Chapter 9. Chemical Formulas

9.1. Molecular Formulas

We begin by defining a few chemical terms. **Molecules** *are collections of atoms bound together in fixed proportions through electronic attractions and repulsions of their electrons and nuclei.* **Chemical compounds** (Latin *com for with* + *ponere* for put) have more than one element in their molecules. **Pure substances** consist of either atoms or molecules of a single element, or molecules of a single compound. **Mixtures** consist of more than one element or compound mixed together. Uniform mixtures of molecules, where all samples have the same composition, are called **Homogeneous mixtures**, or **solutions**. **Heterogeneous mixtures** have varying chemical composition over different spatial regions.

The idea that matter is ultimately made of molecules with *fixed* (constant) rather than varying numbers of atoms for each molecule was the great insight and contribution of John Dalton. It marked the beginning of chemistry as a science near the turn of the Nineteenth Century. Dalton developed a graphical notation scheme that portrays molecules as collections of spherical atoms, and soon chemists began symbolizing the composition of molecules using letters for element symbols, with subscripts to indicate the number of atoms of the element in the molecule. Such chemical notations are called **chemical formulas** and are extremely useful in visualizing the composition of matter (Chapter 6).

Simplest chemical formulas have the general form ΠE_n, where E is an element symbol and n is the number of atoms of element E in the molecule the formula represents. In more complicated formulas E might represent a group of atoms known to bind together, called a *functional group*. Atoms and groups may be arranged in *structural formulas* to depict how they are connected together. Elements are arranged from more electropositive to more electronegative in simple compounds and groups. In the case of *organic* substances, containing carbon, hydrogen and possibly other elements, it is customary to write carbon first followed by hydrogen, then any other elements in alpabetical order, unless the atomic arrangements within the molecule are displayed.

Example 9.1 The chemical formula for carbon dioxide is CO_2, that for dioxygen is O_2, that for acetylene is HCCH, and that for methyl alcohol is CH_3OH.

The names of the first two examples correspond sensibly to the formulas of the substances, that for acetylene is a structural formula (the molecular formula would be C_2H_2). The last example is somewhat cryptic to the unexperienced chemist because it contains the OH group characteristic of alcohols. Nevertheless, *chemical formulas give clear, unambiguous representations of the molecules of substances* in every case. Chemical nomenclature is taken up in Chapter 10.

9.2. Molecular Mass

Since molecules are combinations of atoms, the total mass of a molecule must be the sum of the masses of the atoms of which it is comprised. In equation form:

$$\boxed{\text{molecular mass} \equiv \sum_{i=1}^{N} n_i \; AM_{i,} \qquad (9.1)}$$

where n_i is the number of atoms of the *ith* element in the molecule, AM_i is its atomic mass, and N is the number of elements in the molecule. Input to this formula comes from molecular formulas, specifying the type and number of atoms in molecules, and tables (such as the periodic table) which provide values for atomic masses. The steps in gathering the necessary information and computing the result can be formulated into a simple algorithm:

Molecular Mass from Chemical Formula Algorithm

Purpose: To calculate the molecular mass of a substance from its chemical formula.

Procedure:

Given a chemical formula representing the numbers and types of atoms of each element comprising one molecule of the substance,

1. Look up the atomic mass of each element in the chemical formula.
2. Multiply the atomic mass of each element by the subscript representing the number of atoms of the element in the chemical formula.
3. Sum the products obtained in step 2 to obtain the total mass of the molecule.

Example 9.2 What is the molecular mass of the compound which has the formula $Ca(NO_3)_2$?

It is necessary to understand that the *parentheses in chemical formulas group together collections of atoms of constant composition*; submolecules if you will. The NO_3 group occurs frequently enough in different chemical compounds to have its own name, nitrate. (Nomenclature is not necessary to understand the processes discussed here, but the curious reader can peek ahead at Table 10.1 in the chapter on nomenclature for a list of such groups.) Subscripts on parenthesized groups show how many such groups are found in the molecule. For molecular mass purposes, the formula could have been written just as well as CaN_2O_6. Also note that *the absence of a subscript in a chemical formula indicates that there is only one atom of the element in the molecule* (as with Ca in the example).

