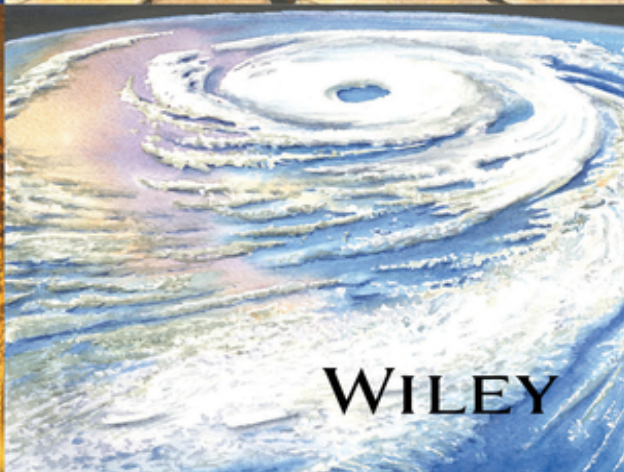


JONATHAN D. RAFF | RONALD A. HITES

ELEMENTS OF ENVIRONMENTAL CHEMISTRY

THIRD EDITION



WILEY

Elements of Environmental Chemistry

Elements of Environmental Chemistry

Third Edition

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O'Neill School of Public and Environmental Affairs

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Note on the Cover:

The illustrations on the cover represent the four “elements” of an environmental chemist’s periodic table (water, earth, fire, and air) viewed through the lens of climate change. The images are watercolor paintings by Jonathan D. Raff and depict arctic sea ice (water), drought (land), a burning forest (fire), and a hurricane viewed from Earth’s orbit (air). This bit of whimsy was suggested by a Sidney Harris cartoon appearing in his book *What’s So Funny About Science?* (William Kaufmann, Los Altos, CA, 1977). A full periodic table of the elements is given in Appendix B.

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To
Malte Thorben Raff
Benjamin Atlee Hites
Gavin James Mahoney

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Preface

Many chemistry and environmental science departments now feature a course on environmental chemistry, and several textbooks support these courses. The coverage and quality of these textbooks varies – in some cases dramatically. Although it is obviously a matter of opinion (depending on the instructor's background and skills), it seems to us that a good environmental chemistry textbook should be quantitative and should develop students' skills with numerous real-world problems.

This book aims at a quantitative approach to environmental chemistry. In fact, one could think of this book as providing the student with the essence of environmental chemistry *and* with a toolbox for solving problems. These skills are transferable to other fields beyond environmental chemistry. With their effort, this book will allow students to understand problem-solving methods in the context of environmental chemistry, and it will provide the basic concepts of environmental chemistry such that these problem-solving skills can be used to understand even more complex environmental challenges.

This is a relatively short book. Its goal is to be tutorial and informal; thus, the text features many quantitative story problems (indicated by bold font). For each problem, a strategy is developed, and the solution is provided. Although short, this book is not intended to be read quickly. It is an interactive textbook, and it is intended to be read with a pencil and calculator in hand so that the reader can follow the problem statement, the strategy for solving the problem, and the calculations used in arriving at an answer. "Reading" this book will do the student little good without actually doing the problems. It is not sufficient for the student to say, "I could do that problem if I had to." The student must work out the problems if he or she is going to learn this material.

In addition to the problems in the text, each chapter ends with a problem set. Besides reinforcing concepts introduced in the chapter, we have tried to incorporate issues from the scientific literature and from the "real world" in these problem-set questions. The answers to these questions are at the back of the book,

and full solutions are in a *Solution Manual* available from the authors to qualified instructors. Most of the problem sets include a problem or two that require a bit more time and the application of simple computing using Excel. These are labeled as such. They could be assigned to small groups of students or held back for the especially competent student.

As a stand-alone text, this book is suitable for a one-semester course (particularly if supplemented with a few lectures on the instructor's favorite environmental topics) aimed at upper-level undergraduate chemistry or civil engineering majors or at first-year graduate students with only a modest physical science background. Because of its tutorial nature, this book would also make a good self-study text for entry-level professionals. A little calculus will help the reader follow the exposition in a few places, but it is not necessary.

The third edition has been revised and rearranged. The first chapter on tool skills has been expanded to include thermodynamic considerations and measurement issues. Chapter 6 on the partitioning of organic compounds has been expanded to cover the fates of organic compounds. The material on mercury, lead, pesticides, polychlorinated biphenyls (PCBs), dioxins, and flame retardants has been expanded and combined into Chapter 7 and supplemented with more references to the literature and to the semi-popular press. The tutorial on organic chemistry names and structures has been kept as Appendix A.

We thank the hundreds of students who used this material in our classes over the years and who were not shy in explaining to us where the material was deficient. Nevertheless, errors likely remain, and we take full responsibility for them.

We would be happy to hear from you. If we have omitted your favorite topic, been singularly unclear about something, or made an error with a problem set solution, please let us know.

Bloomington, IN, USA
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1

Simple Tool Skills

There are several tasks that will occur over and over again as one works as an environmental scientist; we need to master them first. These tasks include unit conversions, estimating, the ideal gas law, stoichiometry, thermodynamic considerations, and measurement issues.

1.1 Unit Conversions

There are several important prefixes that you should know, and these are given in Table 1.1.

For example, a nanogram is 10^{-9} g, a kilometer is 10^3 m, and a petabyte is 10^{15} bytes, which is a lot.

