Finding Empirical and Molecular Formulas by Experiment

6.4

Section Preview/ Specific Expectations

In this section, you will

- **identify** real-life situations in which the analysis of unknown substances is important
- **determine** the empirical formula of a hydrate through experimentation
- **explain** how a carbon-hydrogen analyzer can be used to determine the empirical formula of a compound
- **communicate** your understanding of the following terms: *carbon-hydrogen combustion analyzer, hydrate, anhydrous*

You have learned how to calculate the percentage composition of a compound using its formula. Often, however, the formula of a compound is not known. Chemists must determine the percentage composition and molar mass of an unknown compound through experimentation. Then they use this information to determine the molecular formula of the compound. Determining the molecular formula is an important step in understanding the properties of the compound and developing a way to synthesize it in a laboratory.

In Investigation 6-A, you reacted a known mass of magnesium with oxygen and found the mass of the product. Then you determined the percentage composition and empirical formula of magnesium oxide. This is just one method for determining percentage composition. It is suitable for analyzing simple compounds that react in predictable ways. Chemists have developed other methods for analyzing different types of compounds, as you will learn in this section.

The Carbon-Hydrogen Combustion Analyzer

A large number of important chemicals are composed of hydrogen, carbon, and oxygen. The **carbon-hydrogen combustion analyzer** is a useful instrument for analyzing these chemicals. It allows chemists to determine the percentage composition of compounds that are made up of carbon, hydrogen, and oxygen. The applications of this instrument include forensic science, food chemistry, pharmaceuticals and academic research — anywhere that an unknown compound needs to be analyzed.

The carbon-hydrogen combustion analyzer works because we know that compounds containing carbon and hydrogen will burn in a stream of pure oxygen, O_2, to yield only carbon dioxide and water. If we can find the mass of the carbon dioxide and water separately, we can determine the mass percent of carbon and hydrogen in the compound.

Examine Figure 6.8 to see how a carbon-hydrogen combustion analyzer works. A sample, made up of only carbon and hydrogen, is placed in a furnace. The sample is heated and simultaneously reacted with a stream

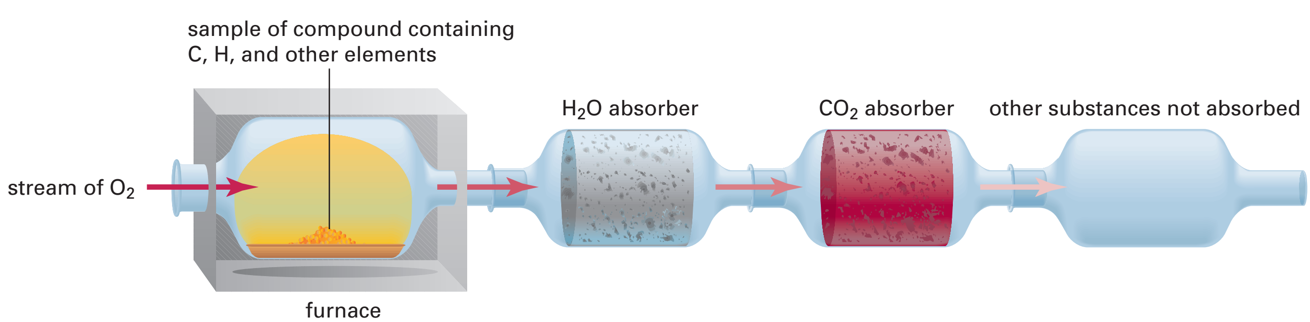

Figure 6.8 A schematic diagram of a carbon-hydrogen combustion analyzer. After the combustion, all the carbon in the sample is contained in the carbon dioxide. All the hydrogen in the sample is contained in the water.

CHECKPOINT

Carbon dioxide reacts with sodium hydroxide to form sodium carbonate and water. Write a balanced chemical equation for this reaction.

of oxygen. Eventually the sample is completely combusted to yield only water vapour and carbon dioxide.

The water vapour is collected by passing it through a tube that contains magnesium perchlorate, $Mg(ClO_4)_2$. The magnesium perchlorate absorbs all of the water. The mass of the tube is determined before and after the reaction. The difference is the mass of the water that is produced in the reaction. We know that all the hydrogen in the sample is converted to water. Therefore, we can use the percentage composition of hydrogen in water to determine the mass of the hydrogen in the sample.