1. From a periodic table, the mass of Ca is 40, that of N is 14 and that of O is 16.
2. Multiply 40 by 1, 14 by 2 and 16 by 6.
3. Molecular mass = $40 \times 1 + 14 \times 2 + 16 \times 6 = 164$

9.3. Chemical Analysis

One of the fundmental tasks of chemistry is the identification of the types and amounts of substances in samples of matter. The branch of chemistry called **analytical chemistry** (Greek *analyein* for resolve) performs *qualitative* (type) and *quantitative* (amount) analysis of substances. Qualitative chemical analysis employs divide-and-conquer heuristics (called "qual schemes") based on selective chemical responses to environment (chemical reactivities, solubilities, etc) to separate substances and identify their components. Quantitative chemical analysis employs precision measurement techniques to determine amounts of substances once they have been identified ("characterized"). Here we will assume that the elements of a substance have been identified (qualitative analysis) and will focus our attention on the problem of determining the amounts of each element, leading to a chemical formula for the substance. There are numerous experimental procedures for determining molecular formulas, some using sophisticated equipment that can measure the properties of individual molecules directly, such as mass spectroscopy. We will begin with a method for determining formulas of compounds based on macroscopic mass measurements that is as old as chemistry itself.

9.4. Empirical Formulas

Macroscopic element mass analyses determine *mass ratios* of the elements in substances, usually reported in terms of *percentage composition*, the mass percent of each element in the compound. According to the Atomic Mol Map of Section 7.5, *number* of atoms in an element is related to the *mass* of the atoms through the atomic mass conversion factor. Thus the Atomic Mol Map can be used to convert element *mass* ratios into element *number* ratios, leading to chemical formulas, called **empirical formulas**. Because the input data involves only ratios of elements, *only relative numbers of atoms in chemical formulas can be deduced from mass percentages*. By convention empirical formulas are expressed in terms of the *simplest* integer ratio of atoms in the chemical formula. We will see how to deduce the *absolute* number of atoms of each element in a molecule in the next section.

When there are several elements in a compound, it is necessary to deduce several ratios of numbers of atoms in the formula. A divide-and-conquer approach computes the number of atoms of each element separately and then combines the results into relative ratios of numbers of elements. Converting percentage composition to absolute masses makes the calculation more manageable. Consider 100 amu of a compound with measured percentages of each element given. (Recall that the atomic mass unit, amu is a measure of mass on the microscopic scale.) There will as many *amu* of each element as there is *percentage* of the element in the 100 amu of the compound. For example, 100 amu of water, which is 11.19% hydrogen by mass, contains 11.19 amu hydrogen. The Atomic Mol Map given in Section 7.5 may then be used to convert the mass of each element into numbers of atoms of the element in the sample.

By convention, molecular formulas contain integer subscripts (because fractions of atoms are hard to imagine), so any fractional number ratios obtained by the above process need to be converted to whole number ratios.

The Empirical Formula Algorithm

Purpose: To determine the empirical (simplest integer) formula of a compound from the mass percentage composition.

Procedure:

1. Assume 100 amu of the compound. Then the number of amu of each element is numerically equal to the mass percentage of that element.
2. For each element in the compound, determine the number of atoms by dividing the amu by the atomic mass of the element.
3. Divide each value from the previous step by the smallest value to obtain ratios of atoms of each element relative to the element having the fewest number of atoms. Each ratio should be an integer or simple fraction, reflecting atom number ratios in the molecule. Since experimental data is not perfectly accurate, some rounding of the values may be necessary to convert decimal values to integers and integer fractions. The fractions may be identifi ed from a table of decimal equivalents of fractions or hand calculations of decimal equivalents.
4. Eliminate any fractions from the previous step by multiplying all fractions by the least common denominator of the fractions. This produces the smallest integer ratio of atoms, called the *empirical or simplest chemical formula*.

Example 9.3 What is the empirical formula for a compound having the composition: 49.0% C, 2.7% H and 48.3% Cl?

1. One hundred amu of the compound contains 49.0 amu C, 2.7 amu H and 48.3 amu Cl.
2. Mol values are 49.0/12.0 = 4.08 for C, 2.7/1.0 = 2.7 for H, and 48.3/35.5 = 1.36 for Cl.
3. Dividing each value from the previous step by the smallest value (1.36) gives 4.08/1.36 = 3 for C, 2.7/1.36 = 1.99 for H, and 1.36/1.36 = 1 for Cl. Round off the value for H to 2.
4. Since there are no fractions to reduce from the previous step, the simplest integer ratio of numbers of atoms is C:H:Cl :: 3:2:1, and the empirical formula is C_3H_2Cl.

