Chapter 1, The stuff of chemistry

All beginnings are obscure.
Hermann Weyl, *Space-Time-Matter*

Chemistry is different from baseball. The most obvious reason is, the stuff of chemistry is so small; it effectively is invisible to our everyday senses. Baseballs may be small—particularly to the batter, but at least we can see them.

The everyday material world is composed of *atoms*. Atoms combine to form *molecules*, and chemistry is *the study of substances (atoms and molecules) and the reactions that transform them into other substances.*

We are going to spend two semesters learning just what this means, but a good place to start is to appreciate that atoms are not something we experience directly, because they are so *incredibly tiny*.

We will see how we know soon, but for now, accept that a typical atom is about 10^{-8} cm across. How small is that? Well, let's make the assumption that atoms are cubes (they are really more like spheres, but treating them as cubes makes things simpler here).

> How many atoms are in a liter of liquid? Answer: About 10^{27}.

Here is how this estimate is made. Since we are dealing with a liquid, let's assume the atoms are right next to each other. (In gas gas, by comparison, atoms are very far apart.) A liter is a cube one tenth of a meter on a side. Since one meter is 100 centimeters, a liter is

$$\left(0.1\ \text{m} \times \frac{100\ \text{cm}}{\text{m}}\right)^3 = 1000\ \text{cm}^3.$$

The volume of our hypothetical atom is

$$\frac{(1 \times 10^{-8}\ \text{cm})^3}{\text{atom}} = \frac{1. \times 10^{-24}\ \text{cm}^3}{\text{atom}}$$

Therfore the number of atoms of this size in one liter is

$$\frac{1000\ \text{cm}^3}{1 \times 10^{-24}\ \text{cm}^3 / \text{atom}} = 1 \times 10^{27}$$

—a billion, billion, billion atoms!

So, right from the start this general chemistry course asks us to suspend our disbelief and devote a school year to learning about the properties and transformations of things we can never hope to see directly!

Having said that, there are some key fact about atoms that ultimately give us a secure handhold. The first fact is: atoms *maintain their identity* in chemical transformations.

Atoms can change partners, but they themselves do not change in chemical processes. This leads to the second fact: atoms combine together in simple *whole number ratios*. This is a consequence of the first fact; since atoms maintain their identity, each combination of atoms must contain an integer number of atoms—never a part of an atom.

A third fact known as *Avogadro's hypothesis*, is that *equal volumes* of different *gases* (at the same temperature and pressure) contain *equal numbers* of particles.

Amedeo Avogadro proposed this in 1811, as an explanation of Gay-Lussac's *Law of combining volumes*: Volumes of reacting gases (at the same temperature and pressure) combine in whole number ratios, and product gas volumes are also in whole number ratios of reactant volumes.

For example, it was found that

2 volumes hydrogen + 1 volume oxygen → 2 volumes water vapor

1 volume nitrogen + 1 volume oxygen → 2 volume nitrogen oxide

3 volumes hydrogen + 1 volume nitrogen → 2 volumes ammonia

Avogadro's hypothesis means that we can interpret these reactions in terms of particles; for example,

2 hydrogen particles + 1 oxygen particle → 2 water particles

■ Avogadro's hypothesis

Avogadro's hypothesis was real genius. I do not know what led Avogadro to make it, but perhaps, with nearly 200 years of hindsight, it was the insight that since gases seemingly provide little resistance to movement (for example, it is easy to run in air, but very hard to run in water), they must be *mostly empty space* and so their *volume depends on the motion of the particles rather than on their size*.

> We will learn that at room temperature and 1 atm pressure, a liter of any gas contains about 3×10^{22} particles. Assume each gas particle takes up the volume of a cube 10^{-8} cm on a side. What percentage of the volume of a gas at room temperature and 1 atm pressure is empty space? Answer: 99.997 %.

Avogadro applied the hypothesis to Gay-Lussac's gas volume data to predict correctly that atoms of the same element could combine together to form *diatomic molecules* and to predict correctly the *absolute proportions* of atoms in gaseous molecules.

For example, Gay-Lussac measured that when 2 volumes of hydrogen reacts with one volume of oxygen, the resulting water vapor takes up two (not three) volumes.

2 volumes hydrogen + 1 volume oxygen → 2 volumes water vapor

Avogadro interpreted this in terms of *numbers of particles*, as follows: In 2 volumes of hydrogen there are twice as many particles as in one volumes of oxygen. Since the volume of the water vapor formed is the same as that of the hydrogen, as many particles of water vapor must be produced as there are particles of hydrogen originally. Since there are only half as many oxygen particles to start with, but since each particle of water vapor contains oxygen, Avogadro assumed that the oxygen particles must have *split in two in the reaction*—that is, that oxygen is really a molecule consisting of two atoms of oxygen (actually, any even number would work; we know now it is just two).

If you continue with this line of reasoning with the other two experiments that Gay-Lussac did, you can see that nitrogen and hydrogen are also splitable molecules. This means, for example, that we can summarize the chemical transformation with the *chemical equation*

$$2\ H_2\,(g) + O_2\,(g) \to 2\ H_2O(g)$$

The coefficients multiplying each *chemical formula* denote the *relative numbers* of particles of each substance. Because atoms are so small, in typical transformation the *absolute numbers* of particles involved are enormous, and in particular, *not* just one or several.

■ Incomplete combustion of acetylene

A vivid demonstration of chemical transformation is the combustion of acetylene, C_2H_2. A balloon filled with acetylene gas is taped to a ring stand, and placed over a flame. The *combustion* of the acetylene is so rapid that not enough oxygen is available. As a result the combustion is *incomplete*; rather than producing carbon dioxide and water vapor,

$$C_2H_2(g) + \tfrac{5}{2}O_2\,(g) \to 2\,CO_2(g) + H_2O(g)$$

the result was soot — elemental carbon and water vapor,

$$C_2H_2(g) + \tfrac{1}{2}O_2\,(g) \to 2\,C(s) + H_2O(g)$$

If you look at this through your child eye, it's really magical to get black soot from a clear, colorless gas.

