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

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

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Jonathan D. Raff and Ronald A. Hites.

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

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

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

$$\text{Rate} = \left(\frac{4.7\times10^{-9}\text{ m}}{\text{s}}\right)\left(\frac{10^9\text{ nm}}{\text{m}}\right) = 4.7\text{ nm/s} \approx 5\text{ nm/s}$$

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 is 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 ($4.7\times1 = 4.7$) and by adding the exponents of 10 ($-9+9=0$) giving a result of $4.7\times10^{0} = 4.7$.

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 Estimating[3]

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 = 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 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 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,

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

6 Amedeo Avogadro (1776–1856), Italian physicist. It is interesting to note that Avogadro's number is close to 2^{79}, or in the interest of defining fundamental constants in terms of integers, is it also $84\,466\,891^3$, where 84 466 891 is a prime number. Of course, it is probably easier to just remember 6.02×10^{23}/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

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

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

$$\left(\frac{V}{n}\right)_{25\,°\mathrm{C}} = 22.4\ \mathrm{L/mol}\left(\frac{288}{273}\right) = 23.6\ \mathrm{L/mol}$$

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 $PV = nRT$

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

What is the mass (weight) of 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:

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

Second, 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/cm^3

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

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

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

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

$$C + O_2 \rightarrow CO_2$$

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).

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

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

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

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

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 $C_9H_{18} + 9O_2 \rightarrow 9CO + 9H_2O$. 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,

$$\frac{M_{CO}}{M_{\text{fuel}}} = \left(\frac{9\ \text{mol CO}}{1\ \text{mol}\ C_9H_{18}}\right)\left(\frac{28\ \text{g}}{\text{mol CO}}\right)\left(\frac{\text{mol}\ C_9H_{18}}{126\ \text{g}}\right) = 2.0$$

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

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

where the symbol $\Delta H^{\circ}_{\text{rxn}}$ 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 $\Delta H^{\circ}_{\text{f}}$ 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 $\Delta H^{\circ}_{\text{rxn}}$ is negative, and an endothermic reaction (one that consumes heat) is associated with a positive $\Delta H^{\circ}_{\text{rxn}}$.

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

(a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
(b) $NO(g) + HO_2(g) \rightarrow NO_2(g) + OH(g)$
(c) $NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$

Strategy: First, find the standard enthalpies of formation ($\Delta H^{\circ}_{\text{f}}$) for each molecule involved in these reactions in a textbook, handbook, or database[8]; 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_2O	l	−286	70
N_2	g	0	192
NH_4NO_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 N_2 and H_2 is 0 kJ/mol by definition. Next, use the equation for ΔH°_{rxn} described above to find the answer.[12]

(Reaction a)

$$\Delta H^\circ_{rxn} = 2\,\text{mol} \times \Delta H_{NH_3(g)} - 1\,\text{mol} \times \Delta H_{N_2(g)} - 3\,\text{mol} \times \Delta H_{H_2(g)}$$

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

(Reaction b)

$$\Delta H^\circ_{rxn} = 1\,\text{mol} \times \Delta H_{NO_2(g)} + 1\,\text{mol} \times \Delta H_{OH(g)} - 1\,\text{mol} \times \Delta H_{NO(g)} - 1\,\text{mol} \times \Delta H_{HO_2(g)}$$

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

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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)

$$\Delta H^{\circ}_{rxn} = 1\,\text{mol} \times \Delta H_{NH_4^+(aq)} + 1\,\text{mol} \times \Delta H_{NO_3^-(aq)} - 1\,\text{mol} \times \Delta H_{NH_4NO_3(s)}$$

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

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 NH_4NO_3(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)

$$\Delta S^\circ = (2\ \text{mol})S_{NH_3(g)} - (1\ \text{mol})S_{N_2(g)} - (3\ \text{mol})S_{H_2(g)}$$
$$= \left(\frac{2\ \text{mol}}{1}\right)\left(\frac{193\ \text{J}}{\text{mol K}}\right) - \left(\frac{1\ \text{mol}}{1}\right)\left(\frac{192\ \text{J}}{\text{mol K}}\right) - \left(\frac{3\ \text{mol}}{1}\right)\left(\frac{131\ \text{J}}{\text{mol K}}\right) = -199\ \text{J/K}$$

