02

CHEMICAL COMPOSITION

B. PERCENT COMPOSITION, EMPIRICAL & MOLECULAR FORMULAS

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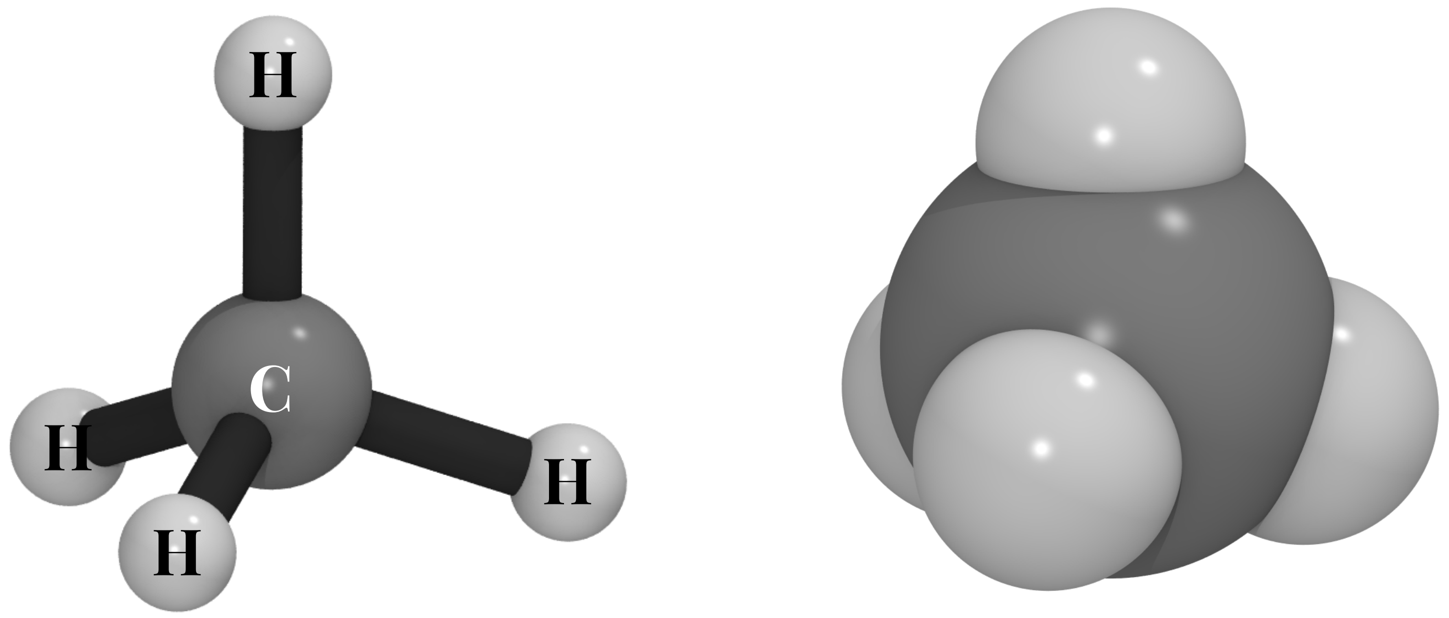
MASS PERCENT I

Objective: *How to think about percent composition*
Be able to calculate mass percentages

Suppose we have a single molecule of methane (CH_4), as shown below. Does this molecule contain more hydrogen or more carbon?



The answer to this question will depend on how we choose to quantify the "amount" of hydrogen or carbon. For instance, the molecule contains more atoms of hydrogen than carbon. Or, we could say that the total volume of the molecule is more hydrogen than it is carbon.

However, a better metric is to consider the mass percent of each element in the molecule or compound.

$$\%\,\mathrm{X} = \frac{\text{total mass of element X}}{\text{total mass of compound}} \times 100\%$$

In terms of *mass*, CH_4 is more carbon than it is hydrogen.

It is easiest to understand this if we consider 1 mol CH_4.

$$\begin{aligned} 1\text{ mol } CH_4 &= 1\text{ mol C} + 4\text{ mol H} \\ &= 1 \times (12.01\text{ g}) + 4 \times (1.008\text{ g}) \\ 1\text{ mol } CH_4 &= 16.042\text{ g} \end{aligned}$$

The mass percent of each element can then be computed:

$$\%\,\mathrm{C} \rightarrow \frac{1 \times (12.01\text{ g})}{16.042\text{ g}} \times 100\% = 74.90\,\%\,\mathrm{C}$$

$$\%\,\mathrm{H} \rightarrow \frac{4 \times (1.008\text{ g})}{16.042\text{ g}} \times 100\% = 25.10\,\%\,\mathrm{H}$$

$$100.00\,\%\text{ total}$$

But what if we had not considered 1 mol? Does it matter?

