DETERMINING EMPIRICAL AND MOLECULAR FORMULAE

Let's start with a few definitions. The empirical formula is the simplest formula for a compound. A molecular formula is the same as or a multiple of the empirical formula, and is based on the actual number of atoms of each type in the compound. For example, if the empirical formula of a compound is C_3H_8 , its molecular formula may be C_3H_8 , C_6H_{16} , etc.

An empirical formula is often calculated from elemental composition data. The weight percentage of each of the elements present in the compound is given by this elemental composition.

Let's determine the empirical formula for a compound with the following elemental composition:

40.00% C, 6.72% H, 53.29% O.

The first step will be to assume exactly 100g of this substance. This means in 100g of this compound, 40.00g will be due to carbon, 6.72g will be due to hydrogen, and 53.29g will be due to oxygen. We will need to compare these elements to each other stoichiometrically. In order to compare these quantities, they must be expressed in terms of moles. So the next task will be to convert each of these masses to moles, using their respective atomic weights:

$$40.00\ \text{g C x}\ \frac{1\ \text{mol C}}{12.01\ \text{g C}} = 3.331\ \text{mol C}$$

$$6.72\ \text{g H x}\ \frac{1\ \text{mol H}}{1.008\ \text{g H}} = 6.667\ \text{mol H}$$

$$53.29\ \text{g O x}\ \frac{1\ \text{mol O}}{16.00\ \text{g O}} = 3.331\ \text{mol O}$$

Take notice that since the composition data was given to four significant figures, the atomic weights used in the calculation were to at least four significant figures. Using fewer significant figures may actually lead to an erroneous formula.

Now that the moles of each element are known, a stoichiometric comparison between the elements can be made to determine the empirical formula. This is achieved by dividing through each of the mole quantities by whichever mole quantity is the smallest number of moles. In this example, the smallest mole quantity is either the moles of carbon or moles of oxygen (3.331 mol):

$$\frac{3.331\ \text{mol C}}{3.331\ \text{mol}} = 1.000\ \text{C} = 1\,\text{C}$$

$$\frac{6.667\ \text{mol H}}{3.331\ \text{mol}} = 2.001\ \text{H} = 2\,\text{H}$$

$$\frac{3.331\ \text{mol O}}{3.331\ \text{mol}} = 1.000\ \text{O} = 1\,\text{O}$$

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The ratio of C:H:O has been found to be 1:2:1, thus the empirical formula is: CH_2O. Again, as a reminder, this is the simplest formula for the compound, and not necessarily the molecular formula. Suppose we know that the molecular weight of this compound is 180g/mol. With this information, the molecular formula may be determined. The formula weight of the empirical formula is 30g/mol. Divide the molecular weight by the empirical formula weight to find a multiple:

$$\frac{180\ \text{g/mol}}{30\ \text{g/mol}} = 6$$

The molecular formula is a multiple of 6 times the empirical formula:

$$C_{(1\ x\ 6)}\ H_{(2\ x\ 6)}\ O_{(1\ x\ 6)}\ \text{which becomes}\ C_6H_{12}O_6$$

Alternatively, the empirical and molecular formula may be determined from experimental data. Suppose we have a compound containing the elements, C, H and S. A 7.96mg sample of this compound is burned in oxygen and found to form 16.65mg of CO_2. The sulfur in 4.31mg of the compound is converted into sulfate by a series of reactions, and precipitated as $BaSO_4$. The $BaSO_4$ was found to have a mass of 11.96mg. The molecular weight of the compound was found to be 168g/mol. Using this data, what is the molecular formula of the compound?

The strategy will be to use stoichiometry to determine the mass percent of each of the elements in the compound, and then use the mass percentages to determine the empirical formula. Notice that since all the data is in milligrams, we may carry out the calculations using milli- units throughout.

The only source of carbon for the CO_2 formed came from the compound, thus, determine the milligrams of carbon found in 16.65mg of CO_2 :

$$16.65\ \text{mg}\ CO_2\ \text{x}\ \frac{1\ \text{mmol}\ CO_2}{44.01\ \text{mg}\ CO_2}\ \text{x}\ \frac{1\ \text{mmol C}}{1\ \text{mmol}\ CO_2}\ \text{x}\ \frac{12.01\ \text{mg C}}{1\ \text{mmol C}} = 4.544\ \text{mg C}$$

Now that the "part" of the sample due to carbon is known, one may calculate the percent carbon in the compound, using the mass the sample as the "whole":

$$\frac{4.544\ \text{mg C}}{7.96\ \text{mg sample}}\ \text{x}\ 100 = 57.1\ \%\text{C}$$

The only source of sulfur for the precipitate of $BaSO_4$, came from the compound, thus, determine the milligrams of sulfur in 11.96 mg of $BaSO_4$:

$$11.96\ \text{mg}\ BaSO_4\ \text{x}\ \frac{1\ \text{mmol}\ BaSO_4}{233.39\ \text{mg}\ BaSO_4}\ \text{x}\ \frac{1\ \text{mmol S}}{1\ \text{mmol}\ BaSO_4}\ \text{x}\ \frac{32.06\ \text{mg S}}{1\ \text{mmol S}} = 1.643\ \text{mg S}$$

Similarly, determine the percent sulfur in the compound, using the mass of sulfur as the "part" and the mass of compound as the "whole":

$$\frac{1.643\,\text{mg S}}{4.31\,\text{mg sample}}\text{ x }100 = 38.1\,\%\text{S}$$

The percentage of hydrogen may determined by difference:

$$\%\text{H} = 100.0\% - 57.1\ \%\text{C} - 38.1\ \%\text{S} = 4.8\ \%\text{H}$$

From the elemental composition, we may determine the empirical formula, in the same manner as used in the first example. First, assume exactly 100g of the compound. In 100 grams of the compound, 57.1g would be due to carbon, 38.0g would be due to sulfur and 4.9g would be due to hydrogen. Convert each of these masses into moles using the corresponding atomic weight for each element:

$$57.1\,\text{g C x }\frac{1\,\text{mol C}}{12.01\,\text{g C}} = 4.75\,\text{mol C}$$

$$4.8\,\text{g H x }\frac{1\,\text{mol H}}{1.008\,\text{g H}} = 4.8\,\text{mol H}$$

$$38.0\,\text{g S x }\frac{1\,\text{mol S}}{32.06\,\text{g S}} = 1.19\,\text{mol S}$$

Now that the moles of each element are known, the empirical formula may be determined by dividing the moles of each element by the smallest number of moles. This yields a ratio of the number of each element in the empirical formula.

$$\frac{4.75\,\text{mol C}}{1.19\,\text{mol}} = 3.99\,\text{C} = 4\,\text{C}$$

$$\frac{1.19\,\text{mol S}}{1.19\,\text{mol}} = 1.00\,\text{S} = 1\,\text{S}$$

$$\frac{4.8\,\text{mol H}}{1.19\,\text{mol}} = 4.0\,\text{H} = 4\,\text{H}$$

The ratio of C:H:S has been found to be 4:4:1, thus the empirical formula is: C_4H_4S. The molar mass of the empirical formula is 84g/mol. Since the molecular weight of the actual compound is 168g/mol, and is double the molar mass of the empirical formula, the molecular formula must be twice the empirical formula:

$$C_{(4\text{ x }2)}\ H_{(4\text{ x }2)}\ S_{(1\text{ x }2)}\text{ which becomes }C_8H_8S_2$$