Pearson New International Edition

Introduction to Environmental Engineering and Science

Gilbert M. Masters Wendell P. Ela

Third Edition

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Mass and Energy Transfer

> When you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of science.
>
> —*William Thomson, Lord Kelvin (1891)*

1 Introduction

This chapter begins with a section on units of measurement. Engineers need to be familiar with both the American units of feet, pounds, hours, and degrees Fahrenheit as well as the more recommended International System of units. Both are used in the practice of environmental engineering.

Next, two fundamental topics, which should be familiar from the study of elementary physics, are presented: the *law of conservation of mass* and the *law of conservation of energy*. These laws tell us that within any environmental system, we theoretically should be able to account for the flow of energy and materials into, and out of, that system. The law of conservation of mass, besides providing an important tool for quantitatively tracking pollutants as they disperse in the environment, reminds us that pollutants have to go somewhere, and that we should be wary of approaches that merely transport them from one medium to another.

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In a similar way, the law of conservation of energy is also an essential accounting tool with special environmental implications. When coupled with other thermodynamic principles, it will be useful in a number of applications, including the study of global climate change, thermal pollution, and the dispersion of air pollutants.

2 Units of Measurement

In the United States, environmental quantities are measured and reported in both the *U.S. Customary System* (USCS) and the *International System of Units* (SI), so it is important to be familiar with both. Here, preference is given to SI units, although the U.S. system will be used in some circumstances. Table 1 lists conversion factors between the SI and USCS systems for some of the most basic units that will be encountered.

In the study of environmental engineering, it is common to encounter both extremely large quantities and extremely small ones. The concentration of some toxic substance may be measured in parts per billion (ppb), for example, whereas a country's rate of energy use may be measured in thousands of billions of watts (terawatts). To describe quantities that may take on such extreme values, it is useful to have a system of prefixes that accompany the units. Some of the most important prefixes are presented in Table 2.

Often, it is the concentration of some substance in air or water that is of interest. Using the metric system in either medium, concentrations may be based on mass (usually mg or g), volume (usually L or m^3), or number (usually mol), which can lead to some confusion. It may be helpful to recall from chemistry that one mole of any substance has Avogadro's number of molecules in it (6.02×10^{23} molecules/mol) and has a mass equal to its molecular weight.

Liquids

Concentrations of substances dissolved in water are usually expressed in terms of mass or number per unit volume of mixture. Most often the units are milligrams (mg),

TABLE 1

Some Basic Units and Conversion Factors

Quantity	SI units	SI symbol ×	Conversion factor =	USCS units
Length	meter	m	3.2808	ft
Mass	kilogram	kg	2.2046	lb
Temperature	Celsius	°C	1.8 (°C) + 32	°F
Area	square meter	m^2	10.7639	ft^2
Volume	cubic meter	m^3	35.3147	ft^3
Energy	kilojoule	kJ	0.9478	Btu
Power	watt	W	3.4121	Btu/hr
Velocity	meter/sec	m/s	2.2369	mi/hr
Flow rate	$meter^3$/sec	m^3/s	35.3147	ft^3/s
Density	kilogram/$meter^3$	kg/m^3	0.06243	lb/ft^3

TABLE 2

Common Prefixes

Quantity	Prefix	Symbol
10^{-15}	femto	f
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	μ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
10	deka	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P
10^{18}	exa	E
10^{21}	zetta	Z
10^{24}	yotta	Y

micrograms (μg), or moles (mol) of substance per liter (L) of mixture. At times, they may be expressed in grams per cubic meter (g/m^3).