(Reaction b)

$$\Delta S^\circ = (1\ \text{mol})S_{NO_2(g)} + (1\ \text{mol})S_{HO(g)} - (1\ \text{mol})S_{NO(g)} - (1\ \text{mol})S_{OH_2(g)}$$
$$= \left(\frac{1\ \text{mol}}{1}\right)\left[\left(\frac{240\ \text{J}}{\text{mol K}}\right) + \left(\frac{184\ \text{J}}{\text{mol K}}\right) - \left(\frac{211\ \text{J}}{\text{mol K}}\right) - \left(\frac{229\ \text{J}}{\text{mol K}}\right)\right] = -16\ \text{J/K}$$

(Reaction c)

$$\Delta S^\circ = (1\ \text{mol})S_{NH_4^+(aq)} + (1\ \text{mol})S_{NO_3^-(aq)} - (1\ \text{mol})S_{NH_4NO_3(s)}$$
$$= \left(\frac{1\ \text{mol}}{1}\right)\left[\left(\frac{113\ \text{J}}{\text{mol K}}\right) + \left(\frac{146\ \text{J}}{\text{mol K}}\right) - \left(\frac{151\ \text{J}}{\text{mol K}}\right)\right] = +108\ \text{J/K}$$

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 NH_4NO_3(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 Gibbs[13] 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 ΔH°_{rxn} 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 NH_4NO_3(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

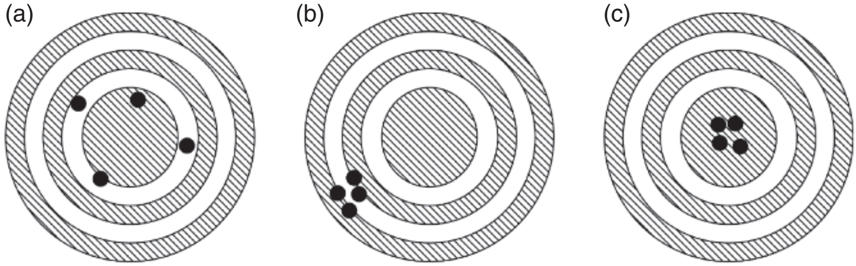

Figure 1.1 The target (a) illustrates good accuracy, but poor precision (the true value of the measurements is the center of the target, and the four solid dots are the measurements themselves), the target (b) shows high precision, but low accuracy, and the target (c) illustrates high precision and high accuracy.

when dealing with legal issues, such a trade off is usually not acceptable, and speed is not an issue (particularly if the lawyers are billing by the hour).

Cost. The cost of making environmental measurements can vary from a few cents (for example measuring the pH of water with pH paper) to a few thousands of dollars per sample (for example, measuring the levels of dioxins in human tissue). In general, the more sensitive and selective methods are more expensive and slower. Some measurements are particularly expensive because of the cost of capital equipment needed to make them. A high-resolution mass spectrometer will be needed for the measurement of dioxins, and that instrument alone may cost a half million dollars or more. This is something to think about if you are considering setting up your own laboratory to make environmental measurements. Operating costs (personnel) usually dwarf capital costs, but not always.

Is there a difference between "accuracy" and "precision?"

Yes, and it is an important difference! "Accuracy" is how close the measurements are to the correct answer, and "precision" is how scattered the measurements are from one another. Figure 1.1 illustrates this concept. Obviously, like marksmanship, one wants both good accuracy *and* good precision, but in any case, it is important to quantify *both* the accuracy and the precision. Here is how to do so.