MASS PERCENT II

Objective: *Understand mass percentages are independent of the amount of sample considered*

Suppose that we were to calculate the mass percentages for 2 mol CH_4 instead.

The total mass of 2 mol CH_4 is now:

$$
\begin{aligned}
2 \text{ mol } CH_4 &= 2 \text{ mol C} + 8 \text{ mol H} \\
&= 2 \times (12.01 \text{ g}) + 8 \times (1.008 \text{ g}) \\
2 \text{ mol } CH_4 &= 32.084 \text{ g}
\end{aligned}
$$

And the mass percentages are then:

$$\% \text{ C} \rightarrow \frac{2 \times (12.01 \text{ g})}{32.084 \text{ g}} \times 100\% = 74.90 \% \text{ C}$$

$$\% \text{ H} \rightarrow \frac{8 \times (1.008 \text{ g})}{32.084 \text{ g}} \times 100\% = 25.10 \% \text{ H}$$

$$100.00 \% \text{ total}$$

These are the same percentages!

It is important to recognize that mass percentages are *independent* of the actual amount of the sample, which is why they are very convenient metric of content for chemists.

Sample Exercise

What is the mass percent of oxygen in each substance?

H_2O (water) and H_2O_2 (hydrogen peroxide)

Again, it is simplest to consider 1 mol of each sample so that we can use the molar mass of each as the total mass.

For H_2O (18.016 g/mol): $\frac{1 \times (16.00 \text{ g})}{18.016 \text{ g}} \times 100\% = 88.81 \% \text{ O}$

For H_2O_2 (34.016 g/mol): $\frac{2 \times (16.00 \text{ g})}{34.016 \text{ g}} \times 100\% = 94.07 \% \text{ O}$

Although 1 mole of H_2O_2 contains twice the moles of O as 1 mole of H_2O, the mass percent of O is not doubled. And, note that while the percent composition is similar, the chemical properties of the substances are quite different!

EMPIRICAL FORMULA

Objective: *Define empirical formula*
Be able to determine empirical formulas

Suppose you have a nitrogen compound (N_xO_y) and you want to figure out what it is, both its chemical formula and name. Through analysis you find the compound is 30.4 % nitrogen by mass. How might you figure out the chemical formula?

Well, since percentages are, by definition, out of "100," it is easiest if we assume we have 100 g of the N_xO_y compound. This means that in 100 g of N_xO_y, there are 30.4 g N and, therefore, also 69.6 g O.

$$\text{Mass Ratio} \rightarrow \begin{cases} 30.4 \text{ g N} \\ 69.6 \text{ g O} \end{cases}$$

So, is the formula then $N_{30.4}O_{69.6}$?

No! Why not? Remember that a chemical formula represents the number of atoms in a compound, not the mass of each, so we must convert these masses to moles of atoms.

$$\text{N} \rightarrow \quad 30.4 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g}} \quad = \quad 2.17 \text{ mol N}$$

$$\text{O} \rightarrow \quad 69.6 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g}} \quad = \quad 4.35 \text{ mol O}$$

So, is the formula then $N_{2.17}O_{4.35}$?

No! Why not? Atoms cannot exist in fractional amounts, so we need a *whole number ratio*, which is achievable if we divide by the smaller mole amount (2.17).

$$\left.\begin{array}{l} \text{N} \rightarrow \quad \dfrac{2.17 \text{ mol N}}{2.17} \quad = \quad 1 \text{ mol N} \\[2ex] \text{O} \rightarrow \quad \dfrac{4.35 \text{ mol O}}{2.17} \quad = \quad 2 \text{ mol O} \end{array}\right\} \rightarrow \text{NO}_2$$

Nitrogen dioxide (NO_2) is called the empirical formula, which represents the simplest or smallest whole number *ratio*.

MOLECULAR FORMULA

Objective: *Define molecular formula*

Be able to determine the molecular formula of a compound based on its empirical formula and molar mass

Now suppose we have dinitrogen tetroxide (N_2O_4), which has a molar mass of 92.02 g/mol. The percent composition by mass of N_2O_4 is actually the same as NO_2!

$$\% \text{N} \rightarrow \frac{2 \times (14.01\ \text{g})}{92.02\ \text{g}} \times 100\% = 30.4\ \%\ \text{N}$$

$$\% \text{O} \rightarrow \frac{4 \times (16.00\ \text{g})}{92.02\ \text{g}} \times 100\% = 69.6\ \%\ \text{O}$$

$$100.0\ \%\ \text{total}$$

Concept Question

If the percent composition of NO_2 and N_2O_4 is identical, how can we differentiate between the two compounds?