■ Building blocks of atoms

So, at the bottom of chemistry is atoms. There must be more to atoms, though, for otherwise atoms would not combine to form molecules. An atom is composed of one or more negatively charged electrons and a positively charged nucleus. Atoms of different elements contain different numbers of electrons. The total electronic charge is balanced by a corresponding positive charge in the nucleus, so that overall atoms are electrically neutral.

How are the electrons and the nucleus of an atom arranged?

Charge-to-mass ratio of the electron

The first step to answering this question is provided by *JJ Thomson's* measurement in 1897 of the ratio of the charge of the electron and its mass. Thomson produced a beam of electrons that he was able to deflect one way by an electric field, and the opposite way by a magnetic field. By adjusting the two fields so that their deflections just cancelled, he was able to determine the velocity of the electrons in the beam as the ratio of the electric and magnetic field strengths,

$$v = E / H$$

Next, he noted the deflection s of the beam in the presence of the electric field alone. This is a measure of the acceleration experienced by the electron,

$$s = \frac{1}{2}\, a\, t^2$$

during the time *t* spent in the electric field. From Newton's law, the acceleration is

$$a = \frac{F(E)}{m}$$

where

$$F(E) = E\, e$$

is the force exerted on the electron of charge e by the electric field of strength E. The time is given by the ratio of the length of the electron path in the electric field to the velocity of the electron

$$t = \ell / v$$

Combining these relations, the *electron charge-to-mass ratio* can be expressed as

$$e / m = \frac{2\, s\, E}{\ell^2\, H^2}$$

Everything on the right-hand side of this equation is known from the measurements.

In this way Thomson found that e / m is 1.76×10^{11} C/kg. The current, more accurate and precise value is $1.758820173647172 \times 10^{11}$ C/kg.

Charge, and so mass of the electron

The next step was the determination in 1906 by *Robert Millikan* and *HA Fletcher* of the charge e itself. They did this by suspending charged droplets of oil in an electric field just sufficient to offset the opposite gravitational field. The upward force due to the electric field is

$$F(E) = Q\, E$$

where Q is the total charge on the oil droplet. Millikan and Fletcher found that Q was always a multiple of 1.6×10^{-19} Coulombs. Accordingly, they reasoned that this value was the fundamental unit of charge, and in particular the charge carried by a single electron.

The current value of the unit of charge is $1.602176462 \times 10^{-19}$ C.

> Use the value of the charge-to-mass ratio, e / m, to compute the *mass of the electron*. Answer: $9.10938188 \times 10^{-31}$ kg.

This is how we know the mass of the electron.

The nucleus

Earlier we estimated that if we assume the linear dimension of atom is 10^{-8} cm, then 1 L (one liter) there is room for approximately 10^{27} atoms,

> Estimate what percentage of the mass of chemical matter is due to electrons. Use the fact that water molecules have 10 electrons, that the approximate linear dimension of a water molecule is 10^{-8} cm, and that 1 L of water weighs 1 kg. Answer: About 0.9%.

From this information we can compute the the percentage of the mass of water is due to its electrons as

$$\frac{10\ \text{electron}}{\text{molecule}} \times \frac{10^{27}\ \text{molecule}}{\text{Liter}} \times \frac{9.10938188 \times 10^{-31}\ \text{kg}}{\text{electron}} \times \frac{\text{Liter}}{\text{kg}} \times 100\,\% = 0.9\,\%$$

Since we have only estimated the number of atoms in 1 kg to one significant figure, we have expressed the result to this many significant figures. This result means that in 1 kg of water, the mass due to electrons is 0.009 kg.

This result is true generally: *In chemical matter, less than 1 % of the mass is due to electrons*! That is, nearly all of the mass of chemical matter is due to something else.

While nearly all of the mass of an atom in its nucleus, nearly all of the space taken up by the atom is due to its electron! In 1911, *Ernst Rutherford* determined directly that indeed nearly all of an atom consists of a *positively charged nucleus of linear dimension* 10^{-12}*cm*, that is, incredibly *smaller* than the atom itself.

Rutherford did this by measuring the deflection of He^{2+} ions—nuclei of helium atoms—by gold atoms. While most ions were not deflected much at all, a few were *deflected by 180 degrees*. Rutherford calculated that the only way this was possible was if the gold atoms consisted of a cloud of electrons surrounding the very dense, positively charged nucleus, for only then could the gold atom transfer enough momentum to the ions to scatter them backwards in the direction from which they came.

Now, we know that atoms have a linear dimension of about 10^{-8} cm. Since the nucleus evidently has a linear dimension 10,000 times smaller, this means: *In chemical matter, space is mostly empty*!

It also means that the nucleus is almost unimaginably dense. To see how dense, we can compute the mass and volume of a carbon atom nucleus. The radius of this nucleus has been measured (by experiments analogous to Rutherford's) to be $r_{\text{nuc}} = 6.0 \times 10^{-13}$ cm. The nucleus is spherical and so its volume is

$$\frac{4}{3}\,\pi\, r_{\text{nuc}}{}^3 = 9.\times 10^{-37}\ \text{cm}^3.$$

The mass of the carbon nucleus can be determined by measuring its deflection in a magnetic field, in a *mass spectrometer*. It is found in this way to be 1.9927×10^{-26} kg.

> Compute the ratio of the mass to the volume give the density of matter in the carbon nucleus. Answer: $2.2\times 10^{10}\ \text{kg}/\text{cm}^3$.

In non-metric units, using the conversions 2.2 lbs/kg, the density is $4.8\times 10^{10}\ \text{lbs}/\text{cm}^3$, that is, *48 billion pounds per* cm^3! This is very dense indeed! By the way, the number of significant figures in this result is limited by the two significant figures in the radius of the nucleus.