Accuracy. The best way to assess accuracy is to measure samples in which the concentrations are known and to see how close one's measurements are to these known values. This is not as simple as it may seem. It is possible to make up a sample with a known amount of the analyte and to measure that, but that is not usually a fair test of the analytical method; for example, it is difficult to simulate the chemical noise of a real sample. In some cases, certified reference standards are available (for example, a fish puree with known amounts of polychlorinated biphenyls is available from the National Institute of Standards and Technology, NIST). In other cases, scientists get together to exchange and analyze real samples and subsequently compare their results to one another's data – this is called a round-robin study. In this case, the true concentration may not be known, but at least everyone is getting the same answer. In some fields, standards are exchanged informally among cognizant laboratories.

On a more routine basis, laboratories often add a known amount of an isotopically labeled target compound (for example, DDT in which all of the carbons are carbon-13 instead of the normal carbon-12) to real samples and measure the concentration of that compound. In this case, one uses an isotopically labeled analogue of the target compound to avoid interfering with the measurement of the unlabeled version of that compound. This is called a surrogate spike experiment, and the results are usually reported as the percent of the spiked compound that is measured relative to the amount added to the sample. Spike recoveries between 80% and 120% are usually acceptable.

Any discussion of accuracy must include a discussion of method calibration. Virtually all environmental measurements require calibration. For example, a gas chromatographic peak area must be calibrated in terms of mass before that mass can be converted into a concentration. There are two ways of doing the calibration: external and internal. External calibration means that a series of samples with known masses are run, and the resulting outputs from those experiments are plotted as a function of the known mass. This is called a calibration curve, and with luck, it is linear. One then uses that calibration curve to convert instrument output to mass. There are some disadvantages with this approach; for example, one needs to keep careful track of the dilutions of the sample during its extraction, clean-up, and analysis.

A more common calibration approach for environmental analyses is called internal standardization. In this case, one adds a known amount of an isotopically labeled version of the analyte to the sample after the sample extraction and clean-up are completed but before instrumental analysis begins. At the end of the measurement, one then compares the instrumental output of the analyte to that of the internal standard to get to the mass of the analyte in the sample. The calculations are really just a series of ratios

$$\left(\frac{\text{mass}_{\text{ana}}^{\text{cal}}}{\text{counts}_{\text{ana}}^{\text{cal}}}\right)\left(\frac{\text{counts}_{\text{std}}^{\text{cal}}}{\text{mass}_{\text{std}}^{\text{cal}}}\right)=\left(\frac{\text{mass}_{\text{ana}}^{\text{real}}}{\text{counts}_{\text{ana}}^{\text{real}}}\right)\left(\frac{\text{counts}_{\text{std}}^{\text{real}}}{\text{mass}_{\text{std}}^{\text{real}}}\right)$$

where *mass* is the weight (in say, ng) of the analyte (subscript *ana*) or the internal standard (subscript *std*) and *counts* is the unitless response from the instrument. The superscripts refer to the masses and the associated counts of the calibration sample (*cal*) and in the real sample (*real*). The terms on the left use data from a calibration experiment in which a known amount of the analyte and the internal standard are analyzed. This result is usually known as the relative response factor (*RRF*) and is specific for each analyte – internal standard pair. An example is essential. Let us say that you are measuring the amount of 1,2-xylene in a 89 m^3

atmospheric sample, and you are using ethylbenzene (a closely related compound) as the internal standard. You first run an experiment with known amounts (say, 350 ng each) of each of these two compounds and obtain the instrument responses (30 884 for xylene and 52 521 for ethylbenzene). The *RRF* is

$$\mathrm{RRF} = \left(\frac{\mathrm{mass}_{\mathrm{ana}}^{\mathrm{cal}}}{\mathrm{counts}_{\mathrm{ana}}^{\mathrm{cal}}}\right)\left(\frac{\mathrm{counts}_{\mathrm{std}}^{\mathrm{cal}}}{\mathrm{mass}_{\mathrm{std}}^{\mathrm{cal}}}\right) = \left(\frac{350\ \mathrm{ng}}{30\,884}\right)\left(\frac{52\,521}{350\ \mathrm{ng}}\right) = 1.70$$