To distinguish between the two, we need to know the molar masses of each: NO_2 = 46.01 g/mol and N_2O_4 = 92.02 g/mol.

The empirical formula gives us the simplest whole number *ratio* of atoms in the compound; however, the molecular formula gives the *actual* formula of the compound. To determine the molecular formula, we need to compare the molar mass to the mass of the empirical formula.

$$\text{molecular formula} = (\text{empirical formula})_n$$

$$n = \frac{\text{molecular formula mass}}{\text{empirical formula mass}}$$

In the case of N_2O_4 and NO_2,

$$n = \frac{92.02\ \text{g}}{46.01\ \text{g}} = 2 \rightarrow (\text{NO})_2$$

Note that the empirical and molecular formulas can *actually* be one and the same—it just depends on the masses!

GUIDED EXAMPLE

Objective: *Be able to determine empirical formulas*

Aluminum oxide (Al_xO_y) is 41.51 % Al and 36.92 % O by mass. Determine the empirical formula for this compound.

Let's write out a general procedure for the steps we will take!

Problem-solving Strategy

1. Assume a 100 g sample.
2. Convert the mass percentages to masses.
3. Convert the masses to moles using molar masses.
4. Divide the mole amounts by the smallest mole value.
   - If the mole ratios contains a fraction, multiply the mole ratio by an integer to obtain whole numbers.
5. Write empirical formula from the simplest whole number ratio obtained from previous step.

First, we assume a 100 g sample to simplify the math.

$$\mathrm{Al_xO_y} \rightarrow \begin{cases} \text{Al} \rightarrow 41.51\ \%\ \text{Al} \rightarrow 41.51\ \text{g Al} \\ \text{O} \rightarrow 36.92\ \%\ \text{O} \rightarrow 36.92\ \text{g O} \end{cases}$$

Now we can convert these masses into mole values.

$$\text{Al} \rightarrow 41.51\ \mathrm{g\ Al} \times \frac{1\ \mathrm{mol\ Al}}{26.98\ \mathrm{g}} = 1.54\ \mathrm{mol\ Al}$$

$$\text{O} \rightarrow 36.92\ \mathrm{g\ O} \times \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g}} = 2.31\ \mathrm{mol\ O}$$

Then, we divide by the smallest mole value to try to obtain a simple *whole number* ratio.

$$\text{Al} \rightarrow \frac{1.54\ \mathrm{mol\ Al}}{1.54} = 1\ \mathrm{mol\ Al}$$

$$\text{O} \rightarrow \frac{2.31\ \mathrm{mol\ O}}{1.54} = 1.5\ \mathrm{mol\ O}$$

Sometimes we end up with fractional mole ratios. In these cases, we can simply multiply the mole ratio by an integer to obtain a simple whole number ratio.

$$\left.\begin{array}{l} \text{Al} \rightarrow 1\ \mathrm{mol\ Al} \times 2 = 2\ \mathrm{mol\ Al} \\ \text{O} \rightarrow 1.5\ \mathrm{mol\ O} \times 2 = 3\ \mathrm{mol\ O} \end{array}\right\} \rightarrow \mathrm{Al_2O_3}$$

PROBLEMS

Fundamental Concepts

1. Cisplatin is found to be 65.02 % Pt, 23.63 % Cl, 9.34 % N, and 2.02 % H by mass. Determine its empirical formula.

2. A certain halohydrocarbon is found to be 71.65 % Cl, 24.27 % C, and 4.07 % H by mass.
   a) Determine the empirical formula.
   b) Determine the molecular formula if the molar mass is found to be 148.44 g/mol.

3. For each set of molecular formulas and molar masses, determine the empirical formula and its mass.
   a) C_6H_6 78.11 g/mol
   b) $C_2H_4Cl_4O_2$ 201.85 g/mol
   c) CCl_4 153.81 g/mol

Problem-Solving Skills

4. Assume you have equal masses of H_2SO_4, $C_{12}H_{22}O_{11}$, and $KClO_3$ samples. Which sample contains the greatest number of oxygen atoms?