The carbon dioxide is captured in a second tube, which contains sodium hydroxide, NaOH. The mass of this tube is also measured before and after the reaction. The increase in the mass of the tube corresponds to the mass of the carbon dioxide that is produced. We know that all the carbon in the sample reacts to form carbon dioxide. Therefore, we can use the percentage composition of carbon in carbon dioxide to determine the mass of the carbon in the sample.

PROBEWARE

If you have access to probeware, do the Chemistry 11 lab, Determining Molecular Mass, or a similar lab available from a probeware company.

The carbon-hydrogen combustion analyzer can also be used to find the empirical formula of a compound that contains carbon, hydrogen, and one other element, such as oxygen. The difference between the mass of the sample and the mass of the hydrogen and carbon produced is the mass of the third element.

Examine the following Sample Problem to learn how to determine the empirical formula of a compound based on carbon-hydrogen combustion data.

CHECKPOINT

If you have a compound containing carbon, hydrogen, and oxygen, what two instruments would you need to determine its molecular formula?

Sample Problem

Carbon-Hydrogen Combustion Analyzer Calculations

Problem

A 1.000 g sample of a pure compound, containing only carbon and hydrogen, was combusted in a carbon-hydrogen combustion analyzer. The combustion produced 0.6919 g of water and 3.338 g of carbon dioxide.

(a) Calculate the masses of the carbon and the hydrogen in the sample.

(b) Find the empirical formula of the compound.

What Is Required?

You need to find

(a) the mass of the carbon and the hydrogen in the sample

(b) the empirical formula of the compound

What Is Given?

You know the mass of the sample. You also know the masses of the water and the carbon dioxide produced in the combustion of the sample.

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FROM PAGE 220

Plan Your Strategy

All the hydrogen in the sample was converted to water. Multiply the mass percent (as a decimal) of hydrogen in water by the mass of the water to get the mass of the hydrogen in the sample.

Similarly, all the carbon in the sample has been incorporated into the carbon dioxide. Multiply the mass percent (as a decimal) of carbon in carbon dioxide by the mass of the carbon dioxide to get the mass of carbon in the sample. Convert to moles and determine the empirical formula.

Act on Your Strategy

(a) Mass of H in sample

$$= \frac{2.02 \text{ g } H_2}{18.02 \cancel{\text{ g } H_2O}} \times 0.6919 \cancel{\text{ g } H_2O} = 0.077\ 56 \text{ g } H_2$$

$$\text{Mass of C in sample} = \frac{12.01 \text{ g C}}{44.01 \cancel{\text{ g } CO_2}} \times 3.338 \cancel{\text{ g } CO_2} = 0.9109 \text{ g C}$$

The sample contained 0.077 56 g of hydrogen and 0.9109 g of carbon.

(b) $\text{Moles of H in sample} = \dfrac{0.07756 \cancel{\text{ g}}}{1.008 \cancel{\text{ g}}/\text{mol}} = 0.07694 \text{ mol}$

$$\text{Moles of C in sample} = \frac{0.9109 \cancel{\text{ g}}}{12.01 \cancel{\text{ g}}/\text{mol}} = 0.07584 \text{ mol}$$

$$\begin{aligned}\text{Empirical formula} &= C_{\frac{0.07584}{0.07584}} H_{\frac{0.07584}{0.07694}} \\ &= C_{1.0}H_{1.0} \\ &= CH\end{aligned}$$

Check Your Solution

The sum of the masses of carbon and hydrogen is 0.077 56 g + 0.9109 g = 0.988 46 g. This is close to the mass of the sample. Therefore your answers are reasonable.

Practice Problems

21. A 0.539 g sample of a compound that contained only carbon and hydrogen was subjected to combustion analysis. The combustion produced 1.64 g of carbon dioxide and 0.807 g of water. Calculate the percentage composition and the empirical formula of the sample.

22. An 874 mg sample of cortisol was subjected to carbon-hydrogen combustion analysis. 2.23 g of carbon dioxide and 0.652 g of water were produced. The molar mass of cortisol was found to be 362 g/mol using a mass spectrometer. If cortisol contains carbon, hydrogen, and oxygen, determine its molecular formula.

CHEM FACT

Cortisol is an important steroid hormone. It helps your body synthesize protein. Cortisol can also reduce inflammation, and is used to treat allergies and rheumatoid arthritis.