By comparison, the density of matter outside of the nucleus, due to the electrons is tiny,

$$\frac{\text{ElectronMass}}{\text{electron}} \times \frac{10\ \text{electron}}{\text{atom}} \times \frac{1\ \text{atom}}{(10^{-8}\ \text{cm})^3} = 9.\times 10^{-6}\ \text{kg}/\text{cm}^3.$$

In non-metric units this density is $0.00002\ \text{lbs}/\text{cm}^3$.

The result of Rutherford's analysis is the *solar system model of the atom*, with the nucleus acting as the Sun, the electrons as the planets, and their coulomb attraction acting as gravity. Nearly all of the mass is contained in nucleus while nearly all of the space is taken up by the electrons. The nucleus is almost unimaginably dense while the density of matter elsewhere, which is nearly everywhere, is vanishingly small.

> Estimate the percentage of the volume of an atom that is *not* empty space. Do this by assuming essentially all of the matter in the atom is in the nucleus. Answer: 9×10^{-11} %.

One of the great conundrums of the physical world is how it can seem so real when in fact it is nearly entirely empty! Perhaps the next time you look at something, you will ponder the fact that what you see is more than 99% empty space.

Protons, neutrons, and isotopes

Nuclei are composed of two kinds of particles, positively charged *protons* and uncharged *neutrons*. The number of protons, Z, is called the *atomic number*. The number of neutrons, N, combines with the atomic number Z to determine the *mass number* A, that is,

$$A = Z + N$$

A particular isotope of an element E (say) is indicated with the notation ${}^{A}_{Z}\mathrm{E}$. For example, the most common form of carbon atoms have 6 protons and so a nuclear charge of $+6$ and atomic number $Z = 6$, 6 neutrons and so $N = 6$ and mass number $A = Z + N = 12$. All of this is abbreviated as ${}^{12}_{6}\mathrm{C}$. Since atoms are electrically neutral, the number of electrons an atom has is equal to the atomic number, that is, the number of protons in the atom nucleus.

■ Relative atomic mass

The chemical properties of an element are determined by the number of electrons its atoms have. However, the atoms of most elements can have alternative numbers of neutrons, and so different possible mass numbers, A. These different kinds of atom of an element are called *isotopes*.

The masses of individual atoms can be determined in a mass spectrometer, by first removing an electron to create a positively charged *ion* (known as a *cation*), using an electric filed to accelerate the ion to a known speed, and then measuring the deflection of the ion in a magnetic field. The amount of deflection depends on how heavy the ion is; lighter ions are deflected more. Different isotopes of the same element show up as ions deflected by slightly different amounts.

The masses of atoms are measured in *relative atomic mass units*, amu's,on a scale for which an atom of carbon with mass number 12 (6 protons and 6 neutrons) is 12 amu exactly (and so with an infinite number of significant figures). Atomic mass units are *dimensionless*, that is, they are just relative numerical values without any units.

The relative number of isotopes of a given element is known as the *natural abundance* of that isotope. Isotopes of the same element behave the same way chemically. Since isotopes have the same number of electrons, this illustrates that chemistry is controlled by the electrons in atoms. Because isotopes of the same element behave the same way chemically, unless special steps are taken, a sample of an element contains mixtures of its isotopes.

Tables of the relative atomic masses of the elements reflect the average mass of an atom of a element, determined by weighting each isotopic mass by the relative abundance of the isotope. To see how this works, let's compute the relative atomic mass of chlorine. The first step is to find out the isotopes of chlorine and their relative abundance. A convenient place to get this data is The WebElements web site,

http://www.webelements.com

Here is the isotope data for chlorine.

Isotope	Relative mass	% Abundance
^{35}Cl	34.968852721	75.78
^{37}Cl	36.96590262	24.22

> Use this data to compute the weighted relative atomic mass of chlorine atoms. Answer: 35.45.

This answer has been rounded to four significant figures since this is what we are justified in using (do you see why?). The result is consistent with the value 35.4527 tabulated on the inside from cover of the text book (presumably computed from more precise abundance data).

■ Absolute atomic mass

Let's summarize what we have learned about *relative* atomic masses. We can use a mass spectrometer to determine the relative masses of atoms. We use a scale on which an atom of ^{12}C is exactly 12 amu. Since the scale is relative, the amu unit has no dimensions. Relative atomic masses are typically tabulated as averages of the relative masses of the naturally occurring isotopes, weighted by the relative abundance of each isotope.

The next question is, what are the *absolute* masses of atoms? That is, for example, what does 12 atomic mass units (*amu*) correspond to in grams? It is crucial that we determine this, because what we are interested in is how many atoms we have, but, since atoms are so tiny, *the only way we will be able to count atoms is by weighing them*.

Absolute mass is determined by a two-step process. First, a *counting unit* for atoms—a *chemist's dozen*—is defined. This unit is called the *mole* (abbreviated mol; from Latin *moles*, meaning *heap* or *pile*). A mole of a substance is defined as the amount that contains the same number of atoms (or molecules, or other entities) as the number of atoms contained in exactly 12 g of ^{12}C. This number is known as *Avogadro's number*, N_0; its value is $6.02214199 \times 10^{23}$ / mol. So, for example, one mole of ^{12}C weighs exactly 12 g. (Note that the value of N_0 would be different if used a different definition of the mole.)

Then, once the counting unit has been defined, we can use its value and an atom's relative atomic mass to determine the absolute atomic mass of an atom, and so molecules. For example, let's compute the absolute mass of one carbon *atom.* We know the mass of one mole and we know how many atoms there are in a mole. So we can write

$$\frac{\text{mass}}{1\ ^{12}\text{C atom}} = \frac{\text{mass}}{\text{mole}} \times \frac{\text{mole}}{\text{atom}} = \frac{12\ \text{g}}{\text{mol}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atom}} = 1.99264647 \times 10^{-23}\ \text{g} / \text{atom}.$$

The result is displayed to nine significant figures, because the relative mass of ^{12}C is known exactly (by definition) and nine is the number of significant figures in Avogadro's number. One-twelfth of the absolute mass of one atom of ^{12}C,

$$\text{amu} = 1.99264647 \times 10^{-23}\ \text{g} / 12 = 1.66053873 \times 10^{-24}\ \text{g}.$$

defines the *atomic mass unit*. In SI units, the atomic mass unit is $1.66053873 \times 10^{-27}$ kg.