5. The percent by mass of nitrogen is 46.7 % for a compound containing only nitrogen and oxygen atoms. Which of the following could this compound be?

   N_2O_5 N_2O NO_2 NO NO_3

6. A metallic oxide is 13.38 % oxygen by mass. If the metal cation has a +4 charge, what is the identity of the metal?

7. A 135 g sample of a liquid hydrocarbon (containing only carbon and hydrogen) is combusted in air. The mass of CO_2 collected was 440 g and the mass of H_2O collected was 135 g. The molar mass of the hydrocarbon is 270 g/mol. What is the molecular formula of the substance?

PROBLEM 1

Cisplatin is found to be 65.02 % Pt, 23.63 % Cl, 9.34 % N, and 2.02 % H by mass. Determine its empirical formula.

— answer —

Objective: *Be able to determine empirical formulas given percent composition by mass*

First, we should assume we have a 100 g sample of cisplatin, which means that in a 100 g sample there are

$$100\text{ g Pt}_a\text{Cl}_b\text{N}_c\text{H}_d \rightarrow \begin{cases} 65.02\text{ g Pt} \\ 23.63\text{ g Cl} \\ 9.34\text{ g N} \\ 2.02\text{ g H} \end{cases}$$

Now, we can convert these masses into moles using the molar masses and divide by the smallest mole value to obtain a mole ratio.

$$\begin{array}{lcrcl cc c}
\text{Pt} & \rightarrow & 65.02\text{ g Pt} \times \dfrac{1\text{ mol Pt}}{195.1\text{ g}} & = & 0.3333\text{ mol Pt} & \rightarrow & \dfrac{0.3333\text{ mol Pt}}{0.3333} & = 1\text{ mol Pt} \\
\text{Cl} & \rightarrow & 23.63\text{ g Cl} \times \dfrac{1\text{ mol Cl}}{35.45\text{ g}} & = & 0.6666\text{ mol Cl} & \rightarrow & \dfrac{0.6666\text{ mol Cl}}{0.3333} & = 2\text{ mol Cl} \\
\text{N} & \rightarrow & 9.34\text{ g N} \times \dfrac{1\text{ mol N}}{14.01\text{ g}} & = & 0.667\text{ mol N} & \rightarrow & \dfrac{0.667\text{ mol N}}{0.3333} & = 2\text{ mol N} \\
\text{H} & \rightarrow & 2.02\text{ g H} \times \dfrac{1\text{ mol H}}{1.008\text{ g}} & = & 2.00\text{ mol H} & \rightarrow & \dfrac{2.00\text{ mol H}}{0.3333} & = 6\text{ mol H}
\end{array}$$

Therefore, the empirical formula of cisplatin $PtCl_2N_2H_6$.

PROBLEM 2

A certain halohydrocarbon is found to be 71.65 % Cl, 24.27 % C, and 4.07 % H by mass.

a) Determine the empirical formula.

b) Determine the molecular formula if the molar mass is found to be 148.44 g/mol.

— answer —

Objective: *Be able to determine empirical formulas given percent composition by mass*

Objective: *Be able to determine molecular formulas given the empirical formula and molar mass*

a) First, we should assume we have a 100 g sample. Then, we can convert these masses into moles using the molar masses and divide by the smallest mole value to obtain a mole ratio.

$$\begin{array}{lllllll} \text{C} & \rightarrow & 24.27\text{ g C} \times \dfrac{1\text{ mol C}}{12.01\text{ g}} & = & 2.021\text{ mol C} & \rightarrow & \dfrac{2.021\text{ mol C}}{2.021} = 1\text{ mol C} \\ \text{H} & \rightarrow & 4.07\text{ g H} \times \dfrac{1\text{ mol H}}{1.008\text{ g}} & = & 4.04\text{ mol H} & \rightarrow & \dfrac{4.04\text{ mol H}}{2.021} = 2\text{ mol H} \\ \text{Cl} & \rightarrow & 71.65\text{ g Cl} \times \dfrac{1\text{ mol Cl}}{35.45\text{ g}} & = & 2.021\text{ mol Cl} & \rightarrow & \dfrac{2.021\text{ mol H}}{2.021} = 1\text{ mol Cl} \end{array}$$

Therefore, the empirical formula of this hydrocarbon is CH_2Cl, which has an empirical formula mass of 49.48 g/mol.

b) The molecular formula is always an integer-multiple of the empirical formula: $(CH_2Cl)_n$. We can find the value of n and thus the molecular formula by comparing the molar mass to the empirical formula mass.

$$n = \frac{\text{molar mass}}{\text{empirical formula mass}} = \frac{144.44\text{ g}}{49.48\text{ g}} = 2 \rightarrow (\mathrm{CH_2Cl})_2 \text{ or } \mathrm{C_2H_4Cl_2}$$

PROBLEM 3

For each set of molecular formulas and molar masses, determine the empirical formula and its mass.