Chemistry Bulletin

Science Technology Society Environment

Accident or Arson?

All chemists who try to identify unknown compounds are like detectives. Forensic chemists, however, actually work with investigators. They use their chemical knowledge to help explain evidence. Forensic chemists are especially helpful in an arson investigation.

Investigating Arson

One of the main jobs of the investigator in a possible arson case is to locate and sample residual traces of accelerants. Accelerants are flammable substances that are used to quickly ignite and spread a fire. They include compounds called hydrocarbons, which contain hydrogen and carbon. Examples of hydrocarbons include petrol, kerosene and diesel.

Portable instruments called *sniffers* can be used to determine the best places to collect samples. These sniffers, however, are not able to determine the type of hydrocarbon present. As well, they can be set off by vapours from burnt plastics. Deciding whether or not a substance is an accelerant is best done by a chemist in a laboratory, using a technique called gas chromatography (GC).

In the Forensic Laboratory

In the laboratory, the sample residue must be concentrated on charcoal or another material. Then the sample is ready for GC analysis. GC is used to separate and detect trace amounts of volatile hydrocarbons and separate them from a mixture. Most accelerants are complex mixtures. They have many components, in different but specific ratios.

GC involves taking the concentrated residue and passing it through a gas column. As the sample residue moves through the column, the different components separate based on their boiling points. The compound with the lowest boiling point emerges from the column and onto a detector first. The other components follow as they reach their boiling points. It is possible to identify each component of a mixture based on the time that it emerges from the column. A detector records this information on a chromatogram. Each component is represented by a peak on a graph. The overall pattern of peaks is always the same for a specific type of accelerant. Therefore, accelerants are identified by their components and the relative proportions of their components.

Only trace amounts of an accelerant need to be collected because current analytical tools are extremely sensitive. If an accelerant is used to start a fire, it is highly likely that there will be trace amounts left over after the fire. The presence of an accelerant at a fire scene strongly suggests that the fire was started intentionally.

Making Connections

1. What other types of crime could be solved by a forensic chemist? Brainstorm a list.
2. What other instruments might a forensic chemist use to identify compounds? Using the Internet or reference books, do some research to find out.

Hydrated Ionic Compounds

You have learned how to find the molecular formula of a compound that contains only hydrogen, carbon, and oxygen. When chemists use this method, they usually have no mass percent data for the compound when they begin. In some cases, however, chemists know most of the molecular formula of a compound, but one significant piece of information is missing.

For example, many ionic compounds crystallize from a water solution with water molecules incorporated into their crystal structure, forming a **hydrate**. Hydrates have a specific number of water molecules chemically bonded to each formula unit. A chemist may know the formula of the ionic part of the hydrate but not how many water molecules are present for each formula unit.

Epsom salts, for example, consist of crystals of magnesium sulfate heptahydrate, $MgSO_4 \cdot 7H_2O$. Every formula unit of magnesium sulfate has seven molecules of water weakly bonded to it. A raised dot in a chemical formula, in front of one or more water molecules, denotes a hydrated compound. Note that the dot does not include multiplication, but rather a weak bond between an ionic compound and one or more water molecules. Some other examples of hydrates are shown in Table 6.4.

Compounds that have no water molecules incorporated into them are called **anhydrous** to distinguish them from their hydrated forms. For example, a chemist might refer to $CaSO_4$ as anhydrous calcium sulfate. This is because it is often found in hydrated form as calcium sulfate dihydrate, shown in Figure 6.9.

mind STRETCH

Suppose there is $MgSO_4 \cdot 7H_2O$ in the chemistry prep room. The experiment you want to do, however, calls for $MgSO_4$. How do you think you might remove the water from $MgSO_4 \cdot 7H_2O$?

Table 6.4 Selected Hydrates

Formula	Chemical name
$CaSO_4 \cdot 2H_2O$	calcium sulfate dihydrate (gypsum)
$CaCl_2 \cdot 2H_2O$	calcium chloride dihydrate
$LiCl_2 \cdot 4H_2O$	lithium chloride tetrahydrate
$MgSO_4 \cdot 7H_2O$	magnesium sulfate heptahydrate (Epsom salts)
$Ba(OH)_2 \cdot 8H_2O$	barium hydroxide octahydrate
$Na_2CO_3 \cdot 10H_2O$	sodium carbonate decahydrate
$KAl(SO_4)_2 \cdot 12H_2O$	potassium aluminum sulfate dodecahydrate (alum)