For those of us forced by convention or national origin to work with the so-called “English units,” here are some other handy conversion factors you should know

$$1 \text{ pound (lb)} = 454 \text{ grams (g)}$$

$$1 \text{ inch (in.)} = 2.54 \text{ centimeters (cm)}$$

$$12 \text{ inches} = 1 \text{ foot (ft)}$$

$$1 \text{ meter (m)} = 3.28 \text{ ft}$$

$$1 \text{ mile} = 5280 \text{ ft} = 1610 \text{ m} = 1.61 \text{ km}$$

$$3.8 \text{ liter (L)} = 1 \text{ US gallon (gal)}$$

A handy formula for converting degrees Fahrenheit to degrees Centigrade is

$$^{\circ}\text{F} = \left(\frac{9}{5}\right)^{\circ}\text{C} + 32$$

Table 1.1 Unit prefixes, their abbreviations, and their meanings.

Prefix	Abbreviation	Multiplier
yocto	y	10^{-24}
zepto	z	10^{-21}
atto	a	10^{-18}
femto	f	10^{-15}
pico	p	10^{-12}
nano	n	10^{-9}
micro	μ	10^{-6}
milli	m	10^{-3}
centi	c	10^{-2}
deci	d	10^{-1}
kilo	k	10^3
mega	M	10^6
giga	G	10^9
tera	T	10^{12}
peta	P	10^{15}
exa	E	10^{18}

There are some other common conversion factors that link length units to common volume and area units

$$1 \text{ L} = 10^3 \text{ cm}^3$$

$$1 \text{ m}^3 = 10^3 \text{ L}$$

$$1 \text{ km}^2 = (10^3 \text{ m})^2 = 10^6 \text{ m}^2 = 10^{10} \text{ cm}^2$$

One more unit conversion that we will find helpful is

$$1 \text{ tonne} = 1 \text{ t} = 10^3 \text{ kg} = 10^6 \text{ g}$$

Yes, we will spell metric *tonnes* like this to distinguish it from English tons, which are 2000 lb and also called “short tons.” One English ton equals one short ton and both equal 0.91 metric tonnes.

Another unit that chemists use to describe distances between atoms in a molecule is the Ångström,¹ which has the symbol Å and represents 10^{-10} m. For example, the C—H bond in an organic molecule is typically 1.1 Å, or 1.1×10^{-10} m. The O—H bond in water is only 0.96 Å long.

¹ Anders Ångström (1814–1874), Swedish physicist.

Let us do some simple unit conversion examples. The point is to carry along the units as though they were algebra and cancel out things as you go. Always write down your unit conversions. We cannot begin to count the number of people who looked foolish at public meetings because they tried to do unit conversions in their head. Even rocket scientists have screwed this up such that they once missed Mars.

Let us assume that human head hair grows at 0.5 in./month. How much hair grows in 1 s? Please use metric units.

Strategy: Let us convert inches to meters and months to seconds. Then depending on how small the result is, we can select the right length units

$$\begin{aligned}\text{Rate} &= \left(\frac{0.5 \text{ in.}}{\text{month}} \right) \left(\frac{2.54 \text{ cm}}{\text{in.}} \right) \left(\frac{\text{m}}{10^2 \text{ cm}} \right) \left(\frac{\text{month}}{31 \text{ days}} \right) \left(\frac{\text{day}}{24 \text{ h}} \right) \left(\frac{\text{h}}{60 \text{ min}} \right) \\ &\quad \left(\frac{\text{min}}{60 \text{ s}} \right) = 4.7 \times 10^{-9} \text{ m/s}\end{aligned}$$

If you find scientific notation confusing, see footnote ². We can put this in more convenient units

$$\text{Rate} = \left(\frac{4.7 \times 10^{-9} \text{ m}}{\text{s}} \right) \left(\frac{10^9 \text{ nm}}{\text{m}} \right) = 4.7 \text{ nm/s} \approx 5 \text{ nm/s}$$

So in 1 s, your hair grows about 5 nm. This is not much, but it obviously adds up second after second.

A word on significant figures: In the above result, the input to the calculation was 0.5 in./month, a datum with only one significant figure. Thus, the output from the calculation should not have more than one significant figure and should be given as 5 nm/s. In general, one should use a lot of significant figures inside the calculation, but round the answer off to the correct number of figures at the end. With a few exceptions, one should be suspicious of environmental results having four or more significant figures – in most cases, two will do. More on this later.

The total amount of sulfur released into the atmosphere per year by the burning of coal is about 75 million tonnes. Assuming this were all solid sulfur, how big a cube would this be? You need the dimension of each side of the cube in feet. Assume the density of sulfur is twice that of water.

Strategy: Okay, this is a bit more than just converting units. We have to convert weight to volume, and this requires knowing the density of sulfur; density has

² We will use scientific notation throughout this book because it is easier to keep track of very big or very small numbers. For example, in the calculation we just did, we would have ended up with a growth rate of 0.000 000 004 7 m/s in regular notation; this number is difficult to read and prone to error in transcription (you have to count the zeros accurately). To avoid this problem, we give the number followed by 10 raised to the correct power. It is also easier to multiply and divide numbers in this format. For example, it is tricky to multiply 0.000 000 004 7 times 1 000 000 000, but it is easy to multiply 4.7×10^{-9} times 1×10^9 by multiplying the leading numbers ($4.7 \times 1 = 4.7$) and by adding the exponents of 10 ($-9 + 9 = 0$) giving a result of $4.7 \times 10^0 = 4.7$.

units of weight per unit volume, which in this case is given to be twice that of water. As you may remember, the density of water is 1 g/cm^3 , so the density of sulfur is 2 g/cm^3 . Once we know the volume of sulfur, we can take the cube root of that volume and get the side length of a cube holding that volume

$$V = (7.5 \times 10^7 \text{ tonnes}) \left(\frac{10^6 \text{ g}}{\text{tonne}} \right) \left(\frac{\text{cm}^3}{2 \text{ g}} \right) = 3.75 \times 10^{13} \text{ cm}^3$$

$$\text{Side} = \sqrt[3]{3.75 \times 10^{13} \text{ cm}^3} = 3.35 \times 10^4 \text{ cm} \left(\frac{\text{m}}{10^2 \text{ cm}} \right) = 335 \text{ m}$$

$$\text{Side} = 335 \text{ m} \left(\frac{3.28 \text{ ft}}{\text{m}} \right) = 1100 \text{ ft}$$

This is huge. It is a cube as tall as the Empire State Building on all three sides. Pollution gets scary if you think of it as being all in one place rather than diluted by the Earth's atmosphere.

