1.15: MOLECULAR FORMULAS AND EMPIRICAL FORMULAS (REVIEW)

Learning objective

- Determine the empirical and molecular formulas from combustion data

Molecular formulas tell you how many atoms of each element are in a compound, and empirical formulas tell you the simplest or most reduced ratio of elements in a compound. If a compound's molecular formula cannot be reduced any more, then the empirical formula is the same as the molecular formula. Combustion analysis can determine the empirical formula of a compound, but cannot determine the molecular formula (other techniques can though). Once known, the molecular formula can be calculated from the empirical formula.

EMPIRICAL FORMULAS

An empirical formula tells us the relative ratios of different atoms in a compound. The ratios hold true on the *molar* level as well. Thus, H_2O is composed of two atoms of hydrogen and 1 atom of oxygen. Likewise, **1.0 mole of H_2O** is composed **of 2.0 moles of hydrogen** and **1.0 mole of oxygen**. We can also work backwards from molar ratios since *if we know the molar amounts of each element in a compound we can determine the empirical formula*.

Example 1.15.1: Mercury Chloride

Mercury forms a compound with chlorine that is 73.9% mercury and 26.1% chlorine by mass. What is the empirical formula?

Let's say we had a 100 gram sample of this compound. The sample would therefore contain 73.9 grams of mercury and 26.1 grams of chlorine. How many moles of each atom do the individual masses represent?

For Mercury:

$$(73.9\ g) \times \left(\frac{1\ mol}{200.59\ g}\right) = 0.368\ moles \tag{1.15.1}$$

For Chlorine:

$$(26.1\ g) \times \left(\frac{1\ mol}{35.45\ g}\right) = 0.736\ mol \tag{1.15.2}$$

What is the molar ratio between the two elements?

$$\frac{0.736\ mol\ Cl}{0.368\ mol\ Hg} = 2.0 \tag{1.15.3}$$

Thus, we have twice as many moles (i.e. atoms) of Cl as Hg. The empirical formula would thus be (remember to list cation first, anion last):

$$HgCl_2 \tag{1.15.4}$$

MOLECULAR FORMULA FROM EMPIRICAL FORMULA

The chemical formula for a compound obtained by composition analysis is always the empirical formula. We can obtain the chemical formula from the empirical formula if we know the molecular weight of the compound. The chemical formula will always be some *integer multiple* of the empirical formula (i.e. integer multiples of the subscripts of the empirical formula). The general flow for this approach is shown in Figure 1.15.1 and demonstrated in Example 1.15.2.

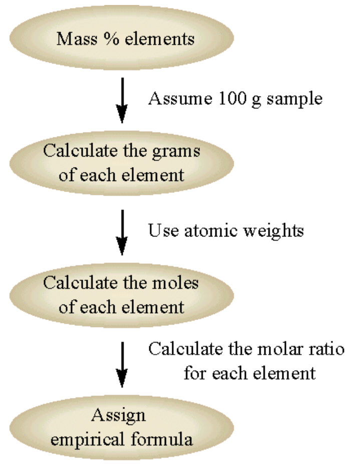


Figure 1.15.1: The general flow chart for solving empirical formulas from known mass percentages.

Example 1.15.2: Ascorbic Acid

Vitamin C (ascorbic acid) contains 40.92 % C, 4.58 % H, and 54.50 % O, by mass. The experimentally determined molecular mass is 176 amu. What is the empirical and chemical formula for ascorbic acid?

Solution

Consider an arbitrary amount of 100 grams of ascorbic acid, so we would have:

- 40.92 grams C
- 4.58 grams H
- 54.50 grams O

This would give us how many moles of each element?

