Chapter 6 Chemical Reactions, Calculations and Energy Considerations

Earlier, we discussed how most people do not really observe an ice-water system as seldom is a question raised about why, counter to our intuition, the ice floats. In a similar way, we pay very little attention to the fact that we are enveloped in a world of chemical reactions. From the life supporting reactions in our bodies to photosynthesis, we are totally dependent on chemistry to enable us to live, eat and reproduce. In addition to the chemical reactions that take place without significant human control, we also employ chemistry for a remarkable number of functions that contribute both positively and negatively to our lives. Try to think of some chemicals that you use in addition to water and oxygen that did not in some way result from the efforts of a chemist. The reaction most familiar to us for better or for worse is the burning of fossil fuels to supply our vast energy needs. For example, many of us use natural gas for heating homes and water and for cooking. Natural gas is composed of very approximately 90% methane (CH_4) thus the burning of methane can be written as:

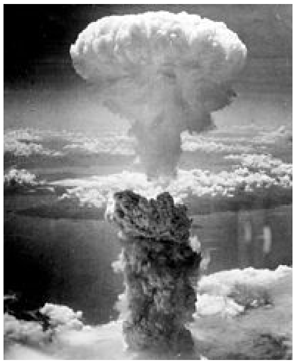
$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O$$

For reactions of this type, the amount of methane provided determines how much reaction takes place because an excess of oxygen is provided by the atmosphere. However, for many reactions, the correct ratio of reactants is often desirable to avoid waste and maximize product yields. To determine the amounts of reactants needed requires the writing of a reaction and subsequent balancing of the reaction to make it into an equation. The equation enables the chemist to calculate the optimal ratio of reactants.

Combustion powers Curiosity to Mars to search for evidence of life including methane.

Balancing reactions. To write a chemical equation, the correct formulas of the reactants and products must first be written down. Between reactants and products, it is common to insert an arrow indicating the direction of the reaction. After the reaction is balanced, the arrow is sometimes replaced with an equal sign. The next goal is to balance the reaction. Balancing is achieved by keeping two thoughts in mind. Lavoisier demonstrated that within measurable limits, mass is conserved in chemical reactions thus the reaction should have the same amount of mass on both sides of the reaction.

Einstein was able to prove that energy and mass are theoretically convertible with the relationship expressed in the famous equation $\mathbf{E = mc^2}$. In a later chapter, we shall see that in nuclear reactions, the amount of mass converted to energy while still a small percentage of the mass of the reactants is measurable. For chemical reactions, either energy input is required or energy is evolved but the mass change while real is significantly below the limits of our best balances.



Nagasaki atomic bomb, 08/09/45

Since nuclei are never changed in chemical reactions, if the number of atoms of each element present in reactants and products is kept the same, the mass will be balanced. This absolutely cannot be done by changing formulas or subscripts of formulas. Balancing can only be accomplished by adjusting coefficients or the numbers in front of each formula until the atoms are balanced. Returning to the burning of methane, the writing of the formulas results in:

$CH_4 + O_2 \rightarrow CO_2 + H_2O$

Simple reactions such as this one can often be balanced by inspection but more complex reactions are best approached if a logical system is used. One method is to first focus on the most complex substance and leave the simplest substance until last. The reason for this is that coefficient changes made to complex substances change the number of several elements while changing the coefficient of the simplest substance changes the fewest number of elements. In the case above, leave the oxygen coefficient until last as it is the simplest substance and only the oxygen numbers are changed by this coefficient. The other three substances have about the same complexity and it does not really matter which one you start with. If you start with the methane, you are putting an understood coefficient of 1 in front of it and you notice when you look at carbon dioxide that putting a 1 there balances the carbons. However, putting a 1 in front of the methane provided 4 hydrogens and looking at the water, a coefficient of 1 would only provide 2 hydrogens. Take the number needed which is 4 and divide by the hydrogen subscript 2 and the resulting 2 is placed in front of the water.

$1\ CH_4 + O_2 \rightarrow 1\ CO_2 + 2\ H_2O$

Looking at the right side of the equation, there are 4 oxygens present so we shift our attention to the oxygen molecule which we decided in the beginning should be left until last. The 4 oxygens divided by its subscript (the number of oxygens per package) gives a coefficient of 2. The 1's are understood and not written.

$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$

To complete the process, you should check to make sure all the elements are balanced. For a second example, inspect the steps for the combustion of propane and ethanol.