> Calculate the mass of one atom of ^{13}C, in amu. One way to do this is to make use of the ratio of the relative masses of ^{12}C and ^{13}C. You can find this information using WebElements. Answer: 13.003354826 amu. Are you surprised by this answer?

> Use your result from the previous problem to calculate the mass of one atom of ^{13}C in grams. Answer: 2.15926×10^{-26} g.

> The simplest atom, ^{1}H, has one proton and one electron. WebElements reports the mass of ^{1}H to be 1.007825035 amu. Use this information and the mass of the electron to compute that the mass of a proton is 1.67262×10^{-27} kg.

■ Calculating chemical amounts

Once we have a table of relative atomic masses, and have defined the atomic mass unit, by means of the definition of Avogadro's number, we have everything we need to *count atoms and molecules by weighing*. This is very important, because what matters in chemical processes is the number of atoms and molecules we have, not how heavy they are. Let's do some example calculations to see how this works. We will see that in every case, the *key step is to convert weights to moles*.

Given mass of an element, how many atoms do we have

> How many atoms are there is 12.56 g of lead, Pb?

The first thing to do is to express the amount of Pb in terms of moles of lead atoms.

> Use the molar mass of Pb, 207.2 g/mol, to compute that this mass of Pb contains 0.06062 mol.

Once we know the amount of Pb we have in moles, we can express this in terms of the number of Pb atoms, using Avogadro's number $N_0 = 6.022137 \times 10^{23}$.

> Show that the result is 3.65×10^{22} atoms.

This problem shows that in common macroscopic amounts of matter there are truly huge numbers of atoms.

Note that, as we will *always* do, we have displayed the final result, 3.650 10^{22} (*Mathematica* doesn't display trailing zeros unless we ask it to), to the correct number of significant figures. In this case the number of significant figures is four, since the mass of Pb is known to four significant figures.

> What mass of naturally occuring gold, Au, contains 1×10^{9} atoms? Answer: $3. \times 10^{-13}$ g.

> What mass of aluminum, Al, contains the same number of atoms as 2.00 g of helium, He? Answer: 13.5 g.

Given mass of a compound, how many molecules do we have?

> How many molecules of acetylene, C_2H_2, are there in 1.00 g?

The first thing we need to do is to compute the molar mass of acetylene. We do this by adding up the relative atomic masses of each atom that occurs in the molecule, being sure to account for multiple occurrences of a given atom, and then interpreting the result as *the number of grams that contain one mole of molecules*.

> Confirm that the molar mass is 26.038 g/mol.

In this case, since we are doing addition, the number of significant figures (five) is chosen so that there are three digits to the right of the decimal place. Once we have the molar mass, we can calculate the number of moles,

$$\frac{1.00\,\mathrm{g}}{26.038\,\mathrm{g}/\mathrm{mol}} = 0.0384\,\mathrm{mol},$$

and then the number of molecules,

$$0.0384\,\mathrm{mol} \times \frac{6.02214 \times 10^{23}}{\mathrm{mol}} = 2.31 \times 10^{22}.$$

Note that here the units applied to Avogadro's number are now molecules/mol; this illustrates that N_0 is just a number (like a dozen), and that it takes on units according to the problem at hand. Note also that there are only three significant figures in this result, since we only know the mass of compound to three significant figures.

> What mass of CO_2 contains the same number of molecules as 2.0 g of methane, CH_4?
> Answer: 5.5 g.

Given mass of a compound, how many atoms do we have?

> How many atoms of oxygen are there in 21.9 g of sulfuric acid, H_2SO_4?

The key to this problem is to realize that the coefficients in the molecular formula are how many of the corresponding atoms there are in one molecule. So, we can determine how many molecules we have, and then multiply by the atom coefficient to get the number of atoms.

> Calculate the molar mass of H_2SO_4. Answer: 98.0778 g/mol.

> Calculate the moles of H_2SO_4. Answer: 0.224 mol.

> Calculate the molecules of H_2SO_4. Answer: 1.34×10^{23} molecules.

> Calculate the atoms of oxygen. Answer: 5.38×10^{23} atom.

There are four times as many oxygen atoms as there are molecules of sulfuric acid, because there are four oxygen atoms in each molecule.

How much mass is needed to have a given number of molecules?

> What mass of acetominophen, $C_8H_9NO_2$, contains 2.00×10^{22} molecules?

The general approach to this kind of problem is to convert the number of molecules to moles, to convert this number of moles to mass.

> Calculate the number of moles of the compound. Answer: 0.0332 mol.

> Calculate the molar mass of the compound. Answer: 151 g/mol.

> Convert the number of moles to mass. Answer: 5.02 g.

How much mass is needed to have a given number of atoms?

> What mass of iron(III) oxide, Fe_2O_3, contains $11.39\ 10^{22}$ atoms of iron.

The new features in this problem is to use the atomic coefficient to convert atoms to molecules.

> Begin by expressing the amount of iron atoms in moles. Answer: 0.1891 mol.

Next, since there are two atoms of iron in each molecule of Fe_2O_3, there are two moles of iron atoms in each mole of Fe_2O_3. Therefore, the number of moles of Fe_2O_3containing the specified number of iron atoms is

$$\text{mol}\,\text{Fe}_2\,\text{O}_3 = \text{mol}\,\text{Fe} \times \frac{1\,\text{mol}\,\text{Fe}_2\,\text{O}_3}{2\,\text{mol}\,\text{Fe}} = 0.09457\,\text{mol}.$$

> To convert this to mass, we need the molar mass of Fe_2O_3, Answer: 159.69 g/mol.

The result is 15.1 g of Fe_2O_3. As always, the result is expressed to the proper number of significant figures.

■ Problems illustrating calculations with moles

We have gotten some practice applying the mole concept to calculate chemical amounts of substances. The key idea is to convert masses to moles, convert between moles of atoms and moles of molecules, and then convert back to mass, if necessary; we *cannot* go from mass of one substance directly to mass of another substance—*we can only do this by working in terms of moles*.