Alternatively, concentrations in liquids are expressed as mass of substance per mass of mixture, with the most common units being parts per million (ppm) or parts per billion (ppb). To help put these units in perspective, 1 ppm is about the same as 1 drop of vermouth added to 15 gallons of gin, whereas 1 ppb is about the same as one drop of pollutant in a fairly large (70 m^3) back-yard swimming pool. Since most concentrations of pollutants are very small, 1 liter of mixture has a mass that is essentially 1,000 g, so for all practical purposes, we can write

$$1\ \text{mg/L} = 1\ \text{g/m}^3 = 1\ \text{ppm (by weight)} \tag{1}$$

$$1\ \mu\text{g/L} = 1\ \text{mg/m}^3 = 1\ \text{ppb (by weight)} \tag{2}$$

In unusual circumstances, the concentration of liquid wastes may be so high that the specific gravity of the mixture is affected, in which case a correction to (1) and (2) may be required:

$$\text{mg/L} = \text{ppm (by weight)} \times \text{specific gravity of mixture} \tag{3}$$

EXAMPLE 1 **Fluoridation of Water**

The fluoride concentration in drinking water may be increased to help prevent tooth decay by adding sodium fluoride; however, if too much fluoride is added, it can cause discoloring (mottling) of the teeth. The optimum dose of fluoride in drinking water is about 0.053 mM (millimole/liter). If sodium fluoride (NaF) is purchased in 25 kg bags, how many gallons of drinking water would a bag treat? (Assume there is no fluoride already in the water.)

Solution Note that the mass in the 25 kg bag is the sum of the mass of the sodium and the mass of the fluoride in the compound. The atomic weight of sodium is 23.0, and fluoride is 19.0, so the molecular weight of NaF is 42.0. The ratio of sodium to fluoride atoms in NaF is 1:1. Therefore, the mass of fluoride in the bag is

$$\text{mass F} = 25 \text{ kg} \times \frac{19.0 \text{ g/mol}}{42.0 \text{ g/mol}} = 11.31 \text{ kg}$$

Converting the molar concentration to a mass concentration, the optimum concentration of fluoride in water is

$$\text{F} = \frac{0.053 \text{ mmol/L} \times 19.0 \text{ g/mol} \times 1{,}000 \text{ mg/g}}{1{,}000 \text{ mmol/mol}} = 1.01 \text{ mg/L}$$

The mass concentration of a substance in a fluid is generically

$$C = \frac{m}{V} \tag{4}$$

where m is the mass of the substance and V is the volume of the fluid. Using (4) and the results of the two calculations above, the volume of water that can be treated is

$$V = \frac{11.31 \text{ kg} \times 10^6 \text{ mg/kg}}{1.01 \text{ mg/L} \times 3.785 \text{ L/gal}} = 2.97 \times 10^6 \text{ gal}$$

The bag would treat a day's supply of drinking water for about 20,000 people in the United States!

Gases

For most air pollution work, it is customary to express pollutant concentrations in volumetric terms. For example, the concentration of a gaseous pollutant in parts per million (ppm) is the volume of pollutant per million volumes of the air mixture:

$$\frac{1 \text{ volume of gaseous pollutant}}{10^6 \text{ volumes of air}} = 1 \text{ ppm (by volume)} = 1 \text{ ppmv} \tag{5}$$

To help remind us that this fraction is based on volume, it is common to add a "v" to the ppm, giving ppmv, as suggested in (5).

At times, concentrations are expressed as mass per unit volume, such as μg/m^3 or mg/m^3. The relationship between ppmv and mg/m^3 depends on the pressure, temperature, and molecular weight of the pollutant. The ideal gas law helps us establish that relationship:

$$PV = nRT \tag{6}$$

where

P = absolute pressure (atm)
V = volume (m^3)
n = mass (mol)

R = ideal gas constant = 0.082056 $\text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
T = absolute temperature (K)

The mass in (6) is expressed as moles of gas. Also note the temperature is expressed in kelvins (K), where

$$\text{K} = {}^\circ\text{C} + 273.15 \tag{7}$$

There are a number of ways to express pressure; in (6), we have used atmospheres. One atmosphere of pressure equals 101.325 kPa (Pa is the abbreviation for Pascals). One atmosphere is also equal to 14.7 pounds per square inch (psi), so 1 psi = 6.89 kPa. Finally, 100 kPa is called a bar, and 100 Pa is a millibar, which is the unit of pressure often used in meteorology.