Now you run a real sample with an unknown mass of xylene to which you have added 200 ng of ethylbenzene as the internal standard and obtain responses of 30 999 for xylene and 65 158 for ethylbenzene. Rearranging the penultimate equation gives

$$\mathrm{mass}_{\mathrm{ana}}^{\mathrm{real}} = \mathrm{RRF} \times \mathrm{counts}_{\mathrm{ana}}^{\mathrm{real}}\left(\frac{\mathrm{mass}_{\mathrm{std}}^{\mathrm{real}}}{\mathrm{counts}_{\mathrm{std}}^{\mathrm{real}}}\right)$$

Putting in the numbers gives

$$\mathrm{mass}_{\mathrm{ana}}^{\mathrm{real}} = 1.70 \times 30\,999\left(\frac{200\ \mathrm{ng}}{65\,158}\right) = 162\ \mathrm{ng}$$

Hence, the concentration of xylene in this sample is 162 ng divided by 89 m^3, which is 1.82 ng/m^3. Luckily, all of these calculations are done for you by the instrument's computer.

The advantage of internal standardization is that the standard is exposed to the same processing procedures and chemical noise as the analyte, and one does not have to know the volumes of any of the samples or their dilution factors. The disadvantage is that isotopically labeled internal standards tend to be expensive, but they do come with more or less certified known concentrations from the vendors. Unfortunately, labeled standards are not available for all compounds of interest.

Precision. Precision is usually easier to assess than accuracy. The simple approach to measuring precision is to measure replicates of a given sample and to see how close the results are to one another. This is usually presented as the standard deviation[16] or standard error of a set of N measurements. The standard error is the standard deviation of a set of measurements divided by $\sqrt{N}$. Because of cost issues, N rarely exceeds 10. In most cases, the precision of a set of measurements is estimated by selected replicates and not by the replication of each measurement. The relative standard error is sometimes given, and it is simply the standard error divided by the mean of a set of concentrations. For many trace level measurements, a relative standard error of ±20% is not uncommon.

As mentioned above, one should be careful with significant figures when reporting environmental concentrations. For example, a level of 2.3456 ppm

16 If terms like "standard deviation" are unfamiliar to you, we recommend taking an introductory statistics class.

suggests that the concentration is known to five significant figures (±0.0001), when a typical relative standard error of ±20% suggests that this concentration is really 2.3456 ± 0.4691 ppm, which has a range of 1.9–2.8 ppm. Clearly, this number should be reported as 2.3 ± 0.5 ppm. It is rare for more than three significant figures to be needed to report environmental measurements. Given that the data always have some built-in imprecision, one should always report the concentrations along with a measure of their precision. In the example here, this is given after the ± symbol. You should always be suspicious when a concentration is reported without any indicated error. Lawyers tend to do this, and they tend to use too many significant figures. For example, a measurement of 1.001 ppm to a lawyer would violate a regulatory standard of 1 ppm, but we know that the number is really 1.0 ± 0.2 ppm.

How can sensitivity of an analytical method be reported?

This is an important question. In the old days, it was not uncommon to find a long list of environmental concentration measurements in which, say, 60–70% of the entries were listed as "not detected." This, of course, led to the question: What, in fact, was the detection limit, and why was it set so high that most of the measurements were below that limit? Nowadays, everyone knows to be careful to select a method and a sample size that allows one to detect the concentrations that are actually present in the samples, but for some samples, the analyte concentrations are occasionally below the limit of detection (called the LOD).[17]

The LOD of a method is only partly related to the ability of the analytical instrument (a mass spectrometer, for example) to detect small amounts of a given element or compound. Many modern instruments can detect sub-picograms of an analyte. The problem is that the analyte of interest is often present in a sample with many chemically similar compounds (chemical noise) and that the sampling methods themselves can add trace amounts of an analyte to a sample (more chemical noise). All of this chemical noise can be reduced (or at least assessed) by using methods of high selectivity and by the analysis of so-called "blanks."