1.2 Estimating³

We often need order of magnitude guesses for many things in the environment. This tends to frighten students because they are forced to think for themselves rather than apply some memorized process. Nevertheless, estimating is an important skill, so we will exercise it. Let us start with a couple of simple examples:

How many cars are there in the United States and in the world?

Strategy: One way to start is to think locally. Among our friends and families, it seems as though about every other person has a car. If we know the population of the United States, then we can use this 0.5 car per person conversion factor to get the number of cars in the United States. It would clearly be wrong to use this 0.5 car per person for the rest of the world (for example, there are not yet 600 million cars in China), but we might use a multiplier based on the size of the economy of the United States vs. the world. We know that the US economy is roughly one-third that of the whole world; hence, we can multiply the number of cars in the United States by three to estimate the number in the world.

³ Students seem to dislike estimating things. To quote from a review of this book on Amazon.com, "Ok, this book is incredibly useless. The chapters themselves do not actually cover the material very well, then [it] asks questions at the end that assume you know every last detail of anything. For example, it asks a question about how many tires are in a dump when they do not tell you the size of the tires. It asks you for the volume of a garage, and it gives you no dimensions or anything to find the dimensions. What was the editor smoking?" While we cannot speak to the smoking habits of our editor, we do point out that if you don't know how big something is you could go out and measure it. After all, we have all seen tires and garages. Our point is to learn to think for yourselves. In the "real world," problems are not handed to you in the form of a self-contained question at the end of a chapter in a textbook.

In the United States, there are now about 330 million people, and about every other person has a car; thus

$$3.3 \times 10^8 \times 0.5 = 1.6 \times 10^8 \text{ cars in the United States}$$

The US economy is about one-third of the world's economy; hence, the number of cars in the world is

$$3 \times 1.6 \times 10^8 \approx 500 \times 10^6 \text{ cars} = 0.5 \times 10^9 \text{ cars}$$

The real number is not known with much precision, but Google tells us the number is on the order of a billion (10^9). Thus, our estimate is low, but it is certainly in the right ballpark. Of course, this number is increasing dramatically as the number of cars in China increases.

The point here is not to get the one and only “right answer” but to get a guess that would allow us to quickly decide about whether or not it is worth getting a more exact answer. For example, let us say that you have just invented some device that will be required on every car in the world, but your profit is only US\$0.10 per car. Before you abandon the idea, you should guess at what your total profit might be. Quickly figuring that there are about 500 million cars and that your profit would be about US\$50 000 000 should grab your attention. Remember, all we are looking for when we make estimates is the right factor of 10—is it 0.1 or 100? We are not interested in factors of 2—we do not care if it is 20 or 40, 10—100 is close enough. Think of the game of horseshoes not golf.

How many people work at McDonald's in the United States?

Strategy: Starting close to home, you could count the number of McDonald's in your town and ratio that number to the population of the rest of the United States. For example, Bloomington, IN, where we live, has three McDonald's “restaurants” serving a population of about 100 000 people. Taking the ratio of this number to the United States' population as a whole gives

$$\left(\frac{3 \text{ McD}}{1 \times 10^5 \text{ people}} \right) 3.3 \times 10^8 = 1 \times 10^4 \text{ restaurants in the United States}$$

Based on local observations and questions of the people behind the counter,⁴ it seems that about 50 people work at each “restaurant”; hence,

$$\left(\frac{50 \text{ employees}}{\text{restaurant}} \right) 1 \times 10^4 \text{ restaurants} \approx 5 \times 10^5 \text{ employees}$$

This is a lot of people working for one company in one country, but of course, most of them are working part-time. According to Google, the truth seems to be that about 500 000 people work at McDonald's in the United States, so our estimate

⁴ Actually when asked, one of the people behind the counter said, “No one really *works* here except me. The others just get in the way.”

is surprisingly (suspiciously?) close, given the highly localized data with which we had to work.

How many American footballs can be made from one pig?

Strategy: Think about the size of a football – perhaps as a size-equivalent sphere – and about the size of a pig – perhaps as a big box – then divide one by the other. Let us assume that a football can be compressed into a sphere and that our best guess is that this sphere will have a diameter of about 25 cm (10 in.). We know or can quickly look up the area of a sphere as a function of its radius (r), and it is $4\pi r^2$. Let us also imagine that a pig is a rectilinear box that is about 1 m long, 1/2 m high, and 1/2 m wide. This ignores the head, the tail, and the feet, which are probably not used to make footballs anyway

$$\text{Pig area} = (4 \times 0.5 \times 1) \text{ m}^2 = 2.0 \text{ m}^2$$

$$\text{Football area} = 4\pi r^2 = 4 \times 3.14 \times \left(\frac{25 \text{ cm}}{2}\right)^2 \approx 2000 \text{ cm}^2$$

$$\text{Number of footballs} = \left(\frac{2.0 \text{ m}^2}{2.0 \times 10^3 \text{ cm}^2}\right) \left(\frac{10^4 \text{ cm}^2}{\text{m}^2}\right) \approx 10 \text{ footballs}$$

This seems about right, and we are not after an exact figure. What we have learned from this estimate is that we could certainly get at least one football from one pig, but it is not likely that we could get 100 footballs from one pig. It is irrelevant if the real number is 5 or 20, given the gross assumptions we have made.