$1\ C_3H_8 + O_2 \rightarrow 3\ CO_2 + H_2O$
$1\ C_3H_8 + O_2 \rightarrow 3\ CO_2 + 4\ H_2O$
$C_3H_8 + 5\ O_2 = 3\ CO_2 + 4\ H_2O$

$C_2H_6O + O_2 \rightarrow CO_2 + H_2O$
$1\ C_2H_6O + O_2 \rightarrow 2\ CO_2 + 3\ H_2O$
$C_2H_6O + 7/2\ O_2 = 2\ CO_2 + 3\ H_2O$
$2\ C_2H_6O + 7\ O_2 = 4\ CO_2 + 6\ H_2O$

Please notice that the third reaction for ethanol has a fractional coefficient (7/2). Clearly, if you are thinking about the reaction on an atomic scale, fractional coefficients do not make sense as half atoms are not possible. However, the coefficients really provide ratios of reactants and products and could represent large scale amounts. For instance, the equation could mean that 1 mole of ethanol

+ 7/2 moles of oxygen should yield 3 moles of carbon dioxide and 3 moles of water. This is perfectly acceptable. Some chemists do not like to leave fractional coefficients in the balanced equation. Since the coefficients represent ratios, it is possible to remove the fraction by multiplying through by the denominator as has been done in the last equation.

Balance the following reactions:

a. ___$C_2H_6(g)$ + ___$O_2(g)$ = ___$CO_2(g)$ + ___$H_2O(g)$

b. ___$Na_2O(s)$ + ___$H_2O(l)$ = ___$NaOH(aq)$

c. ___$KClO_3(s)$ = ___$KCl(s)$ + ___$O_2(g)$

d. ___$Al(s)$ + ___$HCl(aq)$ = ___$AlCl_3(aq)$ + ___$H_2(g)$

e. ___$C_3H_6O(g)$ + ___$O_2(g)$ = ___$CO_2(g)$ + ___$H_2O(g)$

f. ___$Fe(s)$ + ___$O_2(g)$ = ___$Fe_2O_3(s)$

g. __ $N_2(g)$ + __ $H_2(g)$ = __ $NH_3(g)$

h. __ $Al(s)$ + __ $HCl(aq)$ = __ $AlCl_3(aq)$ + __ $H_2(g)$

i. __ $C_6H_{12}O_6(s)$ + __ $O_2(g)$ = __ $CO_2(g)$ __ $H_2O_{(g)}$

Chemical calculations. Chemists use the word stoichiometry to describe calculations that apply to the amounts of reactants and products in a chemical reaction. The coefficients in the balanced reaction give the ratios of the amounts of reactants needed and the amounts of products that could form. Some important points need to be stressed here. First, notice the word "could" in the last sentence. Just because a reaction can be written does not mean it will take place. The reaction might be endothermic which means the reaction is uphill in energy and requires energy input for it to occur. It is also possible that the reactants could react in a different way to give different products. The reaction will usually proceed by the lowest energy pathway. Another issue is the position of equilibrium. Some reactions, albeit a minority, end up with a mixture of starting materials and products or at a position of equilibrium. We will encounter this situation when acids are discussed in the next chapter. The rate of reaction also needs to be considered. Some reactions such as the rusting of iron are slow (fortunately for this reaction) and others are very fast. If the reaction is extremely fast and evolves energy and gases, the reaction might be explosive and very dangerous. Finally, the ratios of the amounts refers to the number of molecules of the substance, not the mass. The coefficients do not give mass ratios. To illustrate, if you wanted to have the same number of marbles as bowling balls, weighing equal amounts would clearly not give the same number of each.

For the reaction, $CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$ the coefficients 1, 2, 1, 2 tell us that 1 molecule of methane reacts with 2 molecules of oxygen to form 1 molecule of carbon dioxide and 2 molecules of water. Since we cannot weigh one atom, chemists usually think of the reaction as telling us that 1 mole of methane reacts with 2 moles of oxygen to form 1 mole of carbon dioxide and 2 moles of water. Recall that a mole is defined as the number of atoms in 12 grams of carbon-12. Experimental measurements reveal that this number now called Avogadro's number is

$6.0221417930\times10^{23}$ units/mole. For most calculations, this is rounded off to 6.022×10^{23} units/mole. The units must be included as a measurement without units is meaningless. If a full grown adult were to tell you that they weigh 68, unless you make an assumption, the 68 would have no meaning. An American would probably assume that the measurement was made in pounds and this would seem like a dangerously low mass. However, if the units kg were attached, the measurement would seem possible.

