PART I

REACTORS AND REACTIONS IN WATER QUALITY ENGINEERING

1

MASS BALANCES

1.1 INTRODUCTION: THE MASS BALANCE CONCEPT

This book deals with the analysis of physical and chemical processes that alter water quality in aquatic systems. The primary systems of interest are the reactors used in water and wastewater treatment operations, although the principles apply equally well to natural aquatic systems, such as rivers, lakes, and oceans.

The first part of this book (Chapters 1–4) deals with reaction engineering and reactor analysis. These terms refer to the overall process of characterizing how the physical features of a system (e.g., volume, mixing characteristics, layout) combine with chemical factors (reaction rates, equilibrium relationships) to control the extent to which a reaction proceeds. In this definition, the word *reactor* is not restricted to engineered systems, but rather refers to any region of space where a reaction is occurring. Thus, a reactor may be as small as a single water droplet or as large as an entire lake. Reactor analysis is an essential step in predicting how a system responds to varying input rates or concentrations, in deciding how big a reactor must be to accomplish a predefined treatment objective, or in comparing different design options. Whatever the specific goal, the analysis consists of writing one or more mass balance equations, determining the values of the parameters in these equations, and then solving the equations for the quantities of interest.

A *mass balance* is an accounting tool that is used to keep track of how much of a substance is present in a given region of space at a given time. In other words, it is a formal statement of the principle of conservation of mass. When analyzing water chemistry problems, mass balances are frequently written to apply the principle of conservation of mass to systems in which there is no gradient of concentration with respect to time or distance. In such cases, the mass balance states that all the components that were originally added to the system must still be there once equilibrium is attained, even though they might be present in a different form. By combining mass balances with the relationships expressed by equilibrium constants and the charge balance, we can determine the speciation of the chemical components of the system at equilibrium.

In this book, mass balances are used most often to characterize systems in which concentrations are a function of time or location, and the mass balance equations are most frequently written in terms of the time derivative of mass. That is, rather than equating the total *amount* of a species i in the system before and after equilibration, the mass balances describe the *rates* at which i enters, exits, reacts, and accumulates in the system. In words,

$$\begin{pmatrix} \text{Rate of change} \\ \text{of mass of } i \\ \text{stored in the} \\ \text{system} \end{pmatrix} = \begin{pmatrix} \text{Rate at which} \\ i \text{ enters the} \\ \text{system from} \\ \text{outside} \end{pmatrix} - \begin{pmatrix} \text{Rate at which} \\ i \text{ exits the} \\ \text{system to} \\ \text{the outside} \end{pmatrix}$$

$$+ \begin{pmatrix} \text{Rate at which} \\ i \text{ is generated} \\ \text{inside the} \\ \text{reactor} \end{pmatrix} - \begin{pmatrix} \text{Rate at which} \\ i \text{ is destroyed} \\ \text{inside the} \\ \text{reactor} \end{pmatrix}$$

This statement is a valid representation of the principle of conservation of mass and is applicable to any item in any reactor. The space defining the reactor (i.e., the space over which the mass balance is being written) is referred to as the *control volume* (CV). To convert the previous statement into

a mathematical form that is applicable to a specific system of interest, it is necessary to

(1) Identify the substance for which the balance is to be written (i.e., what is i?).
(2) Define the system boundaries so that it is clear whether a given molecule of i is inside or outside the CV.
(3) Establish all the ways that i can enter or exit the CV.
(4) Establish all the ways that i can be created or destroyed within the CV.

In carrying out the first two steps, the importance of being precise when identifying both the item of interest and the boundaries of the system deserves emphasis. For instance, if a mass balance is being written for copper, is it a mass balance on total copper, dissolved copper, or free, uncomplexed cupric ion? If the system is a lake, does it include only the aqueous phase above the bottom sediment, or all the material in the water column (solution and suspended solids)? Does it include a portion of the interstitial solution in the lake bed or any rooted aquatic plants? Choosing the system boundaries to include or exclude any of these items is acceptable, and we could write a valid mass balance for any of these choices. However, depending on what we hope to learn by solving the mass balance, one set of system boundaries might be more useful than another.

Three choices for the system boundaries for a mass balance characterizing a water treatment process are shown in Figure 1-1. The flow diagram shown is used in the conventional activated sludge process for biological treatment of wastewater, and also for certain precipitation processes in water and wastewater treatment operations (specifically, precipitation processes that incorporate sludge recycle). The boundaries shown in Figure 1-1a isolate the tank where the key biological or chemical conversions occur, those shown in Figure 1-1b isolate the portion of the system where solid/liquid separation is accomplished, and those shown in Figure 1-1c encompass the entire treatment system. As noted in the previous paragraph, a valid mass balance could be written using any of these choices for the system boundaries, but the type of information that could be derived by solving the mass balance would be different in each case. A numerical example demonstrating this point is presented at the end of this section.

Conceptually, the third and fourth steps needed to write a mass balance are straightforward. In most systems, the only way in which a substance can enter or leave a system is by physical movement (transport), and the only way in which it can be formed or destroyed inside the system is by chemical reactions (including biochemical and nuclear reactions as special types of chemical reactions).