Using density to count atoms

> Calculate the number of atoms of silicon (Si) in 415 cm^3 of the colorless gas disilane, Si_2H_6, at 0°C (32°F) and atmospheric pressure, where its density is 0.00278 g cm^{-3}. (Oxtoby and Nachtrieb, 2e, problem 1.34.)

Density is the amount of mass in a given volume.

> We are given the density and the volume, so we can compute the mass. Answer: 1.15 g.

> Next, we can use the molar mass of disilane, 62.219 g/mol, to calculate the number of moles. Answer: 0.0185 mol.

Finally, we can use the number of silicon atoms in each molecule, that is, the coefficient of Si in the molecular formula, to calculate the number of silicon atoms in the sample.

$$\text{mol disilane} \times \frac{N_0 \text{ molecule}}{\text{mol}} \times \frac{2 \text{ atoms Si}}{\text{molecule}} = 2.23 \times 10^{22} \text{ atoms.}$$

Mass percentage in chemical synthesis

> A pharmacist prepares an anti-ulcer medicine by mixing 286 g of Na_2CO_3 with water, adding 150 g of glycine, $C_2H_5NO_2$, and stirring continuously at 40°C until a firm mass results. She heats the mass gently until all of the water has been driven away. No other chemical changes occur in this step. Compute the mass percentage of carbon in the resulting white crystalline medicine. (Oxtoby and Nachtrieb, 2e, problem 1.40.)

The mass percentage is the mass of carbon divided by the total mass of the medicine, multiplied by 100. The carbon in the medicine comes from both the Na_2CO_3 and the glycine. For each compound, we can calculate the mass of carbon by first determining how many moles of carbon we have, and then using the molar mass of carbon. Pictorially, we can do

$$\text{mass of compound} \xrightarrow{\text{molar mass of compound}} \text{moles of compound}$$
$$\xrightarrow{\text{molecular formulas}} \text{moles of carbon} \xrightarrow{\text{molar mass of carbon}} \text{mass of carbon}$$

Note that we don't need to work in terms of molecules and atoms, since the number of atoms of an element in a molecule is the same as the number of moles of atoms in a mole of molecules.

Here are the details.

> Begin by computing the molar masses of our starting materials. Answer: Na_2CO_3 = 105.99 g/mol, glycine = 75.067 g/mol.

> Next, compute the moles of carbon that come from Na_2CO_3 and glycine: Answer: Na_2CO_3 = 2.698 mol, glycine = 3.996 mol.

> The total number of moles of carbon is the sum of these, and from that compute the mass, using the molar mass of carbon. Answer" 80.4 g.

> The last step is to express this result as a mass percentage. Answer: 18 %.

There are only two significant figures in the result, because we only know the mass of glycine to two significant figures (150 has two, 150. has three), and so the denominator of this expression is known only to two significant figures.

Mass percentage in a compound

> Here is one last example. Calculate the mass percent of hydrogen in 0.692 g of water, H_2O. (Oxtoby and Nachtrieb, 2e, problem 1.47.)

One way to approach this problem is determine how many moles of water we have; next, using the molecular formula, compute how many moles of hydrogen we have; and finally, compute the mass of hydrogen, and so the mass ratio. Here are the details of this method. When you are comfortable with this kind of reasoning, you will have mastered the mole concept.

> The first step is to convert to moles of water. Answer: 0.0384 mol.

> The next step is to convert to moles of hydrogen. Answer: 0.0768 mol.

Since there are two atoms of hydrogen in each molecule, there are two moles of hydrogen in each mole of molecules. (If this is unclear, it may help to think about ears! People have two ears; a dozen people have two dozen ears!)

> Finally, determine the mass of hydrogen. Answer: 0.0774 g.

> From this result compute the mass percent of hydrogen in water. Answer: 11.2 %.

There is another way to solve this problem, by working directly from the molecular formula. The idea is that the relative mass of hydrogen is *independent of how much water we have*; that is, the molar ratio is always 2 mol H to 1 mol H_2O. This means we can evaluate the mass percentage of hydrogen as

$$\frac{2\,\text{mol H} * 1.0079\,\text{g}/\text{mol H}}{1 \times \text{mol H}_2\text{O} \times (2 \times 1.0079 + 15.999)\,\text{g}/\text{mol H}_2\text{O}} \times 100\,\% = 11.2\,\%.$$

This way of solving the problem may not be as clear as the first method we used. To sort through what is being done, it may help if you break it up into pieces. Notice, by the way, that using this method we know the mass percentage to *five* significant figures, since the significance in the result depends only on the significance in the molar masses!

■ Calculating chemical amounts in chemical reactions

The essence of chemistry is the reaction of substances to form other substances. It is easy to extend calculations of chemical amounts to chemical reactions. Here is an example that shows how. Carbon disulfide, CS_2, is a liquid that is used in the production of rayon and cellophane. It is manufactured from methane and elemental sulfur via the reaction

$$CH_4 + 4\,S \rightarrow CS_2 + 2\,H_2S$$

> Calculate the mass of CS_2 that can be prepared by the complete reaction of 67.2 g of sulfur, S. (Oxtoby and Nachtrieb, 2e, problem 1.62.)

The way to solve this kind of problem is to, as usual, work in terms of moles, but to add the new step of using the coefficients of the chemical equation to relate the moles of one substance to the moles of another substance. In this case, we know that there is 1 mole of CS_2 formed for every 4 moles of sulfur consumed.

> The first step is to convert to moles of sulfur. Answer: 2.096 mol.

> Next, use the coefficients of the chemical equation to calculate the moles of CS_2. Answer: 0.524 mol.

> Finally, convert to mass of CS_2. Answer: 39.9 g.

That's all there is to it!

Writing balanced chemical equations

We have seen that the key to doing these problems is using the coefficients of the chemical equation to relate moles of one substance to moles of another. These coefficients are determined by the process of *balancing the chemical equation* so that the total number of moles of each element is the same on left (reactant) and right (product) side of the equation.

