ELEMENTS OF ENVIRONMENTAL CHEMISTRY

Second Edition




RONALD A. HITES
JONATHAN D. RAFF

WILEY

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A Note on the Cover

The illustrations on the cover represent the four "elements" in an environmental chemist's periodic table: air, earth, fire, and water. The images were taken by J. D. Raff and show clouds over the Pacific Ocean (air), a mesa near Capitol Reef National Park, Utah (earth), wildfire smoke obscuring the sun (fire), and ripples in the Pacific Ocean near Monterey Bay, California (water). 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 is given in Appendix C.

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To

Benjamin Atlee Hites

Gavin James Mahoney

Malte Thorben Raff

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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 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 effort, this book will allow students to understand problem-solving methods in the context of environmental chemistry and provide 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 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 really 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. Most of the problem sets include a problem that requires a bit more time and the application of simple computing; we have called these "Group Projects" to encourage students to work together on these problems. 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 chemical 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 hardly necessary.

The Second Edition has been completely revised and rearranged. The former chapter on atmospheric chemistry has been divided into two new chapters: one on atmospheric chemistry and one on climate change. The sequence of the chapters on chemodynamics and pesticides, lead, and mercury has been reversed. A descriptive chapter on polychlorinated biphenyls and dioxins and polybrominated flame retardants has been added at the end. A tutorial on organic chemistry names and structures has been added as an appendix.

We thank Todd Royer and Jeffery White for their insightful comments on parts of the text. We also 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 also thank Robert Esposito, Executive Editor at John Wiley & Sons, for guiding this project to completion.

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.

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October, 2011

Chapter 1
Simple Tool Skills

There are several little tasks that will occur over and over again as we work through problems; we need to master them first. These tasks include unit conversions, estimating, the ideal gas law, and stoichiometry.

1.1. UNIT CONVERSIONS

There are several important prefixes you should know:

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

For example, a nanogram is 10^{-9} grams and a kilometer is 10^{3} meters.

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

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1 pound (lb) = 454 grams (g)
1 inch (in.) = 2.54 centimeters (cm)
12 inches = 1 foot (ft)
1 meter (m) = 3.28 ft
1 mile = 5280 ft = 1610 m
3.8 liter (L) = 1 U.S. gallon (gal)

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

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

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 lbs and also called "short tons." One English ton equals one short ton and both equal 0.91 metric tonne.

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} meters. For example, the C–H bond in an organic molecule is typically 1.1 Å, or 1.1×10^{-10} meters. Likewise, the O–H bond in water is only 0.96 Å long.

Let's do some simple unit conversion examples. The point is to carry along the units as though they were al-

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

gebra 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.

Let's assume that human head hair grows at 0.5 in. per month. How much hair grows in one second? Please use metric units.

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

$$\text{Rate} = \left(\frac{0.5\ \text{in.}}{\text{month}}\right)\left(\frac{2.54\ \text{cm}}{\text{in.}}\right)\left(\frac{\text{m}}{10^2\,\text{cm}}\right)\left(\frac{\text{month}}{31\ \text{days}}\right)$$
$$\times\left(\frac{\text{day}}{24\ \text{h}}\right)\left(\frac{\text{h}}{60\ \text{min}}\right)\left(\frac{\text{min}}{60\ \text{s}}\right) = 4.7\times10^{-9}\,\text{m}/\text{s}$$

If scientific notation is confusing, see footnote 2.

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[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 0.0000000047 m/s in regular notation; that 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 is multiply and divide numbers in this format. For example, it is tricky to multiply 0.0000000047 times 1000000000, 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 $4.7 \times 10^{0} = 4.7$.

We can put this in more convenient units:

$$\text{Rate} = \left(\frac{4.7\times10^{-9}\,\text{m}}{\text{s}}\right)\left(\frac{10^{9}\,\text{nm}}{\text{m}}\right) = 4.7\ \text{nm/s}$$

This is not much, but it obviously mounts up second after second.

A word on significant figures: In the above result, the input to the calculation was 0.5 in. per 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.

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 occupy? You need the dimension of each side of the cube in feet. Assume the density of sulfur is twice that of water.

Strategy: OK, 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 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:

$$V=\left(7.5\times10^{7}\,\text{tonnes}\right)\left(\frac{\text{cm}^{3}}{2\ \text{g}}\right)\left(\frac{10^{6}\text{g}}{\text{tonne}}\right)=3.75\times10^{13}\,\text{cm}^{3}$$

$$\text{Side}=\sqrt[3]{3.75\times10^{13}\ \text{cm}^{3}}=3.35\times10^{4}\text{cm}\left(\frac{\text{m}}{10^{2}\text{cm}}\right)=335\ \text{m}$$

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

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 that diluted by Earth's atmosphere.

1.2. ESTIMATING

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's 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 (e.g., there are not yet 500 million cars in China), but we might just use a multiplier based on the size of the economy of the United States vs. the world. We know that the U.S. 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.