Blanks are control samples in which one would expect to find none of the analytes. A blank could be as simple as a simulated sample known to be clean, which is taken through the entire analytical procedure. For example, if one were measuring dioxins in soil, a blank could be sand that had been heated to 500 °C for 24 h. This is usually known as a laboratory blank, and it covers possible contamination from the laboratory itself (such as from glassware) and from solvents and other reagents. A blank could also be a sample collection system (for example a

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17 Besides the LOD, other commonly encountered terms include the instrument detection limit (IDL), the method detection limit (MDL), and the practical quantitation limit (PQL). All of these terms refer to different aspects of the measurement system. For more details, google "EPA: What does all of this alphabet soup really mean?" This will lead you to a well-written exposition from the U.S. Environmental Protection Agency.

filter used to collect atmospheric particles) that had been taken into the field, but never exposed to the environment. This is called a travel or field blank. In any case, the amount of the analyte in the blank sample is usually not zero, and it is this amount that is considered the true LOD of a method – at least as implemented in a given laboratory. It is this LOD that is a measure of the overall measurement system's sensitivity and not the instrument's sensitivity. It does no good to be able to measure, say, 1 pg in the instrument if the blank level is 10 pg.

In the end, good measurement practice requires two types of quality assurance experiments: A positive control experiment in which one measures a known amount of an analyte and gets the right answer, and a negative control experiment, in which one measures a blank sample and gets nothing or very little. Both of these issues can only be addressed in the context of the environmental measurements that one is planning to make.

What is the right measure of the central tendency of environmental measurements?

Intuitively, one might assume that the best measurement of the central tendency of a set of environmental measurements is their average. After all, this works fine for most things in life. For example, the average IQ of Americans is 100, a number which can be arrived at by measuring the IQ of, say, 10 000 people, adding those numbers together and dividing by 10 000. This is called the arithmetic mean, and for IQs it is given by

$$\overline{\mathrm{IQ}} = \left(\frac{1}{N}\right) \sum_{i=1}^{N} \mathrm{IQ}_i$$

where in our example $N = 10\,000$ and i refers to the individual. This works because, in this case, the IQ values are normally distributed. Here "normally distributed" refers to the classic bell-shaped curve as shown in Figure 1.2. This plot shows the fraction of people in a large population as a function of their IQ. The equation of this curve is well known, and it has certain benchmarks: the mean (100 in this case) and the standard deviation (15 in this case). Tables of the areas under parts of this curve are widely available, and they tell us that about 68% of people have an IQ in the range of 85–115 (the mean ± the standard deviation) and that only 0.1% of the people have an IQ > 145 (the mean + 3 standard deviations). The latter probably includes most of the readers of this book.

It turns out that environmental data are *not* normally distributed. Figure 1.3a shows the distribution of PCB concentrations in the atmosphere around the North American Great Lakes.[18] Note that this distribution is not symmetrical such as

18 Hites, R. A. A statistical approach for left-censored data: Distributions of atmospheric polychlorinated biphenyl concentrations near the Great Lakes as a case study, *Environmental Science & Technology Letters*, **2015**, *2*, 250–254.

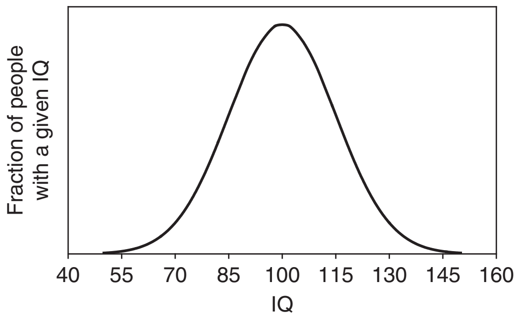

Figure 1.2 Fraction of people having a given IQ. This is a classic normal or bell-shaped distribution. In this case, the normal distribution has a mean of 100 and a standard deviation of 15. In fact, the IQ scale was set up to use this mean and standard deviation.