We are going to learn two methods to balance equations in this course. For now we will learn a method that works well for simple reactions; later, we will learn another method to balance more complicated reactions. We can break down the simple method into four steps.

1. Write the molecular formula of each reactant on the left, of each product on the right, and separate the two groups by and right arrow. Think of each formula as representing one mole of the substance, rather than one molecule (or atom).
2. Assign a coefficient of 1 (which is not written explicitly) to the species which has the largest number of elements.
3. Pick, one by one, those elements that appear in only one other species, and choose the coefficient of that species so that the number of moles of that element is the same on both sides of the equation.
4. (optional): Multiply all of the coefficients by a common factor to eliminate any fractional values.

Let's illustrate this method by balancing

$$Fe + O_2 + H_2O \rightarrow Fe(OH)_2$$

1. This step is already done, by the statement of the problem.
2. Choose the coefficient of $Fe(OH)_2$ to be 1 (not written explicitly).
3. In this step: Fe occurs all alone, and only in Fe, to its coefficient is 1 (not written explicitly); H occurs only in H_2O, as 2 moles of H. There are 2 moles of H in $Fe(OH)_2$, so the coefficient of H_2 is 1; O occurs *unbalanced* only in O_2; it also occurs in H_2O, but its coefficient has already been determined. There are 2 moles of O in $Fe(OH)_2$ that need to be accounted for; 1 mole is already accounted for in H_2O, so 1 more mole is needed. Therefore the coefficient of O_2 is 1/2.

The result of these steps is the balanced equation

$$Fe + \frac{1}{2} O_2 + H_2O \rightarrow Fe(OH)_2$$

If we like, we can multiply each species by 2 (step 4) to rewrite the equation as

$$2\ Fe + O_2 + 2\ H_2O \rightarrow 2\ Fe(OH)_2$$

Doing this is up to you; either form is fine, since all that matters is the **relative** amounts of each species, that is, the **ratios** of their coefficients.

Percentage yield

The arrow, →, in chemical equations denotes that reactants are transformed into products. Later in this course we will learn that in fact this process really occurs in *both* directions. The balance between the forward and reverse reactions determines the *yield* of the reaction. For some reactions, the balance is overwhelmingly on the side of the products, and so we think of these reactions as consuming all of the reactants; we say the reaction proceeds 100%. For other reactions, however, this is not the case, either because the reaction hasn't had enough time to take place completely, or because of back reaction of products to form reactants; in such cases the yield of the reaction is less than it would be if the reaction proceeded 100%.

This idea is quantified by defining the *percentage yield* of a reaction. First we calculate the amount of product we expect, assuming 100% yield; this is called the *theoretical yield*. Then we determine the amount of product actually formed. The percentage yield is the ratio of the *actual yield* to the theoretical yield, expressed as a percent.

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\,\%$$

Here is an example of how this works. Titanium dioxide, TiO_2, reacts with carbon and chlorine to give gaseous $TiCl_4$, by the balanced chemical equation

$$TiO_2 + 2\,C + 2\,Cl_2 \rightarrow TiCl_4 + 2\,CO$$

> The reaction of 7.39 kg of titanium dioxide with excess C and Cl_2 gives 14.24 kg of titanium tetrachloride. Calculate the theoretical yield of $TiCl_4$ (assuming 100% reaction) and its percentage yield. (Oxtoby and Nachtrieb, 2e, problem 1.72.)

> As usual, the first thing to do is to convert the reactant into moles. Answer: 92.5 mol.

> Then, we use the coefficients of the balanced chemical equation to calculate the moles of product. Answer: 92.5 mol.

(In this case, since the coefficients are both the same, we get the same number of moles of product as moles of reactant.)

Finally, we calculate the mass of product. Answer: 17500 g.

This is the theoretical yield. The actual yield is 14.24 kg. Therefore the percentage yield is 81.1 %. There are three significant figures in this results because of the significant figures in the mass of the starting material.

■ Limiting reagent

In the reaction of titanium dioxide,

$$TiO_2 + 2\,C + 2\,Cl_2 \rightarrow TiCl_4 + 2\,CO$$

we assumed that we had excess carbon and chlorine.

> What is the minimum amount of these that we need?

We can say immediately, using the coefficients of the chemical equation. Answer: 185 mol C and 185 mol Cl_2.

As long as we have at least this much carbon and chlorine, all of the titanium dioxide will be consumed, assuming 100% yield. This is a case where the titanium dioxide is the *limiting reagent*.

Limiting reagent in sandwich making

A favorite (and delicious) demonstration of mine is one that Alex Golger prepares to illustrate the concept of limiting reagent. First, let's define the chemical equation for making a sandwich as

$$2\ \text{slice}_{\text{bread}} + \text{slice}_{\text{cheese}} \rightarrow \text{sandwich}$$

Let's say we begin with eleven slices of bread and two pieces of cheese. We are then able to make only two sandwiches. Clearly, the cheese is the *limiting reagent*.

	bread	**cheese**	**sandwich**
start	11 slices	2 slices	0
end	7 slices	0	2

Now, Alex has always anticipates my hunger and so, for example, brings an additional 5 pieces of cheese

	bread	**cheese**	**sandwich**
start	7 slices	5 slices	2
end	1 slice	2 slices	5

With these we are then able to make three more sandwiches for a total of five. In this case, the bread is the limiting reagent, since we need two slices to make a sandwich.

What we need versus what we have

A possible source of confusion in working with limiting reagents is the difference between *what is needed versus what is available*. For example, in the chemical equation,

$$3\ A + 2\ B \rightarrow C$$

the coefficients tell the relative amount of each substance *needed* in the chemical transformation. In this sense, the chemical equation is like a recipe, telling the amount of each ingredient needed to make a given amount of product. The amounts in the recipe can be all multiplied by any factor we choose, to scale the amount of product up or down. That is like multiplying each of the coefficients in a chemical equation by the same factor. For example, we can multiply the chemical equation above by 2 to get

$$6\ A + 2\ B \rightarrow C$$

This new equation contains the same information as the first one, namely the relative amounts of each substance in the transformation.