Just as you can talk about a dozen of any item, you can also talk about a mole of anything. One mole of methane has exactly the same number of molecules as a 1 mole of oxygen. Thus using moles instead of molecules when using the coefficients to determine ratios of reactants and products is perfectly legitimate. Use of moles maintains the correct ratios since a mole of anything contains the same number of particles. The equation for the methane combustion tells us that for each mole of methane that reacts, two moles of oxygen are required. In other words, the equation tells us that we can extract the ratio (2 moles O_2/1 mole CH_4) using the ratio of the coefficients or the inverse (1 mole CH_4 /2 moles O_2) can be used as a unit conversion.

Unit conversions: a very useful calculation tool.
A unit conversion is a ratio that represents equality or unity. Because of the equality, any measurement can be multiplied by a unit conversion without changing the value of the measurement. As a consequence of the change of units, the numbers will also change but the value of the measurement stays the same. As an example, suppose you are 1.80 meters tall and want to know your height in centimeters. By definition, 100 cm = 1 meter. Using algebra, we can divide both sides of the equation by 1 meter yielding:

$$\frac{100\text{ cm}}{1\text{ m}} = 1 \qquad \frac{1\text{ m}}{100\text{ cm}} = 1$$

The ratio is 1 thus the ratio is a unit conversion. We also could have divided both sides of the equation by 100 cm yielding the second unit conversion above. Since unit conversions equal 1, any unit conversion can be inverted and it will still equal 1. Now we take the measurement of 1.80 meters and multiply it by the appropriate unit conversion so that the given units will cancel and the answer will have the desired units.

$$(1.80\text{ m})\frac{(100\text{ cm})}{1\text{ m}} = 180\text{ cm}$$

This simple example could have been performed in your head but this procedure makes more complex calculations more straightforward. Suppose instead you wanted your height in inches. There are exactly (due to definition) 2.54 cm/1 inch and 1 inch/2.54cm. It would be possible to multiply the 180 cm by 1 inch/2.54 cm or unit conversions can be strung one after another to convert the initial measurement to the desired units.

$$(1.80\text{ m})\frac{(100\text{ cm})}{1\text{ m}}\left(\frac{1\text{ inch}}{2.54\text{ cm}}\right) = 70.9\text{ inches}$$

Most Americans are not too familiar with the metric system but scientists generally work with the metric system. One obvious reason for the metric preference is that units are related by powers of 10 rather than by factors of 3, 4, 12, 16, 5280 etc. Name several other advantages of the metric system (meters, kilograms, liters) over the system retained by the U. S. but wisely replaced by the metric system by the U. K. For an introduction to the metric system, see the insert at the end of this chapter.

To be able to perform mole calculations, we need to review the concept of molecular mass as we need the values of molecular mass to calculate moles from mass and mass from moles. The molecular mass is the number of grams needed to provide 1 mole of the substance. Since 12 g of carbon-12 is defined as 1 mole, the amount required for any substance is the amount in grams determined by adding the atomic masses from the formula. For instance, a mole of methane (CH_4) weighs 12.011 + 4(1.008) = 16.043 g/mole. A molecule of methane has a mass that is 16.043 /12 times more massive than a carbon atom so a mole of methane has a mass 16.043 /12 the mass of a mole of carbon-12. Notice the 12.011 was used above because the atomic masses are based on the isotope carbon-12 but carbon in nature has about 1% carbon-13 so the atomic mass of carbon is 12.011. To weigh a mole of carbon on the earth would require 12.011 g, not 12 g. The mass of a mole of ammonium sulfate [$(NH_4)_2SO_4$] would be calculated like this:

$$2[14.007 + 4(1.008)] + 32.07 + 4(15.999) = 132.14\text{ g/mol}$$

If you have 5.00 g of ammonium sulfate, you would have $(5.00\text{ g})\left(\frac{1\text{ mole}}{132.14\text{ g}}\right) = 0.0378$ mole

If you have 0.25 mole of ammonium sulfate, you would have $(0.25\text{ mole})\left(\frac{132.14\text{ g}}{1\text{ mol}}\right) = 33$ g