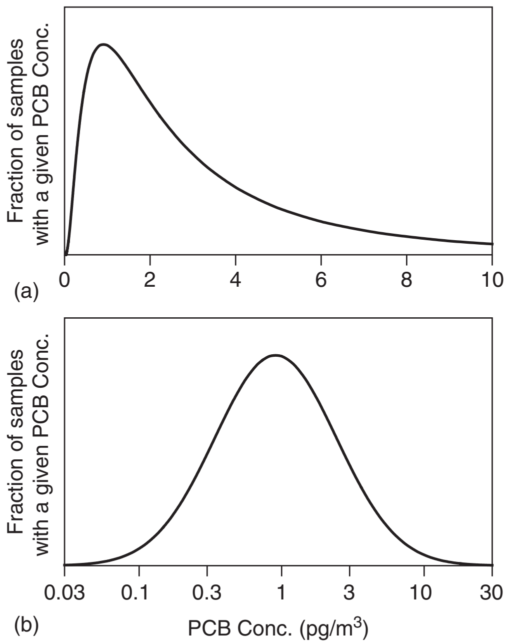

Figure 1.3 (a) Fraction of Great Lakes samples having a given PCB concentration. (b) The same data but plotted on a logarithmic concentration (Conc.) scale. Note in this scale that there is equal spacing for each factor of 10.

noticed above for the distribution of IQs. However, if one transforms the concentration scale by taking the logarithms (see Figure 1.3b), then the symmetrical normal distribution reappears. This means that the logarithms of the concentrations are normally distributed, not the concentrations themselves. This distribution is called the log-normal distribution, and it is common throughout the environmental sciences.[19]

19 Koch, A. L. The logarithm in biology, I. Mechanisms generating the log-normal distribution exactly, *Journal of Theoretical Biology*, **1966**, *12*, 276–290; and Koch, A. L. The logarithm in biology, II. Distributions simulating the log-normal, *Journal of Theoretical Biology*, **1969**, *23*, 251–268.

The main implication of this result it that the central tendency of a set of environmental measurements is the geometric mean – not the arithmetic mean. In other words, one must take the average of the logarithms of the concentrations and then exponentiate the result to get the geometric mean.

$$\log \overline{C}_{\text{geo}} = \left(\frac{1}{N}\right) \sum_{i=1}^{N} \log(C_i)$$

Alternately, one can multiply all the N concentrations times one another and take the Nth root of this product.

$$\overline{C}_{\text{geo}} = \left(\prod_{i=1}^{N} C_i\right)^{1/N}$$

It is even easier to use the built-in "geomean" function in Excel. A corollary here is that none of the values can be zero because, of course, the log(0) is undefined.

Another measure of the central tendency of a set of data is the median. This value does not depend on the distribution function of the data. It is simply the value that bisects the data into two equally numbered halves. For example, out of 100 measurements, 50 of them will be above the median and 50 will be below the median. The median is also called the 50th percentile. The median is usually close to the geometric mean.

What do I do if the LOD is higher than some of my measurements?

Let us imagine that one has measured blank samples with sufficient replication so that one has good confidence in the resulting LOD. One then measures 100 or so real samples and finds that a few of the resulting concentrations are less than the LOD. What to do? Surprisingly, there are at least three schools-of-thought: (i) Delete the offending measurements from subsequent analyses; after all, one does not really know what the numbers should be. The argument against doing this is that one will bias the average of the remaining results to be higher than they should be. (ii) Replace the offending measurements by the LOD/2. The argument against doing this is that one is making up data; see the interesting paper by Helsel.[20] (iii) Subtract the LOD from the all of measurements, deleting any that give a negative concentration. The argument against doing this is that the errors of the difference expand exponentially as this difference gets smaller and one may still be deleting some numbers. We recommend the second strategy, and we recommend using the median as the measure of central tendency. The median will not change until more than half of the measurements have been replaced, and the median does not depend on the log-normal distribution of the data. But the best approach is to make sure your blanks and the resulting LOD values are so low relative to the

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20 Helsel, D. R. Fabricating data: How substituting values for nondetects can ruin results, and what can be done about it, *Chemosphere*, **2006**, *65*, 2434–2439.

measurements that this correction is used only on a small number of samples. If one has >10–20% nondetects in a set of samples, one has a problem, and one needs to either use a more sensitive method or to eliminate the blank problems.