Now, what if we are told that we *have* specific amounts of each substance. These amounts are completely arbitrary and have nothing to do with the coefficients in the chemical equation, that is, with how much we *need*. This is why the amounts that we actually have never affect the coefficients of the chemical equation. For example, say we have 14 moles of A and 19 moles of B. These amounts don't affect the ``recipe'', that is, we *do not* write

$$14\ A + 19\ B \rightarrow C\ \text{(Wrong!)}$$

for this would be confusing what we need (the chemical coefficients) with what we have (the actual amounts present).

Limiting reagent in iron thiocyanate formation

Aqueous solutions of iron(III) ions, $Fe^{3+}(aq)$, and thiocyanate ions, $SCN^{-}(aq)$, are both colorless, but the two ions combine to form iron thiocyanate ions, $Fe(SCN)^{2+}(aq)$, which are reddish brown.

If we have only a small amount of thiocyanate, then no matter how much iron(III) we add, only a small amount of iron thiocyanate will be formed, and so the resulting solution will be only slightly colored. In this case the *thiocyanate is the limiting reagent*. We demonstrated this by combining a 0.0001 M (mol L^{-1}) thiocyanate solution and a 0.2 M iron(III) solution.

If instead we have more thiocyanate than iron(III), then we convert all of the iron(III) to iron thiocyanate. That is, in this case the iron is the limiting reagent. We can demonstrate this by combining a 1.0 M thiocyanate solution with the 0.2 M iron(III) solution. The result was a deeply colored solution.

Limiting reagent in combustion of hydrogen

A vivid demonstration of the effect of a limiting reagent is how reaction of hydrogen and oxygen differs depending on the relative amounts of each present. Consider three balloons ignited with a candle flame.

- The first balloon is filled with pure oxygen. The balloon simply bursts, with no ignition.
- The second balloon is filled with pure hydrogen. The hydrogen combines with the oxygen in the air and reacts quickly to form water vapor. There is a loud noise and a bright ball of flame.
- The third balloon is filled with both hydrogen and oxygen, in a nearly two-to-one ratio. Therefore, the combustion reaction proceeds nearly instantaneously, with a **very** loud noise. The flame ball is much smaller than the case of pure hydrogen, since no mixing with the oxygen in the air is necessary. The reaction is so violent that there is a discernible pressure wave from the explosion.

Let's ignore the oxygen from the air, and calculate the combustion of a mixture of equal volumes of hydrogen and oxygen. We want to know which reactant is the limiting reagent, and how much reactants and products there are before and after the reaction, assuming 100% yield. The balanced chemical equation is

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$$

Since we start with equal volumes of each reactant, we know from Avogadro's hypothesis that we have equal numbers of moles of each gas. Let specify that we have 10.0 moles of each gas.

Here is a *recipe to determine which reagent is limiting:*

> In sequence, calculate how much product can be formed *assuming all of each reactant is consumed*. The reactant that forms the *smallest* amount of product is the limiting reagent.

> Calculate the number of moles of water that 10.0 moles of hydrogen would form. Answer: 10.0 mol.

> Caclculate the number of moles of water that 10.0 moles of oxygen would form. Answer: 20.0 mol.

Since the hydrogen forms the least amount of water, it is the limiting reagent.

When the reaction is over, all of the hydrogen will be consumed (remember, we are assuming 100% yield).

> How much oxygen will have been consumed? Answer: 5.00 mol.

Therefore, at the end of the reaction, 5.0 moles of oxygen will remain.

Here is a summary of the results

	H_2	O_2	H_2O
start	10 mol	10 mol	0 mol
end	0 mol	5 mol	10 mol

The recipe to determine which reagent is limiting *always*, and so I recommend it highly.

■ Study problem on limiting reagent and percentage yield

Here is a study problem which combines the ideas of limiting reagent and percentage yield. Consider the hypothetical balanced chemical equation

$$3\,X + 2\,Y \rightarrow 4\,Z$$

Assume that you combine 11.4 mol of X and 8.97 mol of Y and that the two react with 100% yield.

> Calculate the moles present of each reactant and of the product after the reaction has taken place.

The first step is to determine which is the limiting reagent.

> We do this by comparing how much product can be made if all of each reagent is consumed. Answer: 15.2 mol Z can be made from 11.4 mol of X, 17.9 mol of Z can be made from 8.97 mol Y.

These results show that X is the limiting reagent, and that the theoretical yield of Z is 15.2 mol Z.

> The next step is to compute how much of the Y is consumed by reaction with all of the X. Answer: 7.60 mol.

Therefore, at the end of the reaction, 8.97 mol – 7.60 mol = 1.37 mol of Y remain unused.

> Repeat your calculation assuming 74.0% yield.

Now, if the yield is 74.0%, instead of 100%, then only 74.0% of the of the limiting reagent will be consumed, and only 74.0% of the theoretical yield of Z will be formed..

Here is a summary of the results.

	X	**Y**	**Z**
start	11.4 mol	8.97 mol	0 mol
end, 100 % yield	0 mol	1.37 mol	15.2 mol
end, 74.0 % yield	3.0 mol	3.35 mol	11.2 mol

This problem illustrates all aspects of limiting reagent and percentage yield calculations.

■ Composition of solutions

A convenient way to make specific amounts of substances available for chemical reactions is by means of aqueous solutions. There are three common ways of characterizing the amount of substance—the solute—in the solution.

Molarity, abbreviated M, is the number of moles of solute particles per liter of solution.

Molality, abbreviated m, the number of moles of solute per kilogram of solvent.

Mole fraction, abbreviated X, the moles of one species (either solute or solvent) relative to the total number of moles.

Here is a problem that works with each of these measures of solution composition.