Figure 6.9 **Alabaster is a compact form of gypsum often used in sculpture. Gypsum is the common name for calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$.**

The molar mass of a hydrated compound must include the mass of any water molecules that are in the compound. For example, the molar mass of magnesium sulfate heptahydrate includes the mass of 7 mol of water. It is very important to know whether a compound exists as a hydrate. For example, if a chemical reaction calls for 0.25 mol of copper(II) chloride, you need to know whether you are dealing with anhydrous copper(II) chloride or with copper(II) chloride dihydrate, shown in Figure 6.10. The mass of 0.25 mol of $CuCl_2$ is 33.61 g. The mass of 0.25 mol of $CuCl_2 \cdot 2H_2O$ is 38.11 g.

Calculations involving hydrates involve using the same techniques you have already practised for determining percent by mass, empirical formulas, and molecular formulas.

The following Sample Problem shows how to find the percent by mass of water in a hydrate. It also shows how to determine the formula of a hydrate based on an incomplete chemical formula.

Figure 6.10 If you need 5 mol of $CuCl_2$, how much of the compound above would you use?

Sample Problem

Determining the Formula of a Hydrate

Problem

A hydrate of barium hydroxide, $Ba(OH)_2{\cdot}xH_2O$, is used to make barium salts and to prepare certain organic compounds. Since it reacts with CO_2 from the air to yield barium carbonate, $BaCO_3$, it must be stored in tightly stoppered bottles.

(a) A 50.0 g sample of the hydrate contains 27.2 g of $Ba(OH)_2$. Calculate the percent, by mass, of water in $Ba(OH)_2{\cdot}xH_2O$.

(b) Find the value of x in $Ba(OH)_2{\cdot}xH_2O$.

What Is Required?

(a) You need to calculate the percent, by mass, of water in the hydrate of barium hydroxide.

(b) You need to find how many water molecules are bonded to each formula unit of $Ba(OH)_2$.

What Is Given?

The formula of the sample is $Ba(OH)_2{\cdot}xH_2O$.
The mass of the sample is 50.0 g.
The sample contains 27.2 g of $Ba(OH)_2$.

Plan Your Strategy

(a) To find the mass of water in the hydrate, find the difference between the mass of barium hydroxide and the total mass of the sample. Divide by the total mass of the sample and multiply by 100%.

(b) Find the number of moles of barium hydroxide in the sample. Then find the number of moles of water in the sample. To find out how many water molecules bond to each formula unit of barium hydroxide, divide each answer by the number of moles of barium hydroxide.

Act on Your Strategy

(a) Mass percent of water in $Ba(OH)_2{\cdot}xH_2O$

$$= \frac{\text{(Total mass of sample)} - \text{(Mass of Ba(OH)}_2\text{ in sample)}}{\text{(Total mass of sample)}} \times 100\%$$

$$= \frac{50.0\ \cancel{g} - 27.2\ \cancel{g}}{50.0\ \cancel{g}} \times 100\%$$

$$= 45.6\%$$

(b) $$\text{Moles of Ba(OH)}_2 = \frac{\text{Mass of Ba(OH)}_2}{\text{Molar mass of Ba(OH)}_2}$$

$$= \frac{27.2\ \cancel{g}}{171.3\ \cancel{g}/\text{mol}}$$

$$= 0.159\ \text{mol Ba(OH)}_2$$

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FROM PAGE 224

$$\text{Moles of } H_2O = \frac{\text{Mass of } H_2O}{\text{Molar mass of } H_2O}$$
$$= \frac{50.0\ \cancel{g} - 27.2\ \cancel{g}}{18.02\ \cancel{g}/\text{mol}}$$
$$= 1.27 \text{ mol } H_2O$$

$$\frac{0.159}{0.159} \text{ mol } Ba(OH)_2 : \frac{1.27}{0.159} \text{ mol } H_2O = 1.0 \text{ mol } Ba(OH)_2 : 8.0 \text{ mol } H_2O$$

The value of x in $Ba(OH)_2 \cdot xH_2O$ is 8.
Therefore, the molecular formula of the hydrate is $Ba(OH)_2 \cdot 8H_2O$.