1.3 Ideal Gas Law

We need to remember the ideal gas law for dealing with many air pollution issues. The ideal gas law is

$$PV = nRT$$

where P = pressure in atmospheres (atm) or in Torr (remember 760 Torr = 1 atm),⁵ V = volume in liters (L), n = number of moles, R = gas constant [0.082 (L atm)/(deg mol)], and T = temperature in Kelvin ($K = \text{deg Centigrade} + 273.15$).

The term *moles* (abbreviated here as *mol*) refers to 6.02×10^{23} molecules or atoms; there are 6.02×10^{23} molecules or atoms in a mole. The term *moles* occurs frequently in molecular weights, which have units of grams per mole (or g/mol); for example, the molecular weight of N_2 is 28 g/mol. This number, 6.02×10^{23} per

⁵ We know we should be dealing with pressure in units of Pascals (abbreviation: Pa), but we think it is convenient for environmental science purposes to retain the old unit of atmospheres – we instinctively know what that represents. For the purists among you, 1 atm = 101 325 Pa (or for government work, 1 atm = 10^5 Pa).

Table 1.2 Composition of the Earth's atmosphere without water.

Gas	Symbol	Composition	Molecular weight (g/mol)
Nitrogen	N ₂	78%	28
Oxygen	O ₂	21%	32
Argon	Ar	1%	40
Carbon dioxide	CO ₂	400 ppm	44
Neon	Ne	18 ppm	20
Helium	He	5.2 ppm	4
Methane	CH ₄	1500 ppb	16

mole (note the positive sign of the exponent), is known far and wide as Avogadro's number.⁶

We will frequently need the composition of the Earth's atmosphere.⁷ Table 1.2 gives this composition along with the molecular weight of each gas.

The units “ppm” and “ppb” refer to parts per million or parts per billion. These are fractional units like percent (%), which is parts per hundred. To get from a unitless fraction to these relative units just multiply by 100 for %, by 10⁶ for ppm, or by 10⁹ for ppb. For example, a fraction of 0.0001 is 0.01% = 100 ppm = 100 000 ppb. For the gas phase, %, ppm, and ppb are all on a volume per volume basis (which is the same as on a mole-per-mole basis). For example, the concentration of nitrogen in the Earth's atmosphere is 78 L of nitrogen per 100 L of air or 78 mol of nitrogen per 100 mol of air. It is **not** 78 g of nitrogen per 100 g of air. To remind us of this convention, sometimes these concentrations are given as “ppmV” or “ppbV,” meaning ppm or ppb by volume. This convention applies to only gas concentrations but not to water, solids, or biota (where the convention is weight per weight).

What is the molecular weight of dry air?

Strategy: The value we are after is the weighted average of the components in air, mostly nitrogen at 28 g/mol and oxygen at 32 g/mol (and a tad of argon at 40 g/mol). Thus,

$$\text{MW}_{\text{dry air}} = 0.78 \times 28 + 0.21 \times 32 + 0.01 \times 40 = 29 \text{ g/mol}$$

⁶ Amedeo Avogadro (1776–1856), Italian physicist. It is interesting to note that Avogadro's number is close to 2⁷⁹, or in the interest of defining fundamental constants in terms of integers, is it also 84 466 891³, where 84 466 891 is a prime number. Of course, it is probably easier to just remember 6.02 × 10²³/mol.

⁷ Here, we are ignoring the amount of water in the atmosphere, which varies dramatically from place to place and season to season.

What are the volumes of 1 mol of gas at 1 atm and 0 °C and at 1 atm and 15 °C? This latter temperature is important because it is the average atmospheric temperature at the surface of the Earth.

Strategy: We are after volume per mole, so we can just rearrange $PV = nRT$ and get

$$\frac{V}{n} = \frac{RT}{P} = \left(\frac{0.082 \text{ L atm}}{\text{K mol}} \right) \left(\frac{273 \text{ K}}{1 \text{ atm}} \right) = 22.4 \text{ L/mol}$$

This value at 15 °C is bigger by the ratio of the absolute temperatures (Boyle's law):

$$\left(\frac{V}{n} \right)_{25^\circ\text{C}} = 22.4 \text{ L/mol} \left(\frac{288}{273} \right) = 23.6 \text{ L/mol}$$

It will help to remember the first of these numbers and how to correct for different temperatures.

What is the density of the Earth's atmosphere at 15 °C and 1 atm pressure?

Strategy: Remember that density is weight per unit volume. We can get from volume to weight using the molecular weight, or in this case, the average molecular weight of dry air. Hence, rearranging $PV = nRT$

$$\frac{n}{V} \left(\frac{\text{MW}}{\text{mol}} \right) = \left(\frac{\text{mol}}{23.6 \text{ L}} \right) \left(\frac{29 \text{ g}}{\text{mol}} \right) = 1.23 \text{ g/L} = 1.23 \text{ kg/m}^3$$

What is the mass (weight) of the Earth's atmosphere?

Strategy: This is a bit harder, and we need an additional fact. We need to know the average atmospheric pressure in terms of weight per unit area. Once we have the pressure, we can multiply it by the surface area of the Earth to get the total weight of the atmosphere.