Suppose you want to calculate how many grams of stomach acid (HCl) can be neutralized by a typical dose of milk of magnesia [0.80 g $Mg(OH)_2$]:

$$2\ HCl(aq) + Mg(OH)_2(aq) = MgCl_2(aq) + 2\ H_2O(l)$$

$$0.80\text{ g }Mg(OH)_2 \cdot \frac{1\text{ mole }Mg(OH)_2}{58.32\text{ g }Mg(OH)_2} \cdot \frac{2\text{ mole HCl}}{1\text{ mole }Mg(OH)_2]} \cdot \frac{36.465\text{ g HCl}}{1\text{ mole HCl}} = 1.00\text{ g HCl}$$

It is also possible to calculate the amount of magnesium chloride that should be formed using the mole ratio $\frac{1\text{ mole }MgCl_2}{1\text{ mole }Mg(OH)_2}$ times the molecular mass of magnesium chloride.

1. Determine the following:
   - a. The formula mass of $Ca(NO_3)_2$
   - b. The formula mass of $CuBr_2$
   - c. The number of moles in 5.4 g of water
   - d. The number of moles in 0.36 g of NaCl
   - e. The mass in grams of 5.1×10^{-2} moles of $ZnSO_4$.
   - f.* The mass in grams of 4.5 moles of $Fe(NO_3)_3$

2. Aluminum reacts with hydrochloric acid to give aluminum chloride and hydrogen gas according to the following equation:

   $$2\ Al_{(s)} + 6\ HCl_{(aq)} = 2\ AlCl_{3(aq)} + 3\ H_{2(g)}$$

   If 2.7 grams of aluminum are reacted with an excess of hydrochloric acid, what is the theoretical yield in grams of hydrogen gas?

Energy considerations are an extremely important part of the study of chemical reactivity. Any reaction that can be written can potentially proceed from left to right. But it is equally possible that given the products, a reaction could occur from right to left. It is also possible that neither direction will go because of the existence of alternative reaction pathways that are more favorable in terms of energy or that the rates of either direction are so slow that the reaction will not be noticeable in a reasonable amount of time. Use of energy information enables prediction of the direction, extent and rate of the reaction.

A reaction that evolves heat is said to be exothermic and one that absorbs heat is endothermic. The chemical term for the heat of a reaction run at constant pressure (common because most reactions are run open to the atmosphere) is enthalpy and designated with the symbolism ΔH. As a result of conventions, ΔH is negative for an exothermic reaction and positive for an endothermic reaction. Commonly exothermic reactions go on their own and endothermic reactions require an input of energy if the reaction is to be carried out. The exothermicity and endothermicity of a reaction do not tell us anything about the rate and actually leave out another very important but somewhat abstract consideration called entropy ΔS. For a reaction to actually be favored, the free energy, $\Delta G = \Delta H - T\Delta S$ must be negative. Normally the ΔH term dominates the expression. This means that an exothermic reaction with a negative ΔH will usually have a negative ΔG value and be spontaneous (go left to right). Please note that spontaneous might infer a fast rate to a non-chemist but to a chemist, spontaneous means the free energy is favorable and does not give us any information about the rate. Rusting is a spontaneous reaction but clearly a very slow one.

1st Law of Thermodynamics: Energy is always conserved and cannot be created or destroyed but energy can be converted from one form into another. The total amount of energy and matter in the Universe remains constant, merely changing from one form to another.

2nd Law of Thermodynamics stated several ways:

1. The entropy of the universe increases during any spontaneous process.
2. Energy spontaneously disperses from being localized to becoming spread out if it is not hindered from doing so. Entropy measures the spontaneous dispersal of energy: how much energy is spread out in a process, or how widely spread out it becomes — at a specific temperature.
3. The entropy of an isolated system never decreases, because isolated systems always evolve toward thermodynamic equilibrium, a state with maximum entropy.

For the combustion of four commonly used hydrocarbon sources of energy, methane, propane, butane and octane, inspect the values for enthalpy per mole and per gram for the reaction.

	ΔH (kJ/mol)	ΔH/ (kJ/g)
$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O$	-890	-55.6
$C_3H_8 + 5\,O_2 = 3\,CO_2 + 4\,H_2O$	-2220	-50.5
$C_4H_{10} + 13/2\,O_2 = 4\,CO_2 + 5\,H_2O$	-2877	-49.6
$C_8H_{18} + 25/2\,O_2 = 8\,CO_2 + 9\,H_2O$	-5460	-47.9

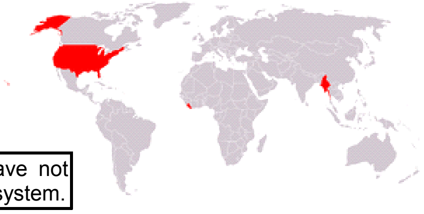
The data above demonstrate that the enthalpy production decreases with the number of carbons. Also less carbon dioxide is produced for the same amount of energy production for methane.