Check Your Solution

Work backward.
According to the formula, the percent by mass of water in $Ba(OH)_2 \cdot 8H_2O$ is:

$$\frac{144.16\ \cancel{g/mol}}{315.51\ \cancel{g/mol}} \times 100\% = 45.7\%$$

According to the question, the percent by mass of water in the hydrate of $Ba(OH)_2$ is:

$$\frac{(50.0\ \cancel{g} - 27.2\ \cancel{g})}{50.0\ \cancel{g}} \times 100\% = 45.6\%$$

Therefore, your answer is reasonable.

Practice Problems

23. What is the percent by mass of water in magnesium sulfite hexahydrate, $MgSO_3 \cdot 6H_2O$?

24. A 3.34 g sample of a hydrate has the formula $SrS_2O_3 \cdot xH_2O$, and contains 2.30 g of SrS_2O_3. Find the value of x.

25. A hydrate of zinc chlorate, $Zn(ClO_3)_2 \cdot xH_2O$, contains 21.5% zinc by mass. Find the value of x.

PROBLEM TIP

This step is similar to finding an empirical formula based on percentage composition.

CHECKPOINT

Write an equation that shows what happens when you heat magnesium sulfate hexahydrate enough to convert it to its anhydrous form.

Determining the Molecular Formula of a Hydrate

As you have just discovered, calculations involving hydrates usually involve comparing the anhydrous form of the ionic compound to the hydrated form. Many chemicals are available in hydrated form. Usually chemists are only interested in how much of the ionic part of the hydrate they are working with. This is because, in most reactions involving hydrates, the water portion of the compound does not take part in the reaction. Only the ionic portion does.

How do chemists determine how many water molecules are bonded to each ionic formula unit in a hydrate? One method is to heat the compound in order to convert it to its anhydrous form. The bonds that join the water molecules to the ionic compound are very weak compared with the strong ionic bonds within the ionic compound. Heating a hydrate usually removes the water molecules, leaving the anhydrous compound behind. In Investigation 6-B, you will heat a hydrate to determine its formula.

Electronic Learning Partner

A video clip describing hydrated ionic compounds can be found on the Chemistry 11 Electronic Learning Partner.

Investigation 6-B

SKILL FOCUS

- Predicting
- Performing and recording
- Analyzing and interpreting
- Communicating results

Determining the Chemical Formula of a Hydrate

Many ionic compounds exist as hydrates. Often you can convert hydrates to anhydrous ionic compounds by heating them. Thus, hydrates are well suited to determining percentage composition experimentally.

In this investigation, you will find the mass percent of water in a hydrate of copper(II) sulfate hydrate, $CuSO_4 \cdot xH_2O$. You will use copper(II) sulfate hydrate for an important reason: The crystals of the hydrate are blue, while anhydrous copper(II) sulfate is white.

Question

What is the molecular formula of the hydrate of copper(II) sulfate, $CuSO_4 \cdot xH_2O$?

Prediction

Predict what reaction will occur when you heat the hydrate of copper(II) sulfate.

Materials

400 mL beaker (if hot plate is used)
tongs
scoopula
electronic balance
glass rod
hot pad
3 g to 5 g hydrated copper(II) sulfate

Safety Precautions

Heat the hydrate at a low to medium temperature only.

Procedure

Note: If you are using a hot plate as your heat source, use the 400 mL beaker. If you are using a laboratory burner, use the porcelain evaporating dish.

1. Make a table like the one below, for recording your observations.

Observations

Mass of empty beaker or evaporating dish	
Mass of beaker or evaporating dish + hydrated copper(II) sulfate	
Mass of beaker or evaporating dish + anhydrous copper(II) sulfate	

A hydrate of copper(II) sulfate (far left) is light blue. It loses its colour on heating.

2. Measure the mass of the beaker and stirring rod. Record the mass in your table.
3. Add 3 g to 5 g hydrated copper(II) sulfate to the beaker.
4. Measure the mass of the beaker with the hydrated copper(II) sulfate. Record the mass in your table.
5. If you are using a hot plate, heat the beaker with the hydrated copper(II) sulfate until the crystals lose their blue colour. You may need to stir occasionally with the glass rod. Be sure to keep the heat at a medium setting. Otherwise, the beaker may break.
6. When you see the colour change, stop heating the beaker. Turn off or unplug the hot plate. Remove the beaker with the beaker tongs. Allow the beaker and crystals to cool on a hot pad.
7. Find the mass of the beaker with the white crystals. Record the mass in your table.
8. Return the anhydrous copper(II) sulfate to your teacher when you are finished. Do not put it in the sink or in the garbage.

