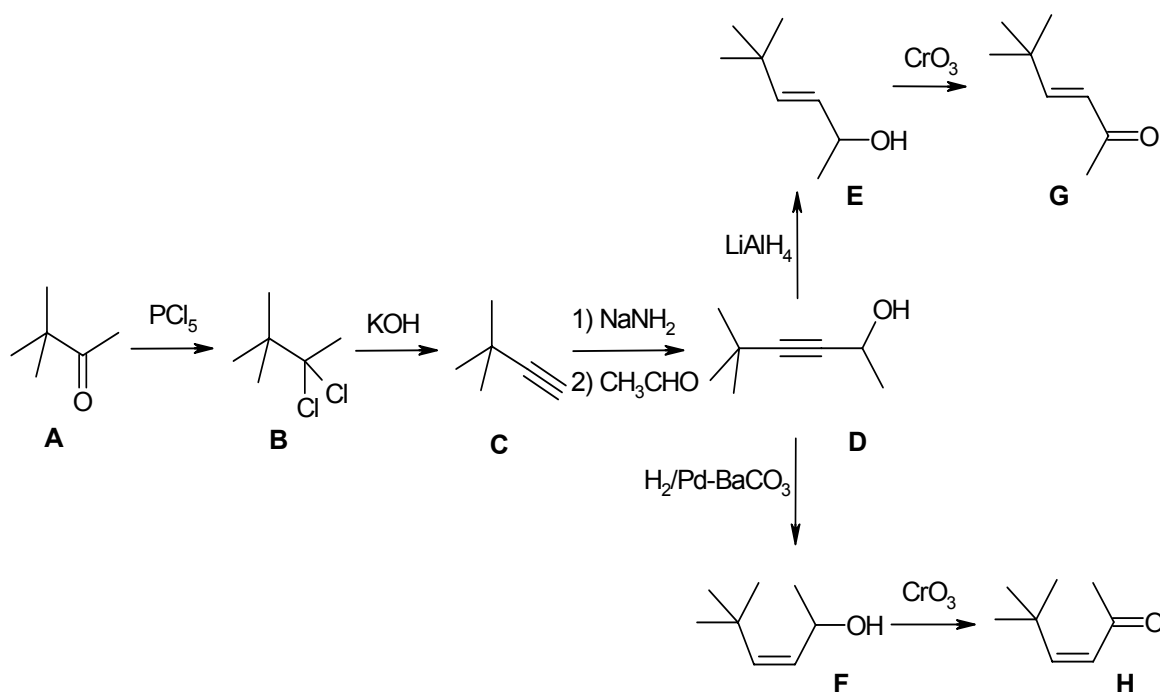
Therefore, the molecular formula of  $\mathbf{A}$  is  $\text{C}_6\text{H}_{12}\text{O}$ . There are 6 isomeric ketones of this molecular formula. Their structures are as follows:



Of these, 3,3-dimethyl-2-butanone alone contains precisely two distinct types of hydrogen atoms. Thus, compound **A** is 3,3-dimethyl-2-butanone (pinacolone):



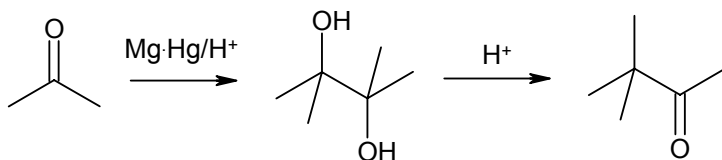
The synthetic sequence starting with **A** is as follows:



Here

- A** = pinacolone;  
**B** = 2,2-dimethyl-3,3-dichlorobutane;  
**C** = 3,3-dimethyl-1-butyne;  
**D** = 5,5-dimethyl-3-hexyne-2-ol  
**E** = *trans*-5,5-dimethyl-3-hexene-2-ol;  
**F** = *cis*-5,5-dimethyl-3-hexene-2-ol;  
**G** = *trans*-5,5-dimethyl-3-hexene-2-one;  
**H** = *cis*-5,5-dimethyl-3-hexene-2-one.