> A solution of acetic acid and water contains 205.0 g/L of acetic acid, CH_3COOH, and 820.0 g/L of water, H_2O. Compute the density of this solution, and then compute the molarity, molality, mole fraction and mass percent of acetic acid in this solution. (Oxtoby and Nachtrieb, 3e, problem 4-24).

Density is defined as the mass of a given volume. We are told that each liter of solution contains 205.0 g of acetic acid and 820.0 g of water. The density evaluates to 1.025 g/mL. (The number of significant figures in the volume is determined by the number of significant figures in the mass specified per liter, in this case four.)

To compute the molarity of the acetic acid, we need to determine the number of moles of acetic acid (the solute) contained in one liter of solution.

> We know the mass of acetic acid in one liter of solution, so we can use its molar mass to get the number of moles of acetic acid in solution. Answer: 3.414 mol.

Since this is the number of moles in one liter, the solution is 3.414 M acetic acid.

> The density of liquid water at 20°C and 1 atm is 1.00 g/cm^3. Calculate the molarity of pure water, that is, the number of moles of water contained in exactly one liter of water. Answer: 55.5 M.

> To compute the molality of the acetic acid, we need to evaluate the moles of acid per kilogram of water. Answer: 4.163 mol/kg.

To evaluate the mole fraction of acetic acid, first we need to know the moles of acid and the moles of water in a given volume of solution. We have already calculated that in one liter there are 3.414 mol of acid.

> Calculate the moles of water in this same volume. Answer: 45.52 mol.

> With this information we can evaluate the mole fraction of acid. Answer: 0.06976.

> Evaluate the mole fraction of water in the solution. Answer: 0.9302.

> Finally,calculate the mass percent of acetic acid. Answer: 20.00 %.

Making a solution of known molarity

How many grams of nickel chloride hydrate, $NiCl_2(H_2O)_6$, are needed to prepare 1.00 L of 0.500 M $NiCl_2$?

> The first step is to calculate the number of moles of $NiCl_2$ needed. Answer: 0.500 mol.

> Next, we compute the number of moles of $NiCl_2(H_2O)_6$ needed. Since there is one mole of $NiCl_2$ per mole of hydrate. Answer: 0.500 mol.

> Finally, we compute the mass of $NiCl_2(H_2O)_6$ needed. Answer: 119 g.

So, to make the solution, we place 119 g $NiCl_2(H_2O)_6$ in a volumetric flask, then carefully add water so that all of the salt dissolves and then continue to add water until the total volume is 1.00 L.

Diluting a solution of known molarity

A stock solution is prepared by placing 25.0 g of ammonium sulfate, $(NH_4)_2SO_4$, in a flask and adding water to bring the total volume to 100.0 mL. Then, 10.00 mL of this solution is combined with 50.00 mL of water. Calculate the molarity of the combined, 60.00-mL solution

The first step is to compute the molarity of the stock solution.

We do this by calculating the number of moles we have. Answer: 0.189 mol.

> Next, calculate the molarity. Answer: 1.89 mol/L.

Next, the key idea is that whenever a solution is diluted, there is *no change in the moles of solute present*. We express this in the equation moles of solute = $V_i\,M_i = V_f\,M_f$. In this problem $V_i = 0.01000$ L, $V_f = 0.06000$ L, and $M_i = 1.89$ mol/L.

> Solve for the final molarity. Answer: 0.315 mol/L.

Note that since we are taking a ratio of volumes we do not need the mL-to-L conversion, that is, we can just take the ratio of volumes in milliliters.

Molarity and titration

A very important example of molarity is to determine the volumes of reactants that would exactly combine with each another. Here is a simple example to illustrate how this works. Let's say we have the reaction

$$2\,\mathrm{A}(aq) + 3\,\mathrm{B}(aq) \rightarrow \mathrm{C}(s)$$

and we know that we have 12.6 mL of A. We find that we have to add 11.2 mL of 1.32 M B to completely react with all of the A. What is the molarity of A?

From the chemical equation, we know that

$$\mathrm{mol\,A} = \mathrm{mol\,B} \times \frac{2\,\mathrm{mol\,A}}{3\,\mathrm{mol\,B}}.$$

From the definition of molarity we know that

$$\text{mol A} = \text{molarity of A} \times \text{liters of A}$$

$$\text{mol B} = \text{molarity of B} \times \text{liters of B}$$

We can combine these equations to get

$$\text{molarity of A} \times \text{liters of A} = \text{molarity of B} \times \text{liters of B} \times \frac{2\text{ mol A}}{3\text{ mol B}}$$

and therefore solve for the molarity of A to be

$$\text{molarity of A} = \text{molarity of B} \times \frac{\text{liters of B}}{\text{liters of A}} \times \frac{2\text{ mol A}}{3\text{ mol B}}$$

> Calculate the molaroity of A. Answer 0.782 mol/L.

Note that, since the volumes appear as a ratio, we do not need to convert them to liters; we would have to do this conversion to calculate the number of moles directly.

Stoichiometry of reactions in solution

Phosphoric acid is made industrially by the reaction of fluroapatite, $Ca_5(PO_4)_3F$, in phosphate rock with sulfuric acid:

$$\begin{aligned} &Ca_5(PO_4)_3F(s) + 2\,H_2SO_4(aq) + 10\,H_2O(l) \rightarrow \\ &\qquad 3\,H_3PO_4 + 5\,(CaSO_4{\cdot}2H_2O)\,(s) + HF(aq) \end{aligned}$$

What volume of 6.3 M phosphoric acid, H_3PO_4, is generated by the reaction of 2.200 metric tons (2200. kg) of fluroapatite?

The first step is to use the chemical equation to find the number of moles of phosphoric acid formed (assuming 100 % yield).

> We do this by converting the mass of fluroapatite to moles. Answer: 4362 mol.

> Next, we use the chemical equation to convert the moles of fluroapatite into moles of acid. Answer: 13090 mol.

> Finally, we use the specified molarity of the acid to determine the volume. Answer: 2100 L.

That is, the reaction can form sufficient fluroapatite to make 2100 L of a 6.3 M solution of phosphoric acid.