EXAMPLE 2 Volume of an Ideal Gas

Find the volume that 1 mole of an ideal gas would occupy at standard temperature and pressure (STP) conditions of 1 atmosphere of pressure and 0°C temperature. Repeat the calculation for 1 atm and 25°C.

Solution Using (6) at a temperature of 0°C (273.15 K) gives

$$V = \frac{1\,\text{mol} \times 0.082056\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 273.15\ \text{K}}{1\ \text{atm}} = 22.414\ \text{L}$$

and at 25°C (298.15 K)

$$V = \frac{1\ \text{mol} \times 0.082056\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 298.15\ \text{K}}{1\ \text{atm}} = 22.465\ \text{L}$$

From Example 2, 1 mole of an ideal gas at 0°C and 1 atm occupies a volume of 22.414 L ($22.414 \times 10^{-3}\ \text{m}^3$). Thus we can write

$$\text{mg/m}^3 = \text{ppmv} \times \frac{1\ \text{m}^3\ \text{pollutant}/10^6\ \text{m}^3\ \text{air}}{\text{ppmv}} \times \frac{\text{mol wt (g/mol)}}{22.414 \times 10^{-3}\ \text{m}^3/\text{mol}} \times 10^3\ \text{mg/g}$$

or, more simply,

$$\text{mg/m}^3 = \frac{\text{ppmv} \times \text{mol wt}}{22.414} \qquad \text{(at 0°C and 1 atm)} \tag{8}$$

Similarly, at 25°C and 1 atm, which are the conditions that are assumed when air quality standards are specified in the United States,

$$\text{mg/m}^3 = \frac{\text{ppmv} \times \text{mol wt}}{24.465} \qquad \text{(at 25°C and 1 atm)} \tag{9}$$

In general, the conversion from ppm to mg/m^3 is given by

$$\text{mg/m}^3 = \frac{\text{ppmv} \times \text{mol wt}}{22.414} \times \frac{273.15\ \text{K}}{T\ (\text{K})} \times \frac{P(\text{atm})}{1\ \text{atm}} \tag{10}$$

EXAMPLE 3 **Converting ppmv to mg/m^3**

The U.S. Air Quality Standard for carbon monoxide (based on an 8-hour measurement) is 9.0 ppmv. Express this standard as a percent by volume as well as in mg/m^3 at 1 atm and 25°C.

Solution Within a million volumes of this air there are 9.0 volumes of CO, no matter what the temperature or pressure (this is the advantage of the ppmv units). Hence, the percentage by volume is simply

$$\text{percent CO} = \frac{9.0}{1 \times 10^6} \times 100 = 0.0009\%$$

To find the concentration in mg/m^3, we need the molecular weight of CO, which is 28 (the atomic weights of C and O are 12 and 16, respectively). Using (9) gives

$$\text{CO} = \frac{9.0 \times 28}{24.465} = 10.3 \text{ mg/m}^3$$

Actually, the standard for CO is usually rounded and listed as 10 mg/m^3.

The fact that 1 mole of every ideal gas occupies the same volume (under the same temperature and pressure condition) provides several other interpretations of volumetric concentrations expressed as ppmv. For example, 1 ppmv is 1 volume of pollutant per million volumes of air, which is equivalent to saying 1 mole of pollutant per million moles of air. Similarly, since each mole contains the same number of molecules, 1 ppmv also corresponds to 1 molecule of pollutant per million molecules of air.

$$1 \text{ ppmv} = \frac{1 \text{ mol of pollutant}}{10^6 \text{ mol of air}} = \frac{1 \text{ molecule of pollutant}}{10^6 \text{ molecules of air}} \tag{11}$$

3 Materials Balance

Everything has to go somewhere is a simple way to express one of the most fundamental engineering principles. More precisely, the *law of conservation of mass* says that when chemical reactions take place, matter is neither created nor destroyed (though in nuclear reactions, mass can be converted to energy). What this concept allows us to do is track materials, for example pollutants, from one place to another with *mass balance* equations. This is one of the most widely used tools in analyzing pollutants in the environment.