- Carbon

$$(40.92 \;\; g\,\cancel{C}) \times \left(\frac{1 \; mol \; C}{12.011 \;\; g\,\cancel{C}}\right) = 3.407 \; mol \; C \tag{1.15.5}$$

- Hydrogen

$$(4.58 \;\; g\,\cancel{H}) \times \left(\frac{1 \; mol \; H}{1.008 \;\; g\,\cancel{H}}\right) = 4.544 \; mol \; H \tag{1.15.6}$$

- Oxygen

$$(54.50 \;\; g\,\cancel{O}) \times \left(\frac{1 \; mol \; O}{15.999 \;\; g\,\cancel{O}}\right) = 3.406 \; mol \; O \tag{1.15.7}$$

Determine the simplest whole number ratio by dividing by the smallest molar amount (3.406 moles in this case - see oxygen):

- Carbon

$$C = \frac{3.407 \; mol}{3.406 \; mol} \approx 1.0 \tag{1.15.8}$$

- Hydrogen

$$C = \frac{4.5.44 \; mol}{3.406 \; mol} = 1.0 \tag{1.15.9}$$

- Oxygen

$$C = \frac{3.406 \; mol}{3.406 \; mol} = 1.0 \tag{1.15.10}$$

The relative molar amounts of carbon and oxygen appear to be equal, but the relative molar amount of hydrogen is higher. Since we cannot have "fractional" atoms in a compound, we need to normalize the relative amount of hydrogen to be equal to an integer. 1.333

would appear to be 1 and 1/3, so if we multiply the relative amounts of each atom by '3', we should be able to get integer values for each atom.

C = (1.0)*3 = 3

H = (1.333)*3 = 4

O = (1.0)*3 = 3

or

$C_3H_4O_3$

This is our ***empirical formula*** for ascorbic acid.

What about the chemical formula? We are told that the experimentally determined molecular mass is **176 *amu***. What is the molecular mass of our empirical formula?

(3*12.011) + (4*1.008) + (3*15.999) = 88.062 *amu*

The molecular mass from our empirical formula is significantly lower than the experimentally determined value. What is the ratio between the two values?

(176 *amu*/88.062 *amu*) = 2.0

Thus, it would appear that our empirical formula is essentially one half the mass of the actual molecular mass. If we multiplied our empirical formula by '2', then the molecular mass would be correct. Thus, the actual molecular formula is:

2* $C_3H_4O_3$ = **$C_6H_8O_6$**

COMBUSTION ANALYSIS

When a compound containing carbon and hydrogen is subject to combustion with oxygen in a special combustion apparatus all the carbon is converted to CO_2 and the hydrogen to H_2O (Figure 1.15.2). The amount of carbon produced can be determined by measuring the amount of CO_2 produced. This is trapped by the sodium hydroxide, and thus we can monitor the mass of CO_2 produced by determining the increase in mass of the CO_2 trap. Likewise, we can determine the amount of H produced by the amount of H_2O trapped by the magnesium perchlorate.

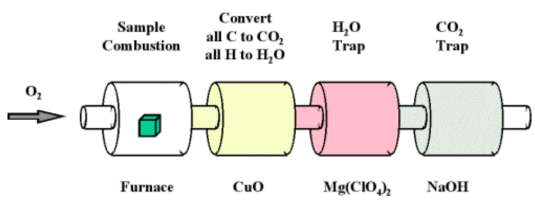


Figure 1.15.2: Combustion analysis apparatus

One of the most common ways to determine the elemental composition of an unknown hydrocarbon is an analytical procedure called combustion analysis. A small, carefully weighed sample of an unknown compound that may contain carbon, hydrogen, nitrogen, and/or sulfur is burned in an oxygen atmosphere,Other elements, such as metals, can be determined by other methods. and the quantities of the resulting gaseous products (CO_2, H_2O, N_2, and SO_2, respectively) are determined by one of several possible methods. One procedure used in combustion analysis is outlined schematically in Figure 1.15.3 and a typical combustion analysis is illustrated in Examples 1.15.3 and 1.15.4.

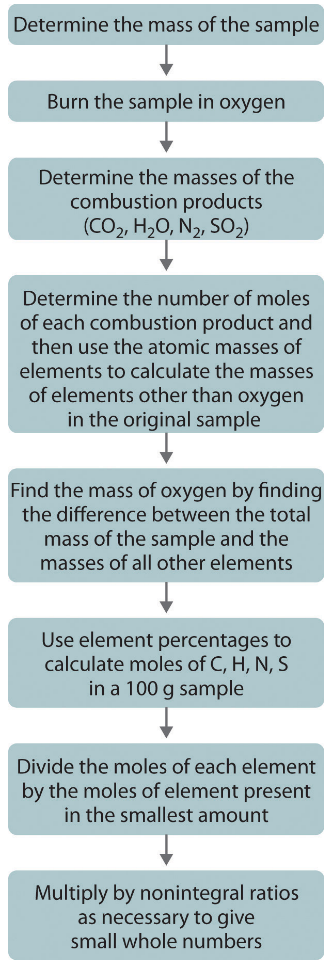


Figure 1.15.3: Steps for Obtaining an Empirical Formula from Combustion Analysis

Example 1.15.3: Combustion of Isopropyl Alcohol

What is the empirical formulate for isopropyl alcohol (which contains only C, H and O) if the combustion of a 0.255 grams isopropyl alcohol sample produces 0.561 grams of CO_2 and 0.306 grams of H_2O?