The metric system. The word metric is derived from Greek or Latin and in both means "relating to measurement." Because it would be very inconvenient to use only one measurement unit as some measurements would require very small numbers and others very large, different units are defined for convenience. For example, if the meter was the only unit available for distance, your height would be a convenient number between about 1.5 and 2.0 meters. However an atom would have a diameter of about 0.0000000001 m or $1\text{x}10^{-10}$ m, and the distance from the earth to the sun would be 149,600,000,000 meters or $1.496\text{x}10^{11}$ m. The very small and very large numbers are difficult to write and relate to. In the metric system, this issue is easily overcome with the use of prefixes that relate the units by convenient powers of 10. The prefixes used commonly by chemists are given below:

pico	10^{-12}
nano	10^{-9}
micro	10^{-6}
milli	10^{-3}
centi	10^{-2}
kilo	10^{3}

Useful metric-American unit conversions:

$$\frac{2.54\text{ cm}}{1\text{ inch}} \quad \frac{1\text{ L}}{1.057\text{ qts}} \quad \frac{28.35\text{ g}}{1\text{ oz}} \quad \frac{1\text{ kg}}{2.20\text{ lb}} \quad \frac{1\text{ km}}{0.621\text{ mile}}$$



Countries in red have not adopted the metric system.

When referring to atomic and molecular dimensions, picometers and nanometers are commonly used and easily interconvertible without a calculator. Contrast the metric system to the American system where inches, feet, yards and miles are related by factors that make calculators almost necessary for conversion. For mass in the metric system, milligram, gram and kilogram quantities are usually convenient. In the American system, ounces, pounds and tons are related by difficult factors and are all too large for most laboratory applications. Volume is really the cube of distance but it is convenient to have volume units. In the metric system, microliters, milliliters and liters are usually convenient for laboratory measurements. Again, in the American system, pints, quarts and gallons are not related by powers of 10 and are usually too big for the laboratory.

There are other compelling reasons for favoring the metric system over the American system. As mentioned, volume is the cube of distance and in the metric system, the units have been defined so that 1 cm^3 is exactly 1 mL. This means that 1000 cm^3 is exactly a Liter. How many gallons could fit into a cubic foot? Since you probably do not know the answer, unless you look up the factor in the Internet, you would probably calculate the relationship using the metric system. Most people estimate the answer by imagining how many gallons of milk could be poured into a cube one foot on a side and come up with a value of about 3 ga/ft^3. This estimate is way off.

$$1\text{ ft}^3\ \frac{(12\text{ inches})^3}{(1\text{ ft})^3}\ \frac{(2.54\text{ cm})^3}{(1\text{ inch})^3}\ \frac{1\text{ mL}}{1\text{ cm}^3}\ \frac{1\text{ L}}{10^3\text{ mL}}\ \frac{1.057\text{ qts}}{1\text{ L}}\ \frac{1\text{ ga}}{4\text{ qts}} = 7.48\text{ gallons}$$

Supposing you were to be asked how much a pint of water weighs? Some of us know from use of a measuring cup that it should weigh about a pound. This is true and there is a saying that a pint is a pound the world around. In science however, the word "about" is usually not good enough and there is about a 4% error with this conversion. In the metric system, water has a density of exactly 1g/mL or 1 g/cm^3 at 3.98°C. Since the density of water is temperature dependent, the mass - volume equivalence is only exact at 3.98°C. At 20°C the density of water is 0.998 g/cm^3 so assuming equivalence introduces a 0.2% error.

Another compelling reason for adopting the metric system is except for the U.S. and a few other countries, most of the world uses the metric system. In the U.S., people working with tools must have two sets of tools, an inconvenient and expensive proposition. Finally, even some abbreviations in the American system do not seem to make sense such as lbs and oz.

Even for temperature measurements, the American system is more difficult. Fahrenheit has 180 divisions between the melting and boiling points of water and sets the freezing point and boiling points of water at the inconvenient values of 32°F and 212°F. In the metric system, water freezes at 0°C and boils at 100°C. While the short term cost of converting from the American system to the metric system would be substantial, in the long run, it should be less expensive and certainly much easier and more convenient.