The first step in a mass balance analysis is to define the particular region in space that is to be analyzed. This is often called the control volume. As examples, the control volume might include anything from a glass of water or simple chemical mixing tank, to an entire coal-fired power plant, a lake, a stretch of stream, an air basin above a city, or the globe itself. By picturing an imaginary boundary around

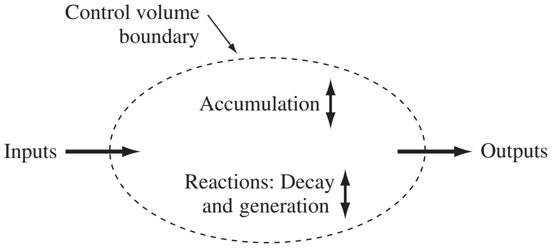

FIGURE 1 A materials balance diagram.

the region, as is suggested in Figure 1, we can then begin to quantify the flow of materials across the boundary as well as the accumulation and reaction of materials within the region.

A substance that enters the control volume has four possible fates. Some of it may leave the region unchanged, some of it may accumulate within the boundary, and some of it may be converted to some other substance (*e.g.,* entering CO may be oxidized to CO_2 within the region). There is also the possibility that more substance may be produced (*e.g.,* CO may be produced by cigarette smoking within the control volume of a room). Often, the conversion and production processes that may occur are lumped into a single category termed *reactions*. Thus, using Figure 1 as a guide, the following materials balance equation can be written for each substance of interest:

$$\begin{pmatrix}\text{Accumulation}\\ \text{rate}\end{pmatrix} = \begin{pmatrix}\text{Input}\\ \text{rate}\end{pmatrix} - \begin{pmatrix}\text{Output}\\ \text{rate}\end{pmatrix} + \begin{pmatrix}\text{Reaction}\\ \text{rate}\end{pmatrix} \tag{12}$$

The reaction rate may be positive if generation of the substance is faster than its decay, or negative if it is decaying faster than it is being produced. Likewise, the accumulation rate may be positive or negative. The *reaction* term in (12) does not imply a violation of the law of conservation of mass. Atoms are conserved, but there is no similar constraint on the chemical compounds, which may chemically change from one substance into another. It is also important to notice that each term in (12) quantifies a mass rate of change (*e.g.,* mg/s, lb/hr) and not a mass. Strictly, then, it is a mass rate balance rather than a mass balance, and (12) denotes that the rate of mass accumulation is equal to the difference between the rate the mass enters and leaves plus the net rate that the mass reacts within the defined control volume.

Frequently, (12) can be simplified. The most common simplification results when *steady state* or *equilibrium* conditions can be assumed. Equilibrium simply means that there is no accumulation of mass with time; the system has had its inputs held constant for a long enough time that any transients have had a chance to die out. Pollutant concentrations are constant. Hence the *accumulation rate* term in (12) is set equal to zero, and problems can usually be solved using just simple algebra.

A second simplification to (12) results when a substance is *conserved* within the region in question, meaning there is no reaction occurring—no radioactive decay, bacterial decomposition, or chemical decay or generation. For such conservative substances, the reaction rate in (12) is 0. Examples of substances that are typically modeled as conservative include total dissolved solids in a body of water, heavy metals in soils, and carbon dioxide in air. Radioactive radon gas in a home or

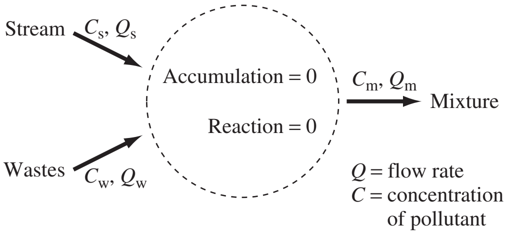

FIGURE 2 A steady-state conservative system. Pollutants enter and leave the region at the same rate.

decomposing organic wastes in a lake are examples of nonconservative substances. Often problems involving nonconservative substances can be simplified when the reaction rate is small enough to be ignored.