There are two ways to get the pressure: First, your average tire repair guy knows this to be 14.7 pounds per square inch (psi), but we would rather use metric units:

$$P_{\text{Earth}} = \left(\frac{14.7 \text{ lb}}{\text{in.}^2} \right) \left(\frac{\text{in.}^2}{2.54^2 \text{ cm}^2} \right) \left(\frac{454 \text{ g}}{\text{lb}} \right) = 1030 \text{ g/cm}^2$$

Second, you might remember from weather reports that the atmospheric pressure averages 30 in. of mercury, which is 760 mm (76 cm) of mercury in a barometer. This length of mercury can be converted to a true pressure by multiplying it by the density of mercury, which is 13.5 g/cm³

$$P_{\text{Earth}} = (76 \text{ cm}) \left(\frac{13.5 \text{ g}}{\text{cm}^3} \right) = 1030 \text{ g/cm}^2$$

Next, we need to know the area of the Earth. We had to look it up – it is $5.11 \times 10^8 \text{ km}^2$. Hence, the total weight of the atmosphere is

$$\begin{aligned} \text{Mass} &= P_{\text{Earth}} A = \left(\frac{1030 \text{ g}}{\text{cm}^2} \right) \left(\frac{5.11 \times 10^8 \text{ km}^2}{1} \right) \left(\frac{10^{10} \text{ cm}^2}{\text{km}^2} \right) \left(\frac{\text{kg}}{10^3 \text{ g}} \right) \\ &= 5.3 \times 10^{18} \text{ kg} \end{aligned}$$

This is equal to 5.3×10^{15} tonnes, which is a lot.

It is sometimes useful to know the volume (in liters) of the Earth's atmosphere if it were all at 1 atm pressure and at 15 °C.

Strategy: Since we have just calculated the weight of the atmosphere, we can get the volume by dividing it by the density of 1.23 kg/m^3 at 15 °C, which we just calculated above

$$V = \frac{\text{Mass}}{\rho} = 5.3 \times 10^{18} \text{ kg} \left(\frac{\text{m}^3}{1.23 \text{ kg}} \right) \left(\frac{10^3 \text{ L}}{\text{m}^3} \right) = 4.3 \times 10^{21} \text{ L}$$

Remember this number.

An indoor air sample taken from a closed two-car garage contains 0.9% of CO (probably a deadly amount). What is the concentration of CO in this sample in units of g/m^3 at 20 °C and 1 atm pressure? CO has a molecular weight of 28.

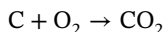
Strategy: Given that the concentration is 0.9 mol of CO per 100 mol of air, we need to convert the moles of CO to a weight, and the way to do this is with the molecular weight (28 g/mol). We also need to convert 100 mol of air to a volume, and the way to do this is with the 22.4 L/mol factor (corrected for temperature, of course)

$$C = \left(\frac{0.9 \text{ mol CO}}{100 \text{ mol air}} \right) \left(\frac{28 \text{ g CO}}{\text{mol CO}} \right) \left(\frac{\text{mol air}}{22.4 \text{ L air}} \right) \left(\frac{273}{293} \right) \left(\frac{10^3 \text{ L}}{\text{m}^3} \right) = 10.5 \text{ g/m}^3$$

Note the factor of 273/293 is needed to increase the volume of a mole of air when going from 0 to 20 °C.

1.4 Stoichiometry

Chemical reactions always occur on an integer molar basis. For example

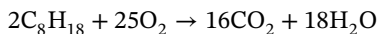


This means 1 mol of carbon (weighing 12 g) reacts with 1 mol of oxygen (32 g) to give 1 mol of carbon dioxide (44 g).

Table 1.3 gives a few atomic weights that every environmental chemist should know.

Assume that gasoline can be represented by C_8H_{18} . How much oxygen is needed to completely burn this fuel? Give your answer in grams of oxygen per gram of fuel.

Strategy: First set up and balance the combustion equation



This stoichiometry indicates that 2 mol of fuel react with 25 mol of oxygen to produce 16 mol of carbon dioxide and 18 mol of water. The molecular

Table 1.3 Environmental chemists' abbreviated periodic table.

Element	Symbol	Atomic weight (g/mol)
Hydrogen	H	1
Carbon	C	12
Nitrogen	N	14
Oxygen	O	16
Sulfur	S	32
Chlorine	Cl	35.5

weight of the fuel is $8 \times 12 + 18 \times 1 = 114$ g/mol, the molecular weight of oxygen is $2 \times 16 = 32$ g/mol, the molecular weight of carbon dioxide is $12 + 2 \times 16 = 44$ g/mol, and the molecular weight of water is $2 \times 1 + 1 \times 16 = 18$ g/mol. We can now set up the reaction in terms of mass

$$\begin{aligned}
 &2 \text{ mol} \times 114 \text{ g/mol fuel} + 25 \text{ mol} \times 32 \text{ g/mol oxygen} \\
 &= 16 \text{ mol} \times 44 \text{ g/mol carbon dioxide} + 18 \text{ mol} \times 18 \text{ g/mol water}
 \end{aligned}$$

which works out to

$$228 \text{ g fuel} + 800 \text{ g oxygen} = 704 \text{ g carbon dioxide} + 324 \text{ g water}$$

Hence, the requested answer is

$$\frac{M_{\text{oxygen}}}{M_{\text{fuel}}} = \left(\frac{800 \text{ g}}{228 \text{ g}} \right) = 3.51$$

Assume that a very poorly adjusted lawnmower is operating such that the combustion reaction is $\text{C}_9\text{H}_{18} + 9\text{O}_2 \rightarrow 9\text{CO} + 9\text{H}_2\text{O}$. For each gram of fuel consumed, how many grams of CO are produced?

Strategy: Again, we need to convert moles to weights using the molecular weights of the different compounds. The fuel has a molecular weight of 126 g/mol, and for every mole of fuel used, 9 mol of CO are produced. Hence,

$$\frac{M_{\text{CO}}}{M_{\text{fuel}}} = \left(\frac{9 \text{ mol CO}}{1 \text{ mol C}_9\text{H}_{18}} \right) \left(\frac{28 \text{ g}}{\text{mol CO}} \right) \left(\frac{\text{mol C}_9\text{H}_{18}}{126 \text{ g}} \right) = 2.0$$

1.5 Thermodynamic Considerations

It is one thing to balance a chemical reaction, but how do we know if it proceeds as it is written? Thermodynamics provides us with the most powerful and simplest

tool for doing this. There are three thermodynamic concepts to consider when determining how energetically favorable or spontaneous a reaction outcome is. They are enthalpy, entropy, and the Gibbs free energy.