- b) Monohydrogenation of a triple bond results in a *trans*-alkene if the reagent is  $\text{LiAlH}_4$  and yields a *cis*-alkene if a palladium catalyst is used. In the latter case, the regioselectivity is determined by the fact that the activated  $\text{H}_2$  molecule is adsorbed on the surface and, therefore, approaches the triple bond from one side.
- c) The simplest synthesis involves reductive dimerization of acetone followed by the pinacol rearrangement:



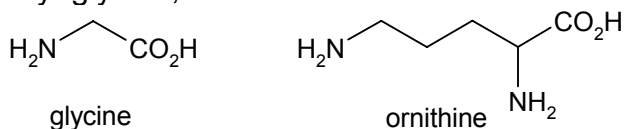
## GRADE 11

### Problem 11-1

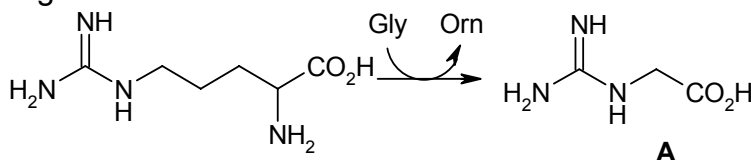
See Problem 9-1.

### Problem 11-2

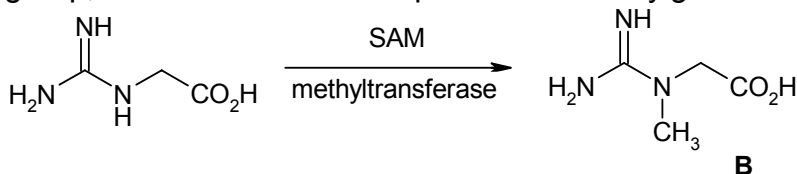
a) Gly=glycine, Orn=ornithine. The structural formulas of these amino acids are:



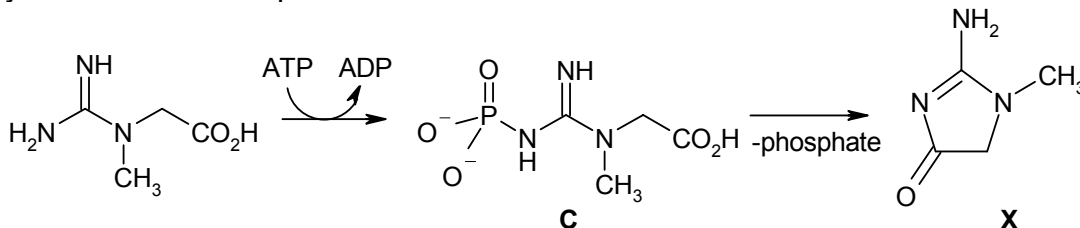
By comparing the structures of glycine and ornithine we conclude that compound **A** is guanidine-acetic acid:



The molecular formula of compound **X** suggests that **X** contains two double bonds. The final steps in the synthesis are phosphorylation and dephosphorylation. Therefore, the formation of **B** involves monomethylation of one of the nitrogen atoms. Since the methylating agent (SAM) attacks the nitrogen nearest to the carboxylic group, we conclude that compound **B** is methylguanidine-acetic acid:

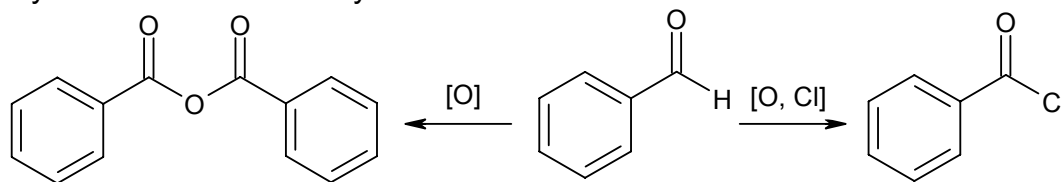


Phosphorylation of the amino group of **B** followed by removal of the phosphate ion yields the final compound **X**:



- b) Suppose that each chicken contains 1 kg of muscle tissue. Together with 300 pounds  $\approx 300 \times 0.4 \text{ kg} = 120 \text{ kg}$  of horse meat, this amounts to 222 kg of muscle tissue. We will take the density of muscle tissue to be  $1 \text{ kg/dm}^3$  (i.e., the density of water). Thus, Justus processed  $222 \text{ dm}^3$  of meat that contained  $222 \times (20 \times 10^{-3}) = 4.44 \text{ mol}$  of compound **C** (creatine phosphate). Since the molecular mass of **C** is  $M(\text{C}_4\text{H}_7\text{N}_3\text{O}) = 113 \text{ g/mol}$ , we conclude that Justus could not have obtained more than  $113 \times 4.44 \times 0.02 = 10 \text{ g}$  of compound **X**.
- c) **X** is creatinine.

- d) The atomic composition of the first and third compounds is given per pair of molecules. The radical is benzoyl ( $C_6H_5CO\cdot$ ). The "bitter almond oil" is benzaldehyde. The products of its mild oxidation and oxidative chlorination are, respectively, benzoyl benzoate and benzoyl chloride:



- e) Justus Liebig and Friedrich Wöhler.

### Problem 11-3

- a) The chemical equation representing the dimerization of vaporized acetic acid (HA) is  $2HA(g) \rightleftharpoons H_2A_2(g)$ .

The average molecular mass of the vapor at 160 °C and 200 °C can be found from the ideal gas equation of state:

$$M_{160} = \frac{m \cdot R \cdot T}{p \cdot V} = \frac{40.7 \times 8.314 \times (273 + 160)}{101.3 \times 20.00} = 72.3 \text{ g/mol.}$$

$$M_{200} = \frac{m \cdot R \cdot T}{p \cdot V} = \frac{33.4 \times 8.314 \times (273 + 200)}{101.3 \times 20.00} = 64.8 \text{ g/mol.}$$

$$M(CH_3CO_2H) = 60.0 \text{ g/mol.}$$

Suppose the mole fraction of the dimer in the equilibrium mixture at 160 °C is  $x$ .

Then we have the equation  $120x + 60.0(1 - x) = 72.3$ , which gives  $x = 0.205$ .

The equilibrium-constant expression is:

$$K_p = \frac{p(H_2A_2)}{p^2(HA)} = \frac{1}{p} \cdot \frac{x(H_2A_2)}{x^2(HA)} = \frac{1}{p} \cdot \frac{x(H_2A_2)}{(1-x(H_2A_2))^2},$$

where  $p$  is the total pressure and  $x$  is the mole fraction of the respective component.

$$\text{For } T=160 \text{ °C we obtain } K_p = \frac{1}{1} \cdot \frac{0.205}{(1-0.205)^2} = 0.324 \text{ atm}^{-1}.$$

Similarly, we find that the mole fraction of the dimer at 200 °C is  $y = 0.080$ . Therefore, the equilibrium constant at this temperature is

$$K_p = \frac{1}{1} \cdot \frac{0.080}{(1-0.080)^2} = 0.095 \text{ atm}^{-1}.$$

- b) The mole fraction of the dimer is 0.205 at 160 °C and 0.080 at 200 °C.  
c) We have:  $\ln K = \text{const} - \frac{\Delta H}{R \cdot T}$ .

Using the values of  $K$  at 160 °C and 200 °C found in part b), we write

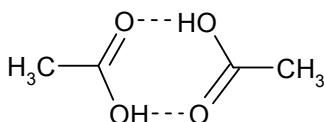
$$\ln K_1 - \ln K_2 = \left( \text{const} - \frac{\Delta H}{RT_1} \right) - \left( \text{const} - \frac{\Delta H}{RT_2} \right).$$

$$\text{or } \ln \frac{K_1}{K_2} = \frac{\Delta H}{R} \cdot \left( \frac{1}{T_2} - \frac{1}{T_1} \right). \text{ Now}$$

$$\Delta_{dim}H = \ln \frac{K_1}{K_2} \cdot \frac{RT_1T_2}{T_1 - T_2} = \ln \frac{0.324}{0.095} \cdot \frac{8.314 \times 433 \times 473}{40} \cdot 10^{-3} = -52.2 \text{ kJ/mol.}$$

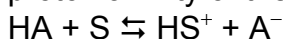
- d) The acetic acid dimer is held together by hydrogen bonds:





Since new chemical bonds are formed, dimerization of acetic acid is an exothermic process. The enthalpy of this reaction is approximately twice the enthalpy of formation of a hydrogen bond.

