

Reading on
MASS BALANCES
(Materials Balances)

... VOLUME ...

$\times 10^3$ mg/g

(1.7)

1.3 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 (e.g., pollutants) from one place to another with mass balance equations.

The first step in a mass balance analysis is to define the particular region in space that is to be analyzed. As examples, the region might include anything from a 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 the region, as is suggested in Figure 1.1, we can then begin to identify the flow of materials across the boundary as well as the accumulation of materials within the region.

A substance that enters the region has three 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 CO₂ within the region). Thus, using Figure 1.1 as a guide, the following materials balance equation can be written for each substance of interest:

$$\left(\frac{\text{Input}}{\text{rate}}\right) = \left(\frac{\text{Output}}{\text{rate}}\right) + \left(\frac{\text{Decay}}{\text{rate}}\right) + \left(\frac{\text{Accumulation}}{\text{rate}}\right) \quad (1.11)$$

Notice that the “decay” term in (1.11) does not imply a violation of the law of conservation of mass. Atoms are conserved, but there is no similar constraint on the chemical reactions, which may change one substance into another.

Frequently, (1.11) can be simplified. The most common simplification results when *steady-state* or *equilibrium* conditions can be assumed. Equilibrium simply means that nothing is changing 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 (1.11) is set equal to zero and problems can usually be solved using just simple algebra.

A second simplification of (1.11) results when a substance is *conserved* within the region in question, meaning that there is no radioactive decay, bacterial decomposition, or chemical reaction occurring. For such conservative substances, the “decay rate” term in (1.11) is zero. 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. Nonconservative substances would include radioactive radon gas in a home or decomposing organic wastes in a lake. Many times problems involving nonconservative substances can be simplified when the reaction rate term is small enough to be ignored.

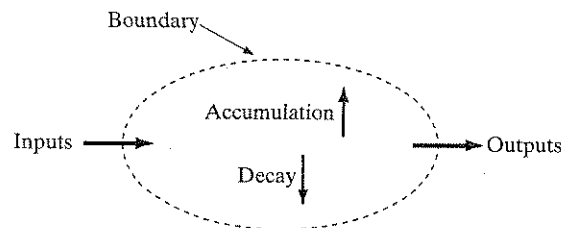


FIGURE 1.1 A materials balance diagram.

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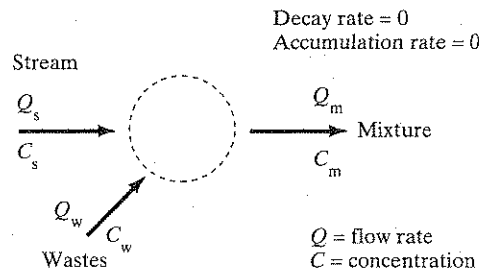


FIGURE 1.2 A steady-state conservative system. Pollutants enter and leave the region at the same rate.

Steady-state Conservative Systems

The simplest systems to analyze are those in which steady state is assumed and the substance in question is conservative. In these cases, (1.11) simplifies to the following:

$$\text{Input rate} = \text{Output rate} \quad (1.12)$$

Consider the steady-state conservative system shown in Figure 1.2.

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 (1.12) allows us to write the following:

$$C_s Q_s + C_w Q_w = C_m Q_m \quad (1.13)$$

The following example illustrates the use of this equation.

EXAMPLE 1.3 Two Polluted Streams

A stream flowing at 10.0 m³/s has a tributary feeding into it with a flow 5.0 m³/s. The stream's concentration of chlorides upstream of the junction is 20.0 mg/L and the tributary chloride concentration is 40.0 mg/L. Treating chlorides as a conservative substance, and assuming complete mixing of the two streams, find the downstream chloride concentration.

Solution We begin by sketching the problem and identifying the region that we want to analyze, as has been done in Figure 1.3.

Rearranging (1.13) to solve for the chloride concentration downstream gives us

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

Note that since the mixture flow is the sum of the two stream flows, $Q_s + Q_w$ has been substituted for Q_m in this expression. All that remains 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 for Q they are m³/s. Taking the product of concentrations and flow rates yields mixed units of mg/L · m³/s, which we could simplify by applying the conversion factor of 10³ L = 1 m³. However, if we did so, we should have to reapply that same conversion factor to

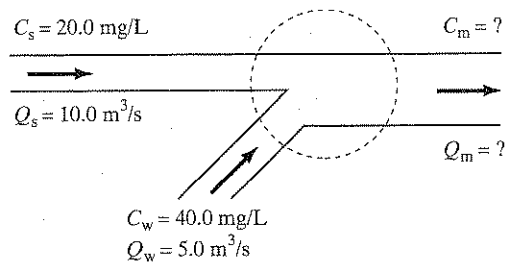


FIGURE 1.3 Flow rate and chloride concentrations for example stream and tributary.

get the mixture concentration back into the desired units of mg/L. In problems of this sort, it is much easier simply to 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 chlorides is thus

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

Steady-state Systems with Nonconservative Pollutants

Many contaminants undergo chemical, biological, or nuclear reactions at a rate sufficient to necessitate treating them as nonconservative substances. If we continue to assume that steady-state conditions prevail so that the rate of accumulation is zero, but now treat the pollutants as nonconservative, then (1.11) becomes

$$\text{Input rate} = \text{Output rate} + \text{Decay rate} \quad (1.14)$$

The decay of nonconservative substances is frequently modeled as a first-order reaction; that is, it is assumed that the rate of loss of the substance is proportional to the amount of the substance that is present. That is,

$$\frac{dC}{dt} = -KC \quad (1.15)$$

where K is a reaction rate coefficient with dimensions of (time^{-1}) , the negative sign implies a loss of substance with time, and C is the pollutant concentration. To solve this differential equation, we can rearrange the terms and integrate

$$\int_{C_0}^C \frac{dC}{C} = \int_0^t (-K) dt$$

which yields

$$\ln(C) - \ln(C_0) = \ln\left(\frac{C}{C_0}\right) = -Kt$$

Solving for concentration gives us

$$C = C_0 e^{-Kt} \tag{1.16}$$

where C_0 is the initial concentration. That is, assuming a first-order reaction, the concentration of the substance in question decays exponentially. This exponential function will appear so often in this text that it will be reintroduced and explored more fully in Chapter 3.

Equation (1.15) indicates the rate of change of *concentration* of the substance. If we assume that the substance is uniformly distributed throughout a volume V , then the total *amount* of substance is CV . The total rate of decay of the amount of a nonconservative substance is thus $d(CV)/dt = V dC/dt$, so using (1.15) we can write for a nonconservative substance:

$$\text{Decay rate} = KCV \tag{1.17}$$

Substituting (1.17) into (1.14) gives us our final simple, yet useful, expression for the mass balance involving a nonconservative pollutant in a steady-state system:

$$\text{Input rate} = \text{Output rate} + KCV \tag{1.18}$$

Implicit in (1.18) is the assumption that the concentration C is uniform throughout the volume V . This complete mixing assumption is common in the analysis of chemical tanks, called *reactors*, and in such cases the idealization is referred to as a *continuously stirred tank reactor (CSTR) model*. In other contexts, such as modeling air pollution, the assumption is referred to as a *complete mix box model*.

EXAMPLE 1.4 A Polluted Lake

Consider a $10.0 \times 10^6 \text{ m}^3$ lake fed by a polluted stream having a flow rate of $5.0 \text{ m}^3/\text{s}$ and pollution concentration equal to 10.0 mg/L (Figure 1.4). There is also a sewage outfall that discharges $0.5 \text{ m}^3/\text{s}$ of wastewater having a pollutant concentration of 100 mg/L . The stream and sewage wastes have a reaction rate coefficient of $0.20/\text{day}$. Assuming the pollution is completely mixed in the lake, and assuming no evaporation or other water losses or gains, find the steady-state concentration.

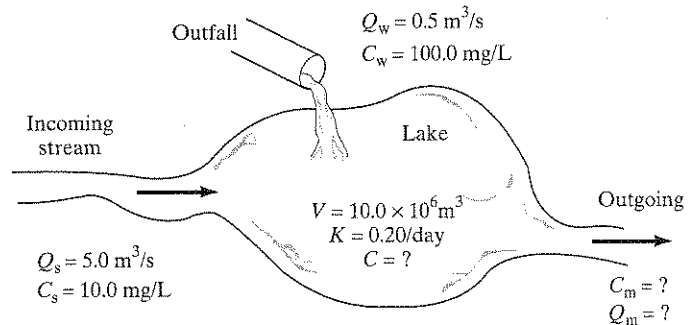


FIGURE 1.4 A lake with a nonconservative pollutant.



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Solution Assuming that complete and instantaneous mixing occurs in the lake implies that the concentration in the lake C is the same as the concentration of the mix leaving the lake, C_m . Using (1.18),

$$\text{Input rate} = \text{Output rate} + KCV \quad (1.18)$$

We can find each term as follows:

$$\begin{aligned} \text{Input rate} &= Q_s C_s + Q_w C_w \\ &= (5.0 \text{ m}^3/\text{s} \times 10.0 \text{ mg/L} + 0.5 \text{ m}^3/\text{s} \times 100.0 \text{ mg/L}) \times 10^3 \text{ L/m}^3 \\ &= 1.0 \times 10^5 \text{ mg/s} \end{aligned}$$

$$\begin{aligned} \text{Output rate} &= Q_m C_m = (Q_s + Q_w)C \\ &= (5.0 + 0.5) \text{ m}^3/\text{s} \times C \text{ mg/L} \times 10^3 \text{ L/m}^3 = 5.5 \times 10^3 C \text{ mg/s} \end{aligned}$$

$$\begin{aligned} \text{Decay rate} &= KCV = \frac{0.20/\text{d} \times C \text{ mg/L} \times 10.0 \times 10^6 \text{ m}^3 \times 10^3 \text{ L/m}^3}{24 \text{ hr/d} \times 3600 \text{ s/hr}} \\ &= 23.1 \times 10^3 C \text{ mg/s} \end{aligned}$$

So from (1.14)

$$1.0 \times 10^5 = 5.5 \times 10^3 C + 23.1 \times 10^3 C = 28.6 \times 10^3 C$$

$$C = \frac{1 \times 10^5}{28.6 \times 10^3} = 3.5 \text{ mg/L}$$

Idealized models involving nonconservative pollutants in completely mixed, steady-state systems are used to analyze a variety of commonly encountered water pollution problems such as the one shown in the previous example. The same simple models can be applied to certain problems involving air quality, as the following example demonstrates.

EXAMPLE 1.5 A Smoky Bar

A bar with volume 500 m^3 has 50 smokers in it, each smoking two cigarettes per hour (see Figure 1.5). An individual cigarette emits, among other things, about 1.4 mg of formaldehyde (HCHO). Formaldehyde converts to carbon dioxide with a reaction rate coefficient $K = 0.40/\text{hr}$. Fresh air enters the bar at the rate of $1000 \text{ m}^3/\text{hr}$, and stale air leaves at the same rate. Assuming complete mixing, estimate the steady-state concentration of formaldehyde in the

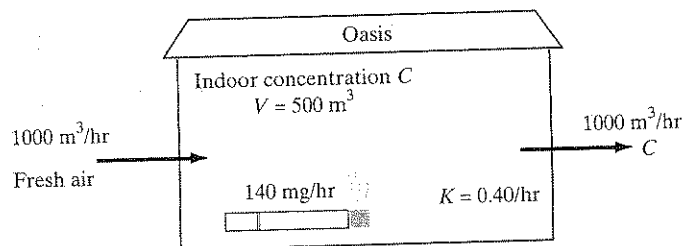


FIGURE 1.5 Tobacco smoke in a bar.

air. At 25 °C and 1 atm of pressure, how does the result compare with the threshold for eye irritation of about 0.05 ppm?

Solution The rate at which formaldehyde enters the bar is

$$\text{Input rate} = 50 \text{ smokers} \times 2 \text{ cigs/hr} \times 1.4 \text{ mg/cig} = 140 \text{ mg/hr}$$

Since complete mixing is assumed, the concentration of formaldehyde C in the bar is the same as the concentration in the air leaving the bar, so

$$\text{Output rate} = 1000 \text{ m}^3/\text{hr} \times C(\text{mg/m}^3) = 1000C \text{ mg/hr}$$

and the decay rate is

$$\text{Decay rate} = KCV = (0.40/\text{hr}) \times (C \text{ mg/m}^3) \times (500 \text{ m}^3) = 200C \text{ mg/hr}$$

So, from (1.14),

$$\text{Input rate} = \text{Output rate} + \text{Decay rate}$$

$$140 = 1000C + 200C$$

$$C = \frac{140}{1200} = 0.117 \text{ mg/m}^3$$

We will use (1.8) to convert mg/m^3 to ppm. The molecular weight of formaldehyde is 30, so

$$\text{HCHO} = \frac{C(\text{mg/m}^3) \times 24,465}{\text{mol wt}} = \frac{0.117 \times 24,465}{30} = 0.095 \text{ ppm}$$

This is nearly double the 0.05 ppm threshold for eye irritation.

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(1.18)