1.5.1 Enthalpy

Chemical reactions either give off heat (this is called exothermic) or they absorb heat from their surroundings (this is called endothermic). Consequently, an exothermic reaction proceeding in the forward direction is endothermic in the reverse direction. The heat we refer to here is the energy that is transferred to the environment when the reaction takes place at a constant temperature and pressure. The amount of heat absorbed during such a chemical reaction is found by subtracting the heat content or enthalpy (denoted as H) of all the reactants from those of the products of a reaction. This is expressed mathematically as

$$\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum \Delta H_{\text{f}}^{\circ}(\text{reactants})$$

where the symbol $\Delta H_{\text{rxn}}^{\circ}$ quantifies the change in enthalpy of the system that accompanies the reaction under standard conditions (25 °C, 1 atm pressure, and 1 mol/L), which is denoted by the “°” superscript. The term $\Delta H_{\text{f}}^{\circ}$ refers to the standard enthalpy of formation, which is the heat evolved or absorbed from the surroundings when the individual elements are combined to form the reactant or product molecule; it is a measure of the strength of molecular bonds formed relative to the strength of bonds in the elements. These values are tabulated in databases and handbooks for a vast number of compounds. Based on this equation, an exothermic reaction (one that releases heat) is one where $\Delta H_{\text{rxn}}^{\circ}$ is negative, and an endothermic reaction (one that consumes heat) is associated with a positive $\Delta H_{\text{rxn}}^{\circ}$.

Calculate values of $\Delta H_{\text{rxn}}^{\circ}$ to determine whether the following three chemical reactions are endo- or exothermic.

- (a) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
- (b) $\text{NO}(\text{g}) + \text{HO}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{OH}(\text{g})$
- (c) $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq})$

Strategy: First, find the standard enthalpies of formation ($\Delta H_{\text{f}}^{\circ}$) for each molecule involved in these reactions in a textbook, handbook, or database⁸; we provide them in Table 1.4.

⁸ Comprehensive tables can be found in the *CRC Handbook of Chemistry and Physics* (CRC Press). For gases and radicals, please see: *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18*. JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, 2015, <http://jpldataeval.jpl.nasa.gov>.

Table 1.4 Thermochemical properties for example problems.

Substance	State ⁹	ΔH_f° (kJ/mol) ¹⁰	S° (J/(mol K)) ¹¹
H ₂	g	0	131
H ⁺	aq	0	0
H ₂ O	l	-286	70
N ₂	g	0	192
NH ₄ NO ₃	s	-366	151
NH ₄ ⁺	aq	-133	113
NO ₃ ⁻	aq	-207	146
NH ₃	g	-46	193
NO	g	90	211
NO ₂	g	33	240
HO ₂	g	12	229
OH	g	37	184
OH ⁻	aq	-230	-11

The standard enthalpy of the hydrogen ion and the elements N₂ and H₂ is 0 kJ/mol by definition. Next, use the equation for $\Delta H_{\text{rxn}}^\circ$ described above to find the answer.¹²

(Reaction a)

$$\Delta H_{\text{rxn}}^\circ = 2 \text{ mol} \times \Delta H_{\text{NH}_3(\text{g})} - 1 \text{ mol} \times \Delta H_{\text{N}_2(\text{g})} - 3 \text{ mol} \times \Delta H_{\text{H}_2(\text{g})}$$

$$\Delta H_{\text{rxn}}^\circ = \left(\frac{2 \text{ mol}}{1} \right) \left(\frac{-46 \text{ kJ}}{\text{mol}} \right) - \left(\frac{1 \text{ mol}}{1} \right) \left(\frac{0 \text{ kJ}}{\text{mol}} \right) - \left(\frac{3 \text{ mol}}{1} \right) \left(\frac{0 \text{ kJ}}{\text{mol}} \right) = -92 \text{ kJ}$$

(Reaction b)

$$\Delta H_{\text{rxn}}^\circ = 1 \text{ mol} \times \Delta H_{\text{NO}_2(\text{g})} + 1 \text{ mol} \times \Delta H_{\text{OH}(\text{g})} - 1 \text{ mol} \times \Delta H_{\text{NO}(\text{g})} - 1 \text{ mol} \times \Delta H_{\text{HO}_2(\text{g})}$$

$$\Delta H_{\text{rxn}}^\circ = \left(\frac{1 \text{ mol}}{1} \right) \left[\left(\frac{33 \text{ kJ}}{\text{mol}} \right) + \left(\frac{37 \text{ kJ}}{\text{mol}} \right) - \left(\frac{90 \text{ kJ}}{\text{mol}} \right) - \left(\frac{12 \text{ kJ}}{\text{mol}} \right) \right] = -32 \text{ kJ}$$

9 This is the physical state of the substance at standard conditions; g is for a gas, aq is for an aqueous solution, l is for a liquid, and s is for a solid.

10 The units used here are based on the Joule, which is named after James Prescott Joule (English physicist, mathematician, and brewer, 1818–1889). However, keep in mind that some tables give energy units in calories; the conversion is 1 cal (calorie) = 4.184 J (Joules).

11 S here represents the entropy of the substance. We will explain more about this later.

12 In the following calculations, we will omit the standard superscript and the reaction subscript.

(Reaction c)

$$\Delta H_{\text{rxn}}^{\circ} = 1 \text{ mol} \times \Delta H_{\text{NH}_4^+(\text{aq})} + 1 \text{ mol} \times \Delta H_{\text{NO}_3^-(\text{aq})} - 1 \text{ mol} \times \Delta H_{\text{NH}_4\text{NO}_3(\text{s})}$$

$$\Delta H_{\text{rxn}}^{\circ} = \left(\frac{1 \text{ mol}}{1} \right) \left[\left(\frac{-133 \text{ kJ}}{\text{mol}} \right) + \left(\frac{-207 \text{ kJ}}{\text{mol}} \right) - \left(\frac{-366 \text{ kJ}}{\text{mol}} \right) \right] = +26 \text{ kJ}$$

Clearly, the first two reactions are exothermic, while the last one is endothermic.