- e) Dimerization of acetic acid occurs not only in gas phase but also in solvents that cannot form hydrogen bonds with acetic acid molecules, such as benzene. In water, there will be virtually no dimer molecules because acetic acid monomers prefer to form hydrogen bonds with the much more abundant water molecules.
- f) The degree of dissociation of an acid (HA) dissolved in a solvent (S) depends on the proton affinity of the solvent,



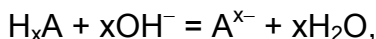
Basic solvents such as pyridine will have a levelling effect on the relative strength of formic and acetic acids, making their differentiation difficult. In contrast, acidic solvents such as propionic acid will amplify the difference. This effect is routinely used in the titrimetric analysis of mixtures of acids.

#### Problem 11-4

- a) Chrysanthemic acid definitely contains oxygen. The mass percent of oxygen in this compound is  $(100 - 71.39 - 9.59) = 19.02\%$ . Then the ratio of the atoms is

$$\text{C} : \text{O} : \text{H} = \frac{71.39}{12.01} : \frac{19.02}{16.00} : \frac{9.59}{1.01} = 5.94 : 1.19 : 9.50 = 5 : 1 : 8.$$

The empirical formula of the compound is, therefore,  $\text{C}_5\text{H}_8\text{O}$ . Since this is a carboxylic acid, its molecular formula must be  $(\text{C}_5\text{H}_8\text{O})_n$ , where  $n$  is an integer greater than 1. Based on the chemical equation representing the titration,