Solution

From this information quantitate the amount of C and H in the sample.

$$(0.561 \;\; g\; \cancel{CO_2}) \left(\frac{1 \; mol \; CO_2}{44.0 \;\; g \; \cancel{CO_2}}\right) = 0.0128 \; mol \; CO_2 \tag{1.15.11}$$

Since one mole of CO_2 is made up of one mole of C and two moles of O, if we have 0.0128 moles of CO_2 in our sample, then we know we have 0.0128 moles of C in the sample. How many grams of C is this?

$$(0.0128 \;\; mol \; \cancel{C}) \left(\frac{12.011 \; g \; C}{1 \;\; mol \; \cancel{C}}\right) = 0.154 \; g \; C \tag{1.15.12}$$

How about the hydrogen?

$$(0.306 \;\; g \; \cancel{H_2O}) \left(\frac{1 \; mol \; H_2O}{18.0 \;\; g \; \cancel{H_2O}}\right) = 0.017 \; mol \; H_2O \tag{1.15.13}$$

Since one mole of H_2O is made up of one mole of oxygen and ***two*** moles of hydrogen, if we have 0.017 moles of H_2O, then we have 2*(0.017) = 0.034 moles of hydrogen. Since hydrogen is about 1 gram/mole, we must have **0.034 grams of hydrogen** in our original sample.

When we add our carbon and hydrogen together we get:

0.154 grams (C) + 0.034 grams (H) = **0.188 grams**

But we know we combusted *0.255 grams* of isopropyl alcohol. The 'missing' mass must be from the oxygen atoms in the isopropyl alcohol:

0.255 grams - 0.188 grams = 0.067 grams oxygen

This much oxygen is how many moles?

$$(0.067 \;\; g\,\cancel{O}) \left(\frac{1 \; mol \; O}{15.994 \;\; g\,\cancel{O}} \right) = 0.0042 \; mol \; O \tag{1.15.14}$$

Overall therefore, we have:

- 0.0128 moles Carbon
- 0.0340 moles Hydrogen
- 0.0042 moles Oxygen

Divide by the smallest molar amount to normalize:

- C = 3.05 atoms
- H = 8.1 atoms
- O = 1 atom

Within experimental error, the most likely empirical formula for propanol would be C_3H_8O

Example 1.15.4: Combustion of Naphalene

Naphthalene, the active ingredient in one variety of mothballs, is an organic compound that contains carbon and hydrogen only. Complete combustion of a 20.10 mg sample of naphthalene in oxygen yielded 69.00 mg of CO_2 and 11.30 mg of H_2O. Determine the empirical formula of naphthalene.

Given: mass of sample and mass of combustion products

Asked for: empirical formula

Strategy:

A. Use the masses and molar masses of the combustion products, CO_2 and H_2O, to calculate the masses of carbon and hydrogen present in the original sample of naphthalene.
B. Use those masses and the molar masses of the elements to calculate the empirical formula of naphthalene.

Solution:

A Upon combustion, 1 mol of CO_2 is produced for each mole of carbon atoms in the original sample. Similarly, 1 mol of H_2O is produced for every 2 mol of hydrogen atoms present in the sample. The masses of carbon and hydrogen in the original sample can be calculated from these ratios, the masses of CO_2 and H_2O, and their molar masses. Because the units of molar mass are grams per mole, we must first convert the masses from milligrams to grams:

$$mass\,of\,C = 69.00\,mg\,CO_2 \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,CO_2}{44.010\,g\,CO_2} \times \frac{1\,molC}{1\,mol\,CO_2} \times \frac{12.011\,g}{1\,mol\,C} \tag{1.15.15}$$