9.5. True Molecular Formulas

A *true* **molecular formula** gives not just the simplest integer ratio of atoms of each element in a compound (relative numbers), but shows the *actual* (or absolute) numbers of atoms of each element in the compound. For example, hydrogen peroxide has the empirical (ratio) formula HO, but a true (absolute) molecular formula H_2O_2. Note that the mass of the true molecular formula is exactly two times the mass of the empirical formula. A *molecular formula is some integer multiple of the simplest ratio formula.* To obtain a true molecular formula from an empirical (simplest ratio) formula, some information about the true molecular formula is needed. Some estimate of the molecular mass of the substance suffices to derive a true molecular formula from an empirical one.[1] The molecular mass does not need to be known with great accuracy because it must be an *integer* multiple of the empirical mass, just as the molecular formula is an integer multiple n of the empirical formula, where n is the ratio of the molecular mass to the empirical mass, usually a one-digit number (n-digit integers can be determined from experimental data that is known to n + 1 significant figures.)

[1] One way to determine the molecular mass of gaseous substances is given in Section 15.4; another is molecular mass spectroscopy, described in the Section 12.3.

The Molecular Formula Algorithm

Purpose: To determine the molecular (or true) formula for a substance from the empirical formula and the molecular mass.

Procedure:

1. Obtain the molecular mass of the simplest formula for the empirical formula using the Molecular Mass from Chemical Formula Algorithm
2. Divide the given molecular mass of the substance by the molecular mass of the simplest formula. The result should be a (small) integer.
3. Multiply the number of atoms of each element in the empirical formula by the integer from the previous step to determine the number of atoms of each element in the molecular, or true formula.

Example 9.4 Given that the molecular mass of the compound of Example 9.3 is known to be 147, determine the true formula for the compound.

1. The molecular mass of the empirical formula (C_3H_2Cl) is 73.5.
2. The molecular mass divided by the empirical formula mass is 147/73.5 = 2
3. The total number of atoms in the true molecular formula for the compound is therefore C = 2 x 3 = 6, H = 2 x 2 = 4, and Cl = 2 x 1 = 2, and the true molecular formula is $(C_3H_2Cl)_2$ or $C_6H_4Cl_2$.[2]

9.6. The Molecular Mol Map

Since molecules are collections of atoms, conversions between the various units of amount of matter can be made in the same way as they are for atoms, namely using a **Molecular Mol Map**. The only difference from the Atomic Mol Map of Section 5.5 is that

[2] Either way of writing the molecular formula is acceptable for mass relationships, but they differ in the suggested bonding arrangements. Formulas of the form A_2 suggest dimers while formulas of the form A suggest monomers.

molecular masses are used for molecules where atomic masses were used for atoms. The remaining conversion factor, Avogadro's number, converts between microscopic and macroscopic amounts equally for atoms or molecules. In fact, by thinking of atoms as special cases of molecules having but a single atom (“monatomic molecules”), the Molecular Mol Map and its heuristic become generalizations of the Atomic Mol Map and its associated heuristic. In this interpretation, molecular mass includes atomic mass; the term molar mass serves for both molecules and atoms, and one symbol, MM stands for both.

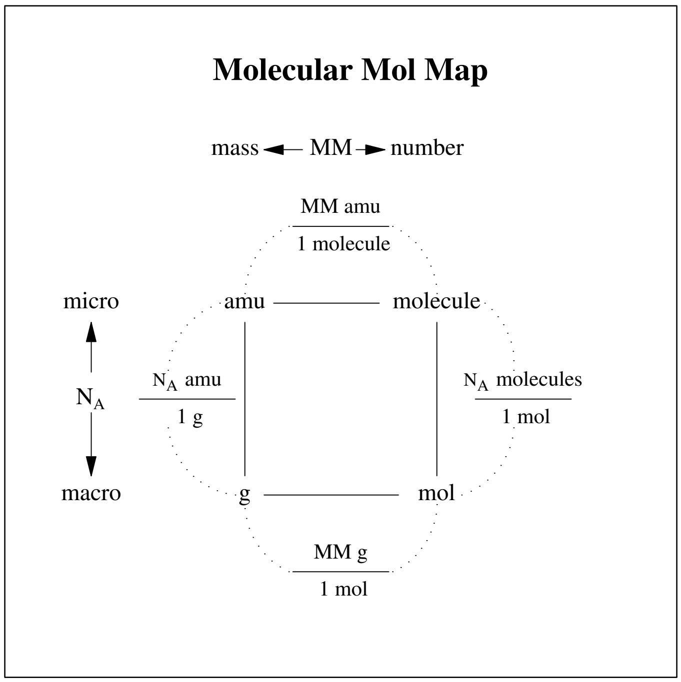

Fig. 9.1 The Molecular Mol Map

The Molecular Mol Map Heuristic

Purpose: To convert from one measure of amount of matter to another.