1.7 Problem Set

1.1 What is the average spacing between carbon atoms in diamond, the density of which is 3.51 g/cm^3?

1.2 At Nikel, Russia, the annual average concentration of sulfur dioxide is observed to be 50 μg/m^3 at 15 °C and 1 atm. What is this concentration of SO_2 in parts per billion?

1.3 Some modern cars do not come with an inflated spare tire. The tire is collapsed and needs to be inflated after it is installed on the car. To inflate the tire, the car comes with a pressurized can of carbon dioxide with enough gas to inflate three tires. Please estimate the weight of this can. *Warning: estimates required.*

1.4 Enrico Fermi (1901–1954), an Italian physicist, was known for his work on the first nuclear reactor in Chicago, and he won a Nobel Prize for this work. He was also known for asking doctoral students the following question during their oral candidacy exams: "How many piano tuners are in Chicago?" How would you answer this question? *Warning: estimates required.*

1.5 What would be the difference (if any) in the weights of two basketballs, one filled with air and one filled with helium? Please give your answer in grams. Assume the standard basketball has a diameter of 9.4 in. and is filled to a pressure of 8.0 psi. Sorry for the English units, but basketball was invented in the United States.

1.6 Acid rain was at one time an important point of contention between the United States and Canada. Much of this acid was the result of the emission of sulfur oxides by coal-fired electricity-generating plants in southern Indiana and Ohio. These sulfur oxides, when dissolved in rainwater, formed sulfuric acid and hence "acid rain." How many metric tonnes of Indiana coal, which averages 3.5% sulfur by weight, would yield the H_2SO_4 required to produce a 0.9-inch rainfall of pH 3.90 precipitation over a 10^4 mi^2 area?

1.7 Assume a power generation station consumes 3.5 million liters of oil/day, that the oil has an average composition of $C_{18}H_{32}$ and density 0.85 g/cm^3, and that the gas emitted from the exhaust stack of this plant contains 45 ppm of NO. How much NO is emitted per day? You may ignore NO in the stoichiometry.

1.8 Imagine that 300 tonnes of dry sewage is dumped into a small lake, the volume of which is 300 million liters. How many tonnes of oxygen are needed to completely degrade this sewage? You may assume the dry sewage has an elemental composition of $C_6H_{12}O_6$.

1.9 Assume an incorrectly adjusted lawnmower is operated in a closed two-car garage such that the combustion reaction in the engine is $C_8H_{14} + 15/2O_2 \rightarrow 8CO + 7H_2O$. How many grams of gasoline must be burned to raise the level of CO by 1000 ppm? *Warning: estimates required.*

1.10 The average concentration of polychlorinated biphenyls (PCBs) in the atmosphere around the Great Lakes is about 2 ng/m^3. What is this concentration in molecules/cm^3? Assume the average molecular weight of PCBs is 320.

1.11 This quote appeared in *Chemical and Engineering News* (September 3, 1990, p. 52), “One tree can assimilate about 6 kg of CO_2 per year or enough to offset the pollution produced by driving one car for 26 000 miles.” Is this statement likely correct? Justify your answer quantitatively. Assume gasoline has the formula C_9H_{16}, that its combustion is complete, and that the car gets 20 mpg.

1.12 Pretend you are an environmental chemist attending a dinner party in Washington with influential lawmakers.[21] While discussing your research with a senator over a martini, you realize that he or she has no idea what you are talking about when you describe concentrations of pollutants in terms of mixing ratios. Please describe to him or her how much a part per thousand (ppth), a part per million (ppm), and a part per billion (ppb) are in terms of drops of vermouth in bathtubs of gin. (Thanks goes to James N. Pitts, Jr., who used a similar analogy.) *Warning: estimates required.*

1.13 Water is ubiquitous in the atmosphere and consequently absorbs to all surfaces you might encounter in the environment (soil, vegetation,

21 You never know, but it might happen! Be prepared.

windows, buildings, etc.). If a window pane was uniformly covered with a single layer (a monolayer) of water, what would that surface coverage be in molecules/cm^2?