1.5.2 Entropy

Whether a chemical reaction is endo- or exothermic does not necessarily tell us whether a reaction will proceed spontaneously. While, in general, exothermic reactions tend to be spontaneous and endothermic reactions not, there are some chemical reactions that are spontaneous and absorb heat from their surroundings. Examples include the dissolution of $\text{NH}_4\text{NO}_3(\text{s})$ in water or the transition of water from liquid to gas phase upon boiling. Thus, enthalpy alone is not the only factor determining the spontaneity of a reaction.

The other factor that determines whether a reaction is spontaneous is entropy, which is a measure of disorder in a system. Indeed, the second law of thermodynamics applied to chemical reactions states that a reaction is spontaneous when it leads to an increase in entropy. A positive entropy of reaction (ΔS°) implies that a reaction proceeds with an increase in the disorder of a system. If a reaction is accompanied by a decrease in the disorder of a system, ΔS° is negative. Reactions that increase the entropy of a system often have the following qualities: (i) there is an increase in the number of products relative to reactants; (ii) phase changes that go from a more ordered condensed phase to a less ordered phase (such as a solid to a liquid or a liquid to a gas); and (iii) dissolution processes (for example, the dissolution of a solid in water). In addition to these considerations, it is important to note that the entropy of a system increases with temperature.

The entropy associated with the transition from reactants to products can be determined by subtracting the entropy of a reaction's final state from that of its initial state, or

$$\Delta S^{\circ} = \sum S^{\circ}(\text{products}) - \sum S^{\circ}(\text{reactants})$$

With this equation, we can predict the entropy change associated with a chemical reaction.

Calculate the entropy changes (ΔS°) accompanying the three chemical reactions used in the previous example problem.

Strategy: The approach is similar to the one in the previous example. First, we find the standard entropies (S°) for each molecule involved in the reactions in a textbook, handbook, or database; for ease, we tabulated them for you in the previous example. Next, we calculate ΔS° by subtracting the total entropy of the

reactants from the products

(Reaction a)

$$\begin{aligned}\Delta S^\circ &= (2 \text{ mol})S_{\text{NH}_3(\text{g})} - (1 \text{ mol})S_{\text{N}_2(\text{g})} - (3 \text{ mol})S_{\text{H}_2(\text{g})} \\ &= \left(\frac{2 \text{ mol}}{1}\right)\left(\frac{193 \text{ J}}{\text{mol K}}\right) - \left(\frac{1 \text{ mol}}{1}\right)\left(\frac{192 \text{ J}}{\text{mol K}}\right) - \left(\frac{3 \text{ mol}}{1}\right)\left(\frac{131 \text{ J}}{\text{mol K}}\right) = -199 \text{ J/K}\end{aligned}$$

(Reaction b)

$$\begin{aligned}\Delta S^\circ &= (1 \text{ mol})S_{\text{NO}_2(\text{g})} + (1 \text{ mol})S_{\text{H}_2\text{O}(\text{g})} - (1 \text{ mol})S_{\text{NO}(\text{g})} - (1 \text{ mol})S_{\text{OH}_2(\text{g})} \\ &= \left(\frac{1 \text{ mol}}{1}\right)\left[\left(\frac{240 \text{ J}}{\text{mol K}}\right) + \left(\frac{184 \text{ J}}{\text{mol K}}\right) - \left(\frac{211 \text{ J}}{\text{mol K}}\right) - \left(\frac{229 \text{ J}}{\text{mol K}}\right)\right] = -16 \text{ J/K}\end{aligned}$$

(Reaction c)

$$\begin{aligned}\Delta S^\circ &= (1 \text{ mol})S_{\text{NH}_4^+(\text{aq})} + (1 \text{ mol})S_{\text{NO}_3^-(\text{aq})} - (1 \text{ mol})S_{\text{NH}_4\text{NO}_3(\text{s})} \\ &= \left(\frac{1 \text{ mol}}{1}\right)\left[\left(\frac{113 \text{ J}}{\text{mol K}}\right) + \left(\frac{146 \text{ J}}{\text{mol K}}\right) - \left(\frac{151 \text{ J}}{\text{mol K}}\right)\right] = +108 \text{ J/K}\end{aligned}$$

Our entropy calculations tell us that reactions a and b lead to a decrease in the entropy, which suggests they are not spontaneous, and that reaction c leads to an increase in entropy, which suggests it is spontaneous.

1.5.3 Gibbs Free Energy

From our discussion of enthalpy and entropy, we observe that spontaneous reactions often (with some exceptions) release energy and tend to occur in the direction that maximizes disorder. For some reactions that fulfill both criteria, it is easy to predict whether they are spontaneous. However, how do we know whether a reaction is spontaneous when its enthalpy and entropy do not fall into those categories? By this, we mean, those reactions that are exothermic, but have negative entropies, or are endothermic and have positive entropies [for example, the dissolution of $\text{NH}_4\text{NO}_3(\text{s})$ in our example problem]? To decide whether a reaction is spontaneous or not, one must consider the balance between the change in enthalpy and entropy. This is evaluated by calculating the change in the Gibbs¹³ free energy (ΔG°) associated with a reversible reaction occurring under standard conditions. This can be done by subtracting the Gibbs free of a reaction's final state from that of its initial state just as we did above when deriving the enthalpy of a reaction; however, it is more instructive here to calculate it from

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Note here that temperature acts to amplify the influence of entropy on the overall Gibbs free energy of the system.¹⁴

¹³ “Gibbs free energy” is named after J. Willard Gibbs (1839–1903), who was an American theoretical physicist who helped found modern-day statistical mechanics and thermodynamics.