Procedure:

1. Identify from the statement of the problem the (given) starting and (requested) ending points on the Molecular Mol Map.
2. Determine a path on the map which leads from the starting point to the ending point.
3. Identify the conversion factors connecting the points along the path.
4. Apply the conversion factors on the edges of the Molecular Mol Map path to the given (starting point) quantity to obtain the requested (ending point) quantity.

The Molecular Mol Map summarizes solutions to a variety of calculations involving determining one of the quantities at one corner from that of any other corner. Two examples illustrate how to use the Molecular Mol Map, one simple, the other more complicated.

Example 9.5 "How many *molecules* are in one *gram* of water?"

The Molecular Mol Map shows two possible routes between g and molecules. Either path should give the same final answer. We will choose the path which connects at amu. For practice, convince yourself the same result is obtained by the path connecting at mol.

$$1 \text{ g water} \times \left(\frac{6.02\text{x}10^{23} \text{ amu}}{1 \text{ g}}\right) \times \left(\frac{1 \text{ molecule water}}{18 \text{ amu water}}\right) = 3.3 \text{ x}10^{22} \text{ molecules water}$$

Before looking at the solution to the next example, try to solve it yourself.

Example 9.6 "How many *atoms of hydrogen* are in one *gram* of water?"

In this case, only part of the solution is given by the Molecular Mol Map. We can find the units g and molecules, but atoms are off the map. Nevertheless, we can use the map to get from g to molecules, and a little reflection on the formula for water, H_2O, provides the conversion between molecules of water and atoms of hydrogen in water. We use the same conversions as in Example 9.5 with one additional conversion to get to the final destination:

$$1 \text{ g } H_2O \times \left(\frac{6.02\text{x}10^{23} \text{ amu}}{1 \text{ g}}\right) \times \left(\frac{1 \text{ molecule } H_2O}{18 \text{ amu } H_2O}\right) \times \left(\frac{2 \text{ atoms H}}{1 \text{ molecule } H_2O}\right) = 6.7\text{x}10^{22} \text{ atoms H}$$

9.7. An Extended Molecular Mol Map

We have seen how mass percentages connect relative amounts of matter in mixtures to absolute amounts of the components (Example 2.10). Since the Molecular Mol Map is used to convert between various measures of amounts of matter, and percentage converts between the amount of matter in a mixture to the amount of pure matter, it would be natural to add (mass) percentage to the mol map, connecting g (of pure substance) with g in a mixture.

Matter can be measured in terms of volume in addition to mass and number. The connection between the mass of a given amount of matter and the volume it occupies is the density (Eq. 2.21 and Example 2.10). This suggest adding another node to the mol map connected to grams.

Chemical solutions are molecular mixtures (cf. Chapter 17). Quantities which convert between amounts of solution components and total amount of solution are conversion factors (ratios having two different units). One common solution conversion factor is **molarity**, M, which measures the mols of one substance in a given number of liters of solution:

$$\boxed{M_A \equiv \frac{n_A}{V_{solution}}, \qquad (9.2)}$$

where M_A is the molarity with respect to component A, n_A is the mols of substance A in $V_{solution}$ liters of solution.

Adding density and percentage and solution compositions to the Molecular Mol Map adds new dimensions (cf. Section 2.8) of volumes and mixtures to those of mass and number for pure substances. The depiction of an extended mol map presents somewhat of a challenge, as graphical images are limited to two or three dimensions. A number of arrangements are possible, with one given in Fig. 9.2. The important thing to note is that conversion maps consist of graphs containing nodes and edges with a given relative topology (connectivity); how the components are arranged in any absolute representation is rather arbitrary. How to apply the map to calculations is the critical factor.