Steady-State Conservative Systems

The simplest systems to analyze are those in which steady state can be assumed (so the accumulation rate equals 0), and the substance in question is conservative (so the reaction rate equals 0). In these cases, (12) simplifies to the following:

$$\text{Input rate} = \text{Output rate} \tag{13}$$

Consider the steady-state conservative system shown in Figure 2. The system contained within the boundaries might be a lake, a section of a free flowing stream, or the mass of air above a city. One input to the system is a stream (of water or air, for instance) with a flow rate Q_s (volume/time) and pollutant concentration C_s (mass/volume). The other input is assumed to be a waste stream with flow rate Q_w and pollutant concentration C_w. The output is a mixture with flow rate Q_m and pollutant concentration C_m. If the pollutant is conservative, and if we assume steady state conditions, then a mass balance based on (13) allows us to write the following:

$$C_s Q_s + C_w Q_w = C_m Q_m \tag{14}$$

The following example illustrates the use of this equation. More importantly, it also provides a general algorithm for doing mass balance problems.

EXAMPLE 4 Two Polluted Streams

A stream flowing at 10.0 m^3/s has a tributary feeding into it with a flow of 5.0 m^3/s. The stream's concentration of chloride upstream of the junction is 20.0 mg/L, and the tributary chloride concentration is 40.0 mg/L. Treating chloride as a conservative substance and assuming complete mixing of the two streams, find the downstream chloride concentration.

Solution The first step in solving a mass balance problem is to sketch the problem, identify the "region" or control volume that we want to analyze, and label the variables as has been done in Figure 3 for this problem.

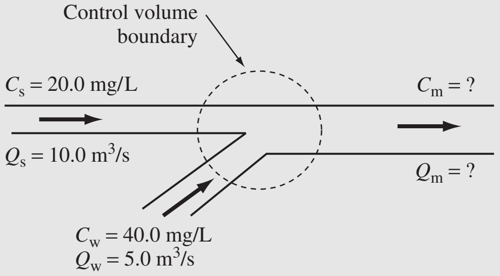

FIGURE 3 Sketch of system, variables, and quantities for a stream and tributary mixing example.

Next the mass balance equation (12) is written and simplified to match the problem's conditions

$$\xcancel{\begin{pmatrix}\text{Accumulation}\\ \text{rate}\end{pmatrix}} = \begin{pmatrix}\text{Input}\\ \text{rate}\end{pmatrix} - \begin{pmatrix}\text{Output}\\ \text{rate}\end{pmatrix} + \xcancel{\begin{pmatrix}\text{Reaction}\\ \text{rate}\end{pmatrix}}$$

The simplified (12) is then written in terms of the variables in the sketch

$$0 = C_s Q_s + C_w Q_w - C_m Q_m$$

The next step is to rearrange the expression to solve for the variable of interest—in this case, the chloride concentration downstream of the junction, C_m. Note that since the mixture's flow is the sum of the two stream flows, $Q_s + Q_w$ can be substituted for Q_m in this expression.

$$C_m = \frac{C_s Q_s + C_w Q_w}{Q_m} = \frac{C_s Q_s + C_w Q_w}{Q_s + Q_w}$$

The final step is to substitute the appropriate values for the known quantities into the expression, which brings us to a question of units. The units given for C are mg/L, and the units for Q are m^3/s. Taking the product of concentrations and flow rates yields mixed units of mg/L · m^3/s, which we could simplify by applying the conversion factor of 10^3 L $= 1$ m^3. However, if we did so, we should have to reapply that same conversion factor to get the mixture concentration back into the desired units of mg/L. In problems of this sort, it is much easier to simply leave the mixed units in the expression, even though they may look awkward at first, and let them work themselves out in the calculation. The downstream concentration of chloride is thus

$$C_m = \frac{(20.0 \times 10.0 + 40.0 \times 5.0)\ \text{mg/L} \cdot \text{m}^3\text{/s}}{(10.0 + 5.0)\ \text{m}^3\text{/s}} = 26.7\ \text{mg/L}$$

This stream mixing problem is relatively simple, whatever the approach used. Drawing the system, labeling the variables and parameters, writing and simplifying the mass balance equation, and then solving it for the variable of interest is the same approach that will be used to solve much more complex mass balance problems later in this chapter.