Analysis

1. (a) Determine the percent by mass of water in your sample of hydrated copper(II) sulfate. Show your calculations clearly.
   (b) Do you expect the mass percent of water that you determined to be similar to the mass percents that other groups determined? Explain.
2. (a) On the chalkboard, write the mass of your sample of hydrated copper(II) sulfate, the mass of the anhydrous copper(II) sulfate, and the mass percent of water that you calculated.
   (b) How do your results compare with other groups' results?

Conclusion

3. Based on your observations, determine the molecular formula of $CuSO_4 \cdot xH_2O$.

Applications

4. Suppose that you heated a sample of a hydrated ionic compound in a test tube. What might you expect to see inside the test tube, near the mouth of the test tube? Explain.
5. You obtained the mass percent of water in the copper sulfate hydrate.
   (a) Using your observations, calculate the percentage composition of the copper sulfate hydrate.
   (b) In the case of a hydrate, and assuming you know the formula of the associated anhydrous ionic compound, do you think it is more useful to have the mass percent of water in the hydrate or the percentage composition? Explain your answer.
6. Compare the formula that you obtained for the copper sulfate hydrate with the formulas that other groups obtained. Are there any differences? How might these differences have occurred?
7. Suppose that you did not completely convert the hydrate to the anhydrous compound. Explain how this would affect
   (a) the calculated percent by mass of water in the compound
   (b) the molecular formula you determined
8. Suppose the hydrate was heated too quickly and some of it was lost as it spattered out of the container. Explain how this would affect
   (a) the calculated percent by mass of water in the compound
   (b) the molecular formula you determined
9. Suggest a source of error (not already mentioned) that would result in a value of x that is
   (a) higher than the actual value
   (b) lower than the actual value

Section Wrap-up

In section 6.4, you learned several practical methods for determining empirical and molecular formulas of compounds. You may have noticed that these methods work because compounds react in predictable ways. For example, you learned that a compound containing carbon and hydrogen reacts with oxygen to produce water and carbon dioxide. From the mass of the products, you can determine the amount of carbon and hydrogen in the reactant. You also learned that a hydrate decomposes when it is heated to form water and an anhydrous compound. Again, the mass of one of the products of this reaction helps you identify the reactant. In Chapter 7, you will learn more about how to use the information from chemical reactions in order to do quantitative calculations.

Section Review

1. K/U Many compounds that contain carbon and hydrogen also contain nitrogen. Can you find the nitrogen content by carbon-hydrogen analysis, if the nitrogen does not interfere with the combustion reaction? If so, explain how. If not, explain why not.

2. I What would be the mass of a bag of anhydrous magnesium sulfate, $MgSO_4$, if it contained the same amount of magnesium as a 1.00 kg bag of Epsom salts, $MgSO_4 \cdot 7H_2O$? Give your answer in grams.

3. K/U A compound that contains carbon, hydrogen, chlorine, and oxygen is subjected to carbon-hydrogen analysis. Can the mass percent of oxygen in the compound be determined using this method? Explain your answer.

4. C Imagine that you are an analytical chemist. You are presented with an unknown compound, in the form of a white powder, for analysis. Your job is to determine the molecular formula of the compound. Create a flow chart that outlines the questions that you would ask and the analyses you would carry out. Briefly explain why each question or analysis is needed.

5. MC A carbon-hydrogen analyzer uses a water absorber (which contains magnesium perchlorate, $Mg(ClO_4)_2$) and a carbon dioxide absorber (which contains sodium hydroxide, NaOH). The water absorber is always located in front of the carbon dioxide absorber. What does this suggest about the sodium hydroxide that is contained in the CO_2 absorber?

6. I A hydrate of zinc nitrate has the formula $Zn(NO_3)_2 \cdot xH_2O$. If the mass of 1 mol of anhydrous zinc nitrate is 63.67% of the mass of 1 mol of the hydrate, what is the value of x?

7. K/U A 2.524 g sample of a compound contains carbon, hydrogen, and oxygen. The sample is subjected to carbon-hydrogen analysis. 3.703 g of carbon dioxide and 1.514 g of water are collected.
   (a) Determine the empirical formula of the compound.
   (b) If one molecule of the compound contains 12 atoms of hydrogen, what is the molecular formula of the compound?