¹⁴ Why is this called “free” energy? The term “free” energy comes from the fact that the ΔG is essentially the net amount of energy available to do work if the heat is transformed to work.

From this equation, we see that for a spontaneous equation (for example, one that is exothermic and has a positive entropy), $\Delta G^\circ < 0$, and we say the reaction is exergonic. Reactions having $\Delta G^\circ > 0$ are not spontaneous, and we classify them as endergonic. The sign of ΔG° tells us which direction the reaction prefers to move. Thus, if a reaction has a negative ΔG° , it will proceed from reactants to products; if $\Delta G^\circ > 0$, the reverse reaction is favored. If $\Delta G^\circ = 0$, then the system is considered to be at equilibrium. Thus, the magnitude of ΔG° is an indication of how far from the equilibrium a reaction is. This relatively simple calculation is powerful because it allows us to predict if a chemical reaction is favorable and in which direction it will proceed to reach equilibrium.

Calculate the standard Gibbs free energy (ΔG°) at 25°C of the three chemical reactions used in the previous example problems.

Strategy: We already calculated the $\Delta H_{\text{rxn}}^\circ$ and ΔS° for these reactions. To derive ΔG° , we simply subtract $T\Delta S^\circ$ from the enthalpy. Note that we used units of kJ/mol for enthalpy and J/(mol K) for entropy; when calculating ΔG° , we need to be sure the enthalpy and entropy terms have the same units.

$$\text{(Reaction a)} \quad \Delta G^\circ = (-9.2 \times 10^4 \text{ J}) + (298 \text{ K})(199 \text{ J/K}) = -3.3 \times 10^4 \text{ J} = -33 \text{ kJ}$$

$$\text{(Reaction b)} \quad \Delta G^\circ = (-3.2 \times 10^4 \text{ J}) + (298 \text{ K})(16 \text{ J/K}) = -2.7 \times 10^4 \text{ J} = -27 \text{ kJ}$$

$$\text{(Reaction c)} \quad \Delta G^\circ = (2.6 \times 10^4 \text{ J}) - (298 \text{ K})(108 \text{ J/K}) = -6.2 \times 10^3 \text{ J} = -6.2 \text{ kJ}$$

Each value refers to the Gibbs free energy change when 1 mol of reactants reacts, which means we could also write the units as kJ/mol. Notice how for dissolution of $\text{NH}_4\text{NO}_3(\text{s})$ in water (reaction c), the reaction is endothermic, but ends up being spontaneous because the reaction results in such a large increase in entropy.

We end this section by reminding you of some of the caveats of using thermodynamics to predict reaction outcomes. Thermodynamics can only tell you whether a reaction is spontaneous or how far away from equilibrium you may be. It says nothing about how fast a reaction will proceed. We will look in more detail at how fast reactions occur in Chapter 2 when we discuss chemical kinetics. Also, keep in mind that we have applied our Gibbs free energy calculations to elementary reactions. Multistep reactions require knowledge of the actual mechanism, which allows us to follow changes in free energy at intermediate stages of the reaction.

1.6 Measurement Issues

How does one measure concentrations of elements and compounds in the environment?¹⁵

¹⁵ For an overview of this subject see Keith, L. H. et al. Principles of environmental analysis, *Analytical Chemistry*, **1983**, 55, 2210–2218.

It should come as no surprise that environmental chemists spend a lot of time measuring concentrations of some element (such as lead) or some compound (such as DDT) in environmental samples (such as fish). We call the target chemical being analyzed the “analyte.” To make these measurements properly and convincingly, there are some general issues that one should consider. The first issue is usually the selection of the analytical measurement technique itself. There are four parameters to think about when making this decision. They are the following:

Selectivity. This means that one needs an analytical method that responds to just the target analyte(s). For example, if you are trying to measure lead in drinking water, you need to be sure that the method responds to only lead and not, for example, to mercury. This is a particular problem when measuring organic compounds; for example, if you are trying to measure 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (which is very toxic), you need to be sure the method does not also respond to, say, 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (which is not as toxic). Interferences from nontargeted compounds are often called “chemical noise.”

Sensitivity. Environmental concentrations are often at very low levels. For example, a remediation level for dioxins in soil may be in the range of a few parts per billion. This requires measurement technology that is very sensitive and that can respond to a few nanograms or picograms of the targeted analyte. For organic compounds, this requirement frequently leads the analyst to gas chromatography (GC) or liquid chromatography (LC) coupled to mass spectrometry (MS). Incidentally, these methods can also be very selective. For metals, this requirement is often met by using atomic absorption spectrometry (AAS) and, more recently, inductively coupled plasma (ICP)-MS. The sample size is related to the method of sensitivity. If one has a lot of sample, then one may be able to use a less sensitive analytical method. For example, 1 L of water or 100 g of fish tissue may be suitable for some analyses, but in other cases, notably air, much larger samples may be needed. Of course, when considering the sensitivity of an analytical method, one has to keep in mind the chemical noise problem mentioned above. If the chemical noise is coming from the sampling or analytical methods themselves, then one may need a larger sample to overwhelm this chemical noise.

Speed. Sometimes one needs an answer right away. For example, when dealing with a public health issue (such as brominated flame retardants in milk), one needs an answer quickly so that one can advise the public on the risks, if any, before they have consumed too much milk. The general rule of thumb is that as the selectivity and sensitivity of an analytical method increase so does the time it takes to get an answer. In some cases, this trade-off may be warranted; for example, it may be acceptable to just know the total organic bromine levels in milk without knowing the structures of the compounds in question. In other cases, notably