– answer –

Objective: *Be able to determine empirical formulas and molecular formulas*

Notice that we are given molecular formulas and the associated masses. Remember that the molecular formula is always a whole number multiple (*n*) of the empirical formula:

$$\text{molecular formula} = (\text{empirical formula})_n \quad ; \quad n = \frac{\text{molecular formula mass}}{\text{empirical formula mass}}$$

First, we can simplify each of the molecular formula into the *simplest* whole number ratio of atoms, which will give us the empirical formula. Note that sometimes the molecular formula and the empirical formula are the same (e.g. CCl_4).

Second, the empirical formula mass can be determined by computing directly based off of the empirical formula or by dividing the molecular mass by the value of n.

Molecular Formula	Molecular Formula Mass		n	Empirical Formula	Empirical Formula Mass
C_6H_6	$78.11\ \mathrm{g/mol}$	→	6	CH	$13.02\ \mathrm{g/mol}$
$C_2H_4Cl_4O_2$	$201.85\ \mathrm{g/mol}$	→	2	CH_2Cl_2O	$100.93\ \mathrm{g/mol}$
CCl_4	$153.81\ \mathrm{g/mol}$	→	1	CCl_4	$153.81\ \mathrm{g/mol}$

PROBLEM 4

Assume you have equal masses of H_2SO_4, $C_{12}H_{22}O_{11}$, and $KClO_3$ samples. Which sample contains the greatest number of oxygen atoms?

– answer –

Objective: *Understand the information given by percent composition by mass*

There are two ways you can solve this problem. The first way involves assuming some mass (let's say 100 g) of each sample and using stoichiometry to determine the number oxygen atoms in each compound. Doing so would indicate the answer is H_2SO_4.

$$100 \text{ g H}_2\text{SO}_4 \times \frac{1\text{mol H}_2\text{SO}_4}{98.09 \text{ g}} \times \frac{4 \text{ mol O}}{1 \text{ mol H}_2\text{SO}_4} \times \frac{6.022 \times 10^{23} \text{ atoms O}}{1 \text{ mol O}} = 2.46 \times 10^{24} \text{ atoms O}$$

$$100 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1\text{mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.34 \text{ g}} \times \frac{11 \text{ mol O}}{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} \times \frac{6.022 \times 10^{23} \text{ atoms O}}{1 \text{ mol O}} = 1.93 \times 10^{24} \text{ atoms O}$$

$$100 \text{ g KClO}_3 \times \frac{1\text{mol KClO}_3}{122.55 \text{ g}} \times \frac{3 \text{ mol O}}{1 \text{ mol KClO}_3} \times \frac{6.022 \times 10^{23} \text{ atoms O}}{1 \text{ mol O}} = 1.47 \times 10^{24} \text{ atoms O}$$

Another way to solve this problem is to compute the percent mass of O in each compound, which will give an indirect measure of the number of atoms of O in each sample. Doing so would also indicate the answer is H_2SO_4.

$$\text{H}_2\text{SO}_4\text{: } \frac{4\times16.00}{98.09}\times100\% = 65.25\% \text{ O} \quad \text{C}_{12}\text{H}_{22}\text{O}_{11}\text{: } \frac{11\times16.00}{342.34}\times100\% = 51.41\% \text{ O} \quad \text{KClO}_3\text{: } \frac{3\times16.00}{122.55}\times100\% = 39.17\% \text{ O}$$

PROBLEM 5

The percent by mass of nitrogen is 46.7 % for a compound containing only nitrogen and oxygen atoms. Which of the following could this compound be? N_2O_5 N_2O NO_2 NO NO_3

– answer –

Objective: *Be able to determine empirical formulas and molecular formulas*

To solve this problem, we can determine the empirical formula of the nitrogen-oxygen compound given the percent composition. But first we need to determine the percent mass of O in the compound: $100.0 - 46.7 = 53.3\%\ \mathrm{O}$.

$$\mathrm{N} \rightarrow 46.7\ \mathrm{g\ N} \times \frac{1\ \mathrm{mol\ N}}{14.01\ \mathrm{g}} = 3.33\ \mathrm{mol\ N} \rightarrow \frac{3.33\ \mathrm{mol\ N}}{3.33} = 1\ \mathrm{mol\ N}$$

$$\mathrm{O} \rightarrow 53.3\ \mathrm{g\ O} \times \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g}} = 3.33\ \mathrm{mol\ O} \rightarrow \frac{3.33\ \mathrm{mol\ O}}{3.33} = 1\ \mathrm{mol\ O}$$

This means that empirical formula and the compound is NO (nitrogen monoxide).