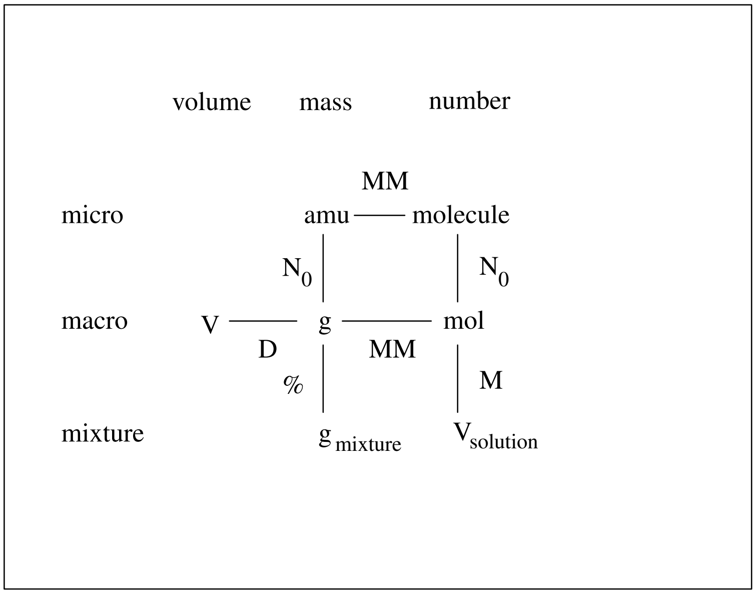

Fig. 9.2 An Extended Molecular Mol Map

The Extended Molecular Mol Map presents a much larger variety of possible computations connecting given nodes than the basic Molecular Mol Map. We will demonstrate a couple of possibilities.

Example 9.7 "How many *grams* of sugar are contained in one *liter* of soda pop?"

Grams are connected to solution volume through solution molarity and component molar mass. Soda pop is an aqueous (water) solution of carbon dioxide (to give a tangy taste), sugar (for sweetness), various flavor and color agents and preservatives. It is a about 0.30 M in sugar, $C_6H_{12}O_6$, MM = 180 g/mol.

$$1 \text{ liter soda pop } \left(\frac{0.30 \text{ mol sugar}}{1 \text{ liter solution}}\right) \times \left(\frac{180 \text{ g sugar}}{1 \text{ mol sugar}}\right) = 54 \text{ g sugar}$$

Example 9.8 "How many *milliliters* of pure gold are contained in one *ton* of gold ore?" The Extended Molecular Mol Map shows a connection between grams of a mixture (ore) and volume of pure substance (V), passing through grams of pure substance (g). To proceed, it is necessary to know how to get on the map from the given input (tons of gold ore). The Mass Conversion Map of Fig. 2.5 is useful here, knowing that there are 2000 lb in one ton. To complete the problem, we need to know the density of gold and the mass percentage gold in the ore. Element densities are listed in various handbooks; $D_{Au} = 19.3 \frac{g}{mL}$. Gold ores contain on average about 10 parts per million gold (by mass). This is a fraction which can be converted to a percentage through the definition, Eq. 2.10, but to be used as conversion factors, percentages should be converted to fractions anyway (as explained in Sections 2.4 and 9.4). Here is one solution:

$$1 \text{ ton ore} \times \left(\frac{2000 \text{ lb}}{1 \text{ ton}}\right) \times \left(\frac{1 \text{ kg}}{0.0454 \text{ lb}}\right) \times \left(\frac{10 \text{ g gold}}{10^6 \text{ g ore}}\right) \times \left(\frac{1 \text{ mL}^3}{19.3 \text{ g gold}}\right) = 0.023 \text{ mL gold}$$

Summary

Matter is composed of molecules consisting of atoms bound together by electron-proton interactions. Molecular formulas show the composition of molecules using element symbols and subscripts indicating the number atoms of each element in the molecule. Molecular formulas can be determined according to the atomic theory from analytical experiments giving percentage element composition and estimates of molar mass. The Molecular Mol Map summarizes strategies for converting between different microscopic and macroscopic measures of amounts of matter.

CHEMICAL FORMULA EXERCISES

1. What is the molecular mass of magnesium phosphate, $Mg_3(PO_4)_2$?
2. What is the empirical formula of a compound which is 65.191% Br and 34.809% O by mass?
3. What is the true molecular formula for the bromine oxide of the previous question, if the molecular mass is 1104.
4. How many *mol* of ice are in 3 g ice and in 3 molecules of ice?
5. How many different kinds of questions can be based on the Molecular Mol Map?
6. How many molecules are in one CC of water?

CHEMICAL FORMULA EXERCISE HINTS

1. Subscripts on parenthesized groups of chemical formulas indicate how many such groups are in the molecule.
2. Assume 100 grams of compound.
3. The true formula is an integer multiple of the empirical formula.
4. Ice is just another form of water. The formula (H_2O) and MM (18) are the same.
5. Count the paths.
6. The density of water is 1 g/ CC (Cubic Centimeter).