ELEMENTS OF ENVIRONMENTAL CHEMISTRY

Ronald A. Hites

Indiana University

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ELEMENTS OF ENVIRONMENTAL CHEMISTRY

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To my family

Bonnie

Veronica, Karin, and David

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. This bit of whimsy was suggested by a Sidney Harris cartoon appearing in his book *What's So Funny About Science?* (Wm. Kaufmann, Inc., Los Altos, CA, 1977).

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PREFACE

Many chemistry and environmental science departments now feature a course on environmental chemistry, and several textbooks support these courses. As you might expect, 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 me that a good textbook on environmental chemistry should include, at a minimum, the following topics: steady- and non-steady-state modeling, chemical kinetics, stratospheric ozone, photochemical smog, the greenhouse effect, carbonate equilibria, the application of partition coefficients (K_{ow}, etc.), pesticides, and toxic metals. In addition, we must always remember that environmental chemistry is a quantitative science; thus, a good textbook for environmental chemistry should also develop students' quantitative skills by providing numerous real-world problems.

This book aims for a quantitative approach to most of these topics. 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. The latter skills are transferable to other fields beyond environmental chemistry. Hopefully, this book will allow students to understand methods of problem solving in the context of environmental chemistry and provide the basic concepts of environmental chemistry, so that these problem-solving techniques can be used to understand even complex environmental challenges.

This is a short book, in some ways modeled after *Elements of Style* by W. Strunk and E.B. White and *Consider a Spherical Cow* by J. Harte. Like those classic texts, the goal of this textbook is to be tutorial and informal;[1] thus, the text features many quantitative story problems (indicated by bold font). For each problem, a strategy is developed and the solution provided. This book is not intended to be read as a novel. It is an interactive textbook, and it is intended to be read with a pencil in hand so that the student can follow along with 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 to say to yourself, "I could do that problem if I really had to." You must do all of the problems if you are going to learn this material. In addition to the problems in the text, each chapter ends with a problem set covering the quantitative aspects of the material. Answers to these problems are at the back of the book, and full solutions to the problem set questions are available on the John Wiley & Sons web site at http://www.wiley.com. Do all the problems in all the problem sets!

This book stems from a course I taught for 25 years at Indiana University to first-year graduate students, who for the most part came into our program with under-

[1] Note the occasional "jokes" in the footnotes.

graduate degrees in biology. Thus, 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. This book would also make a good companion text for courses wanting to add a patina of environmental topics to an otherwise dull subject and for courses that cover other environmental sciences such as ecology. Because of its tutorial nature, it 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 really necessary.

I thank Philip S. Stevens and Jeffrey R. White for their insightful comments on parts of the text. I also thank the hundreds of students who used this material in my classes over the years and who were not shy in explaining to me where the material was deficient. Nevertheless, errors likely remain, and I take full responsibility for them.

I would be happy to hear from you. If I have omitted your favorite topic or if I have been singularly unclear about some topic, please let me know. If you disagree with my problem set solutions, please let me know.

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CHAPTER 1

SIMPLE TOOL SKILLS

There are a variety of little tasks that will occur over and over again as we work through quantitative problems, and 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 and should probably memorize.

Femto	(f)	10^{-15}
Pico	(p)	10^{-12}
Nano	(n)	10^{-9}
Micro	(μ)	10^{-6}
Milli	(m)	10^{-3}
Centi	(c)	10^{-2}
Kilo	(k)	10^{3}
Mega	(M)	10^{6}
Giga	(G)	10^{9}
Tera	(T)	10^{12}

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

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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:

1 pound (lb) = 454 g
1 inch (in.) = 2.54 cm
12 in. = 1 foot (ft)
1 m = 3.28 ft
1 mile = 5280 ft = 1609 m
3.79 L = 1 U.S. gallon (gal), liquids only

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

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

One more unit conversion that we will find very helpful is

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

Yes, we will spell metric *tonne* like this to distinguish it from 1 U.S. short ton, which is 2000 lb. One short ton equals 0.91 metric tonnes.

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! I cannot begin to count the number of people who looked foolish at public meetings because they tried to do unit conversions in their heads.

Human head hair grows about one half of an inch per 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.

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

If scientific notation is confusing to you, learn to use it.[1] We can put this hair growth rate in more convenient units:

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

[1] 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 0.000,000,0047 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 to multiply and divide numbers in this format. For example, it is tricky to multiply 0.000,000,0047 by 1000,000,000, but it is easy to multiply 4.7×10^{-9} by 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 $4.7 \times 10^0 = 4.7$.

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 have been given as 5 nm/s. In general, one should use a lot of significant figures inside the calculation, but round off the answer 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.

$$V = (7.5 \times 10^7\,\mathrm{t})\left(\frac{\mathrm{cm}^3}{2\,\mathrm{g}}\right)\left(\frac{10^6\,\mathrm{g}}{\mathrm{t}}\right) = 3.8 \times 10^{13}\,\mathrm{cm}^3$$

$$\mathrm{Side} = \sqrt[3]{3.8 \times 10^{13}\mathrm{cm}^3} = 3.35 \times 10^4\,\mathrm{cm}\left(\frac{\mathrm{m}}{10^2\,\mathrm{cm}}\right)$$

$$= 335\,\mathrm{m}$$

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

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 ESTIMATING

We often need order of magnitude guesses for many things in the environment. This is an important skill, so let us start with a couple of examples.

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

Strategy. Among our friends and families, it seems like about every other person has a car. If we know the population of the United States, then we can use this 0.5 cars per person conversion factor to get the number of cars in the United States. It would be wrong to use this 0.5 cars per person for the rest of the world (e.g., there are not 500 million cars in China—yet), but we might just use a multiplier based on the size of the economy of the United States versus 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 3 to estimate the number of cars in the world.

In the United States, there are now about 295 million people and almost every other person has a car; thus,

$$2.95 \times 10^8 \times 0.5 = 1.5 \times 10^8 \text{ cars in the United States}$$

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

$$3 \times 1.5 \times 10^8 \approx 5 \times 10^8$$

The real number is not known with much precision, but in 2005, it is likely on the order of $\sim 6 \times 10^8$ cars. Thus, our estimate is a bit low, but it is certainly in the right ballpark. Of course, this number will increase dramatically as the number of cars in China increases.

How many people work at McDonalds in the world?

Strategy. Starting close to home, you could count the number of McDonalds in your town and ratio that number to the population of the rest of the United States. For example, Bloomington, Indiana, where I live, has four McDonald "restaurants" serving a population of about 120,000 people. Ratioing this to the U.S. population as a whole

$$\left(\frac{4\,\text{McD}}{1.2 \times 10^5\ \text{people}}\right) 2.95 \times 10^8 = 9800$$

restaurants in the United States