PROBLEM 5

A metallic oxide is 13.38 % oxygen by mass. If the metal cation has a +4 charge, what is the identity of the metal?

– answer –

Objective: *Be able to determine empirical formulas and molecular formulas*

First, understand that the empirical formula for such an ionic compound must be MO_2 because the metal cation is M^{4+} and the anion is O^{2-}. This means that the mole ratio of M:O is 1:2.

Because we are given the mass percentages, we can set up the following work to determine the empirical formula. What we do not know though is the identity of the metal M and its molar mass. Let's say that the molar mass of the M is x g/mol though. That means we would have $\frac{86.62}{x}$ mol M as shown below. So we need to figure out the value of x to identify the metal M.

$$\text{M} \quad \rightarrow \quad 86.62 \text{ g M} \times \frac{1 \text{ mol M}}{x \text{ g}} = \frac{86.62}{x} \text{ mol M} \quad \rightarrow \quad \frac{86.62/x \text{ mol N}}{86.62/x} = 1 \text{ mol M}$$

$$\text{O} \quad \rightarrow \quad 13.38 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g}} = 0.8362 \text{ mol O} \quad \rightarrow \quad \frac{0.8362 \text{ mol O}}{86.62/x} = 2 \text{ mol O}$$

Because we already know the mole ratio of M:O is 1:2, the quantity $\frac{86.62}{x}$ mol M must be the smaller mole amount by which we need to divide each quantity to derive the empirical formula. We can solve the portion related to oxygen to extract the molar mass (x) and identify M as Pb.

$$\frac{0.8362 \text{ mol O}}{86.62/x} = 2 \text{ mol O} \rightarrow x = 207.2$$

PROBLEM 6

A 135 g sample of a liquid hydrocarbon (containing only carbon and hydrogen) is combusted in air. The mass of CO_2 collected was 440 g and the mass of H_2O collected was 135 g. The molar mass of the hydrocarbon is 270 g/mol. What is the molecular formula of the substance?

– answer –

Objective: *Be able to determine empirical formulas and molecular formulas*

First, realize that the combustion of this compound can be expressed as the unbalanced chemical equation: C_xH_y (*l*) + O_2 (*g*) → CO_2 (*g*) + H_2O (*g*).

Second, understand that all of the carbon in the hydrocarbon must be converted into the 440 g of CO_2 and all of the hydrogen in the hydrocarbon must be converted into the 135 g of H_2O. This means that we can determine the amount (moles) of C and H in the hydrocarbon as:

$$440\text{ g CO}_2 \times \frac{1\text{ mol CO}_2}{44.01\text{ g}} \times \frac{1\text{ mol C}}{1\text{ mol CO}_2} = 9.99_8\text{ mol C} \qquad 135\text{ g H}_2\text{O} \times \frac{1\text{ mol H}_2\text{O}}{18.02\text{ g}} \times \frac{2\text{ mol H}}{1\text{ mol H}_2\text{O}} = 14.9_8\text{ mol H}$$

From this information, we can now determine the empirical formulas of the hydrocarbon as C_2H_3 (empirical mass = 27.05 g/mol).

$$\begin{array}{llllllll} \text{C} & \rightarrow & 9.99_8\text{ mol C} & \rightarrow & \dfrac{9.99_8\text{ mol C}}{9.99_8} = 1\text{ mol C} & \times 2 & = & 2\text{ mol C} \\ \text{H} & \rightarrow & 14.9_8\text{ mol H} & \rightarrow & \dfrac{14.9_8\text{ mol H}}{9.99_8} = 1.50\text{ mol H} & \times 2 & = & 3\text{ mol H} \end{array}$$

Because we know the molar mass of the hydrocarbon, we can determine the molecular formulas:

$$n = \frac{\text{molar mass}}{\text{empirical formula mass}} = \frac{270\text{ g}}{27.05\text{ g}} = 10 \rightarrow (\text{C}_2\text{H}_3)_{10}\text{ or C}_{20}\text{H}_{30}$$