$$= 1.883 \times 10^{-2}\,g\,C \tag{1.15.16}$$

$$mass\,of\,H = 11.30\,mg\,H_2O \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,H_2O}{18.015\,g\,H_2O} \times \frac{2\,molH}{1\,mol\,H_2O} \times \frac{1.0079\,g}{1\,mol\,H} \tag{1.15.17}$$

$$= 1.264 \times 10^{-3}\,g\,H \tag{1.15.18}$$

B To obtain the relative numbers of atoms of both elements present, we need to calculate the number of moles of each and divide by the number of moles of the element present in the smallest amount:

$$moles\;C = 1.883 \times 10^{-2}\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 1.568 \times 10^{-3}\,molC \tag{1.15.19}$$

$$moles\;H = 1.264 \times 10^{-3}\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 1.254 \times 10^{-3}\,molH \tag{1.15.20}$$

Dividing each number by the number of moles of the element present in the smaller amount gives

$$H : \frac{1.254 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.000 \;\; C : \frac{1.568 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.250 \tag{1.15.21}$$

Thus naphthalene contains a 1.25:1 ratio of moles of carbon to moles of hydrogen: $C_{1.25}H_{1.0}$. Because the ratios of the elements in the empirical formula must be expressed as small whole numbers, multiply both subscripts by 4, which gives C_5H_4 as the empirical formula of naphthalene. In fact, the molecular formula of naphthalene is $C_{10}H_8$, which is consistent with our results.

Exercise 1 1.15.4

a. Xylene, an organic compound that is a major component of many gasoline blends, contains carbon and hydrogen only. Complete combustion of a 17.12 mg sample of xylene in oxygen yielded 56.77 mg of CO_2 and 14.53 mg of H_2O. Determine the empirical formula of xylene.
b. The empirical formula of benzene is CH (its molecular formula is C_6H_6). If 10.00 mg of benzene is subjected to combustion analysis, what mass of CO_2 and H_2O will be produced?

Answer a

The empirical formula is C_4H_5. (The molecular formula of xylene is actually C_8H_{10}.)

Answer b

33.81 mg of CO_2; 6.92 mg of H_2O

EXERCISE 2

Elemental analysis of an organic compound indicates its composition to be 37.82% carbon, 6.36% hydrogen, and 55.82% chlorine.

a. What is the empirical formula for this compound?

b. Mass spectral analysis indicates a molar mass of 129 g/mol. What is the molecular formula for this compound?

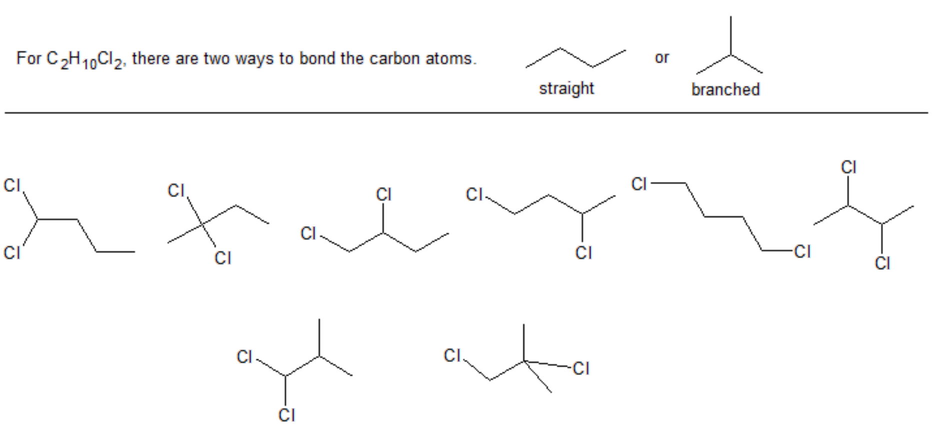
c. Draw all the possible bond-line structures with this molecular formula.

Solutions to Exercise 2

a. C_2H_5Cl with a molar mass of 64.5 g/mol

b. $C_4H_{10}Cl_2$

c. There 8 possible structures with the molecular formula $C_4H_{10}Cl_2$. It can help to start with the different carbon backbones and then systematically add any branches (substituents).



CONTRIBUTORS AND ATTRIBUTIONS

- Mike Blaber (Florida State University)