In the United States, there are now about 300 million people,[3] and about every other person has a car; thus

$$3 \times 10^8 \times 0.5 = 1.5 \times 10^8 \text{ cars in the United States}$$

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

$$3 \times 1.5 \times 10^8 \approx 500 \times 10^6 \text{ cars}$$

The real number is not known with much precision, but Google tells us the number is 600–700 million cars. Thus, our estimate is a bit 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 make a decision about whether or not it is worth getting

[3]Notice the use of one significant figure here. Given that this is a seat-of-the-pants estimate, there is no reason to use more digits.

a more exact answer. For example, let's say that you have just invented some device that will be required on every car in the world, but your profit is only \$0.10 per car. Before you abandon the idea, you should guess at what your total profit might be. Quickly figuring that there are on the order of 500 million cars and that your profit would be on the order of \$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 to 100? We are not interested in factors of 2 – we don't 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, Indiana, where we live has six McDonald's "restaurants" serving a population of about 80,000 people. Ratioing this to the U.S. population as a whole

$$\left(\frac{6 \text{ McD}}{8 \times 10^4 \text{people}}\right) 3 \times 10^8 = 2 \times 10^4 \text{restaurants in the U.S.}$$

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

$$\left(\frac{50 \text{ employees}}{\text{restaurant}}\right) 2 \times 10^4 \text{restaurants} \approx 10^6 \text{employees}$$

This estimate might be on the high side – Indiana seems to have a lot of circumferentially challenged people, so Indiana may have more than its share of McDonald's outlets. Thus, let's round this down to just 700,000 employees. This is still a lot of people working for one company in one country. According to Google, the truth seems to be that, in 2010, about 500,000 people worked at McDonald's in the United States, so our estimate is not too bad and is in fact surprisingly 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's assume that a football can be compressed into a sphere, and 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's also imagine that a pig is a rectilinear box that is about 1 m long, ½ m high, and ½ m wide. This ignores the head, the tail, and the feet, which are probably not used to make footballs anyway:

$$\text{Pig area} = (4 \times 0.5 \times 1)\ \text{m}^2 + (2 \times 0.5 \times 0.5)\ \text{m}^2 = 2.5\ \text{m}^2$$

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

$$\#\text{footballs} = \left(\frac{2.5 \text{ m}^2}{2000 \text{ cm}^2}\right)\left(\frac{10^4 \text{ cm}^2}{\text{m}^2}\right) \approx 10 \text{ footballs}$$

This seems about right, but 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)],[4] V = volume in liters (L), n = number of moles, R = gas constant (0.082 L atm deg^{-1} mol^{-1}), and T = temperature in deg Kelvin (K = 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. By the way, this number is remarkably close to 2^{79}, which you may use instead.

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[4]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).

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} (note the positive sign of the exponent) is known far and wide as Avogadro's number.[5]

We will frequently need the composition of Earth's dry atmosphere. The table below gives this composition along with the molecular weight of each gas:

Gas	Symbol	Composition	Molecular Weight
Nitrogen	N_2	78%	28
Oxygen	O_2	21%	32
Argon	Ar	1%	40
Carbon dioxide	CO_2	390 ppm	44
Neon	Ne	18 ppm	20
Helium	He	5.2 ppm	4
Methane	CH_4	1.5 ppm	16

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 10^6 for ppm, or by 10^9 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 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

[5]Amedeo Avogadro (1776–1856), Italian physicist.

"ppmv" or "ppbv." 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 perhaps a tad of argon at 40 g/mol). Thus,

$$\begin{aligned} MW_{\text{dry air}} &= 0.78 \times 28 + 0.21 \times 32 + 0.01 \times 40 \\ &= 29 \text{ g/mol} \end{aligned}$$

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 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):

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

It will help to remember both of these numbers or, at least, how to get from one to the other.

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

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

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

What is the mass (weight) of 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 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:

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

Second, remember from the TV 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/cm^3:

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

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

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

This is equal to 5.3×10^{15} metric tonnes.

It is useful to know what the volume (in liters) of Earth's atmosphere would be 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 by the density of 1.23 kg/m^3 at 15°C, which we just calculated above:

$$V = \frac{\text{Mass}}{\rho} = 5.3\times 10^{18}\ \text{kg}\left(\frac{\text{m}^3}{1.23\ \text{kg}}\right)\left(\frac{10^3\,\text{L}}{\text{m}^3}\right)$$
$$V_{T=288\text{K},\ P=1\ \text{atm}} = 4.3\times 10^{21}\ \text{L}$$

Remember this number.

An indoor air sample taken from a closed 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):

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

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

1.4. STOICHIOMETRY

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

$$C + O_2 \rightarrow CO_2$$

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).

The following table gives a few atomic weights you should know. The complete periodic table is provided as Appendix C.