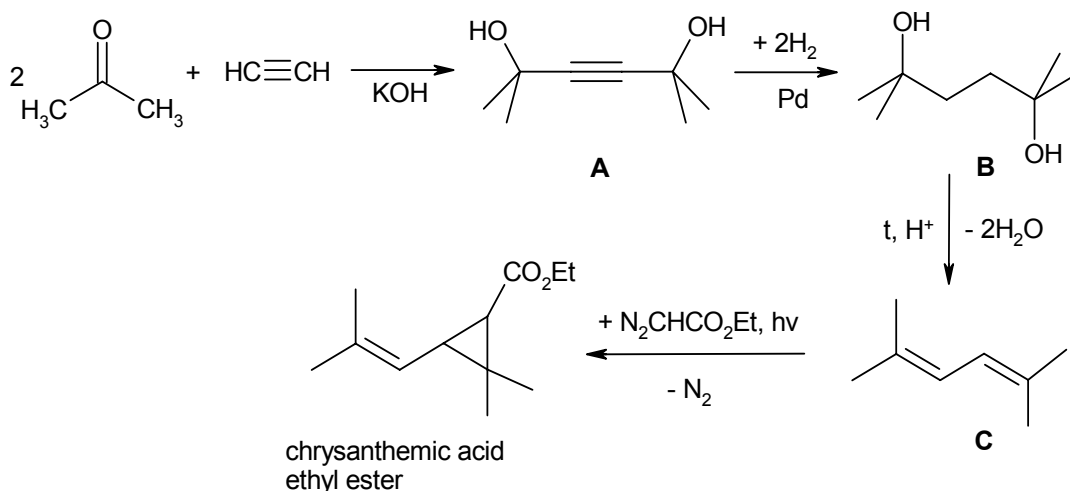


the molecular mass of chrysanthemic acid is

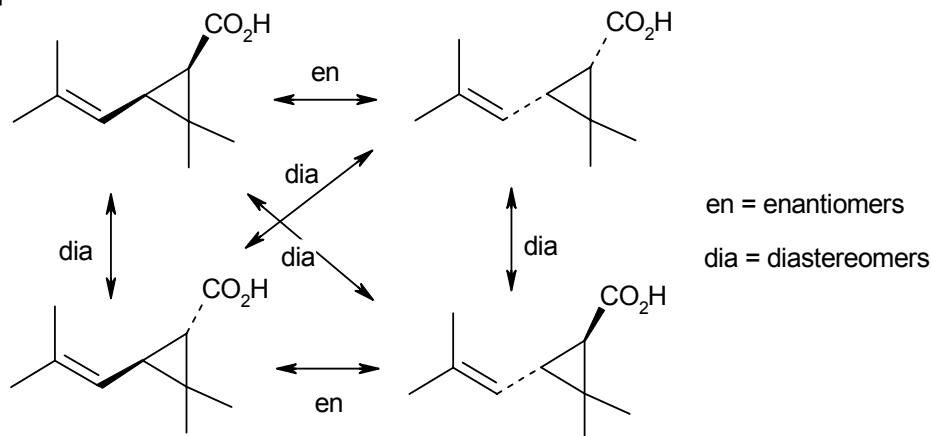
$$M = \frac{123.5 \times 10^{-3}}{0.0436 \times 0.01685} x = 168x \text{ g/mol, where } x \geq 1.$$

This allows us to conclude that  $x=1$  and  $n=2$ . Hence, the molecular formula of chrysanthemic acid is  $\text{C}_{10}\text{H}_{16}\text{O}_2$ .

- b) Condensation of acetone and acetylene in the presence of a base yields 2,5-dimethyl-3-hexyne-2,5-diol (compound **A**). Addition of a water molecule to the triple bond produces 2,5-dimethylhexane-2,5-diol (compound **B**), which is then dehydrated to give a conjugated diene, 2,5-dimethyl-2,4-hexadiene (**C**). In the final step of the synthesis, light-induced decomposition of ethyl diazoacetate generates a carbene which reacts with one of the two equivalent  $\text{C}=\text{C}$  bonds to give chrysanthemic acid ethyl ester:

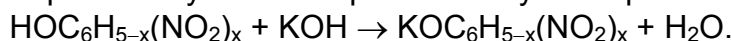


- c) Chrysanthemic acid contains two non-equivalent chiral carbon atoms and, hence, exists as  $2^2 = 4$  stereoisomers. The *cis*- and *trans*-forms of the cyclopropane ring are related to each other as diastereomers. Each of these diastereomers exists as a pair of enantiomers:



### Problem 11-5

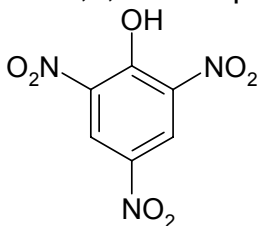
- a) Nitration of phenol can produce mono-, di-, and trinitrophenols. The general formula of these compounds is  $\text{HOC}_6\text{H}_{5-x}(\text{NO}_2)_x$ , where  $x = 1, 2,$  or  $3$ . Neutralization of nitrophenols by KOH is represented by the equation:



The amount of KOH required for the titration is  $19.52 \times 0.05124 = 1.000$  mmol. The molar mass of the acid is  $\frac{0.229 \text{ g}}{0.001 \text{ mol}} = 229 \text{ g/mol}$ . Therefore,  $x=3$ , and the molecular

formula of **A** is  $\text{HOC}_6\text{H}_2(\text{NO}_2)_3$ .

- b) **A** is 2,4,6-trinitrophenol or picric acid:



- c) Picric acid is a stronger acid than phenol because the three electron-withdrawing nitro groups reduce the electron density in the benzene ring and polarize the O–H bond, thereby facilitating heterolytic dissociation of the O–H bond (ionization).
- d) Explosive decomposition of picric acid can result in a number of products, e.g.,  $\text{C}_6\text{H}_3\text{N}_3\text{O}_7 \rightarrow \text{C} + \text{CO} + \text{N}_2 + \text{H}_2\text{O}$ .