1.14 About 800 million liters of oil were released into the Gulf of Mexico during the 2010 Deepwater Horizon oil spill. What would be the dimensions of a cubic container (in feet of each equal side) necessary to hold it all? If the oil from this spill formed a film on the ocean surface that was one molecule thick, how much area would it cover? *Warning: estimates required.*

1.15 Nanoparticle silver is beginning to find many applications, some of which will lead to these particles entering the environment, thus understanding the fate of these nanoparticles is important. To get an idea of the silver concentrations with which one many be dealing, it is useful to know the number of silver atoms in a given nanoparticle. For this exercise, please estimate the number of silver atoms in a 10-nm diameter nanoparticle.

1.16 The detection limit of many chlorinated pollutants (such as DDT, chlordane, and PCBs) is on the order of 5 pg introduced into a gas chromatographic column. Assume that a sample of human adipose tissue contains 34 parts per trillion (ppt) of DDT, that the extraction procedure is 75% efficient, and that the equivalent of 5% of the final sample can be injected into the gas chromatograph for one analysis. What is the minimum size (in g) of adipose tissue that must be removed from a volunteer in order to detect this amount of DDT?

1.17 Given the following data, what is the concentration (in pg/m^3) of pyrene in this particular atmospheric sample? The volume of air sampled was 827 m^3; the amount of the internal standard (d_{10}-anthracene) added to the sample was 200 ng; the gas chromatograph peak area of pyrene was 35 300 counts; and the peak area of d_{10}-anthracene was 14 600 counts. In a preliminary calibration experiment, 200 ng of pyrene gave a peak area of 156 000 counts, and 200 ng of d_{10}-anthracene gave 97 300 counts.

1.18 The World Health Organization sets a standard of less than 0.2 mg for each 60-kg person per week as an acceptable mercury intake. In Canada, fish from the Great Lakes is considered edible if their mercury content is below 0.5 ppm. Are these values compatible?

1.19 A poorly trained environmental science student reported an atmospheric concentration of SO_2 of 75 ppb on a weight per weight basis. Please convert this number to the correct units.

1.20 Calculate the Gibbs free energy from enthalpy and entropy for the following reactions; use these values to evaluate whether the respective reactions are spontaneous.

a. $CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$
b. $2NO_2(g) + H_2O(l) \rightarrow HONO(aq) + HNO_3(aq)$
c. The dissolution of urea crystals, $(NH_2)_2CO$, in water

1.21 [EXCEL] A graduate student was asked to determine the association (if any) between two methods for the measurement of PCBs in fish. He or she obtained the following results (in ppm) for seven different samples using two different analytical methods. Is there a statistical association between the methods, and if so, how strong is it? *Hint*: Plot these data.

Sample no.	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Method A	9.0	18.2	17.5	14.2	11.0	10.1	12.2
Method B	7.5	15.5	14.3	12.2	19.0	8.5	9.8

1.22 [EXCEL] The following are a set of measurements of a fictitious pollutant in human blood.[22] The units are ng/g (or ppb). Assume the LOD for this set of data is 8 ppb. Calculate the geometric means and medians for the following four cases: (a) all of the data, (b) all of the data with values less than the LOD deleted, (c) all of the data with values less than the LOD replaced by LOD/2, and (d) the LOD subtracted from all of the values and any negative values deleted. What do you conclude?

6.45	10.82	16.30	24.92	31.20
6.88	12.04	16.61	26.15	31.25
7.05	13.82	17.83	28.72	34.12
8.89	13.95	20.20	30.21	36.71
9.72	14.64	22.89	30.39	37.99
10.80	15.93	24.82	30.88	49.49

22 Yes, we know we are violating our significant figure rule. But these are not real data.