Physical transport processes include advection, diffusion, and dispersion, all of which can move molecules across the system boundaries either into or out of the CV. *Advection*, or
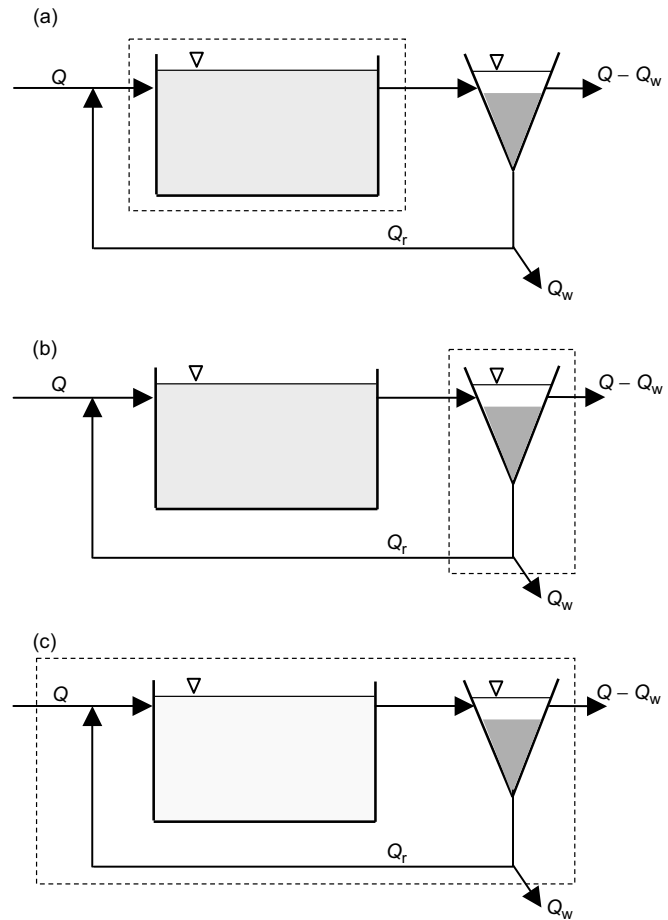

FIGURE 1-1. Three different choices (indicated by the broken lines) for the boundaries of the control volume for a mass balance in a system consisting of a reactor and a settling basin, with recycle of settled solids to the reactor influent. Q, Q_r, and Q_w are the influent flow rate, the flow rate of the recycle stream, and the flow rate of the waste (sludge) stream, respectively.

bulk flow, is flow in response to a driving force (e.g., a pressure gradient) that acts on all molecules in a region of space to move them in a given direction. This process contrasts with *diffusion*, which is the net effect of random molecular movement caused by the molecules' thermal-kinetic energy. Although the diffusive motion of any individual molecule is random, when the random motion of all the molecules is coupled with a concentration gradient, the net effect is transport in the direction that diminishes local concentration differences.

Dispersion might be considered as a cross between advection and diffusion. When a force is applied to a fluid, different portions of the fluid tend to move at different velocities. In laminar flow in a pipe, the parabolic distribution of velocities leads to some molecules of fluid (and any chemicals in that fluid) advancing through the pipe faster than others; in this case, the velocity is a well-defined

function of distance from the wall. In laminar flow in porous media, packets of fluid pass through some pores quickly and other pores much more slowly, leading to differences in the rate of transport of chemicals by different packets. In contrast to the situation in pipes, the velocity profile in the latter situation does not bear any well-defined relationship to location in the flow pattern. The same statement is true in turbulent flow, in which eddies form and transport mass from one point to another; in this case, the velocity of each packet of fluid is characterized by fluctuations around a mean value, although the mean velocity of the bulk fluid might remain constant.

In all the systems described above, the portion of the transport of mass that is different from the average advective transport is attributed to *dispersion*. In cases where dispersive transport is dominated by random fluctuations in velocity (such as the latter two situations described in the preceding paragraph), it can be modeled and analyzed identically to diffusion, with packets of water in dispersive mixing being the analogs of molecules in diffusive mixing. A thorough description of dispersion, especially as it applies to porous media, is given by Bear (1979).

Chemical reactions can also alter the mass of i in the region of space enclosed by the system boundaries. However, in the case of chemical reactions, the key processes are creation of i from other molecules, or conversion of i into other molecules, within (as opposed to across) the system boundaries.

Based on the preceding discussion, the determination of whether or not a transport or reaction process should be included in a mass balance on i for a specific situation can be made by applying two simple rules:

(1) Terms describing physical transport are included in the mass balance if and only if they cause i to cross the system boundaries. If a molecule of i moves from one point to another strictly within or strictly outside the CV, such movement is not reflected in the mass balance.

(2) Terms describing chemical reactions in which i participates are included if the reactions occur within the system boundaries and are excluded if they occur outside the system boundaries.

An easy way to decide whether a physical transport process should be included in a mass balance expression is to imagine that the system is enclosed in a permeable balloon. If the process carries molecules of i across the surface of the balloon, it must be included in the mass balance; on the other hand, if it causes molecules of i to move around either inside or outside the balloon, but does not carry i across the surface, it should not be included.

To understand the basic principle and the essential simplicity of a mass balance, it might be useful to consider an analogy between a mass balance and the accounting that applies to a savings account. When balancing a savings account, we need to consider deposits and withdrawals, which might be considered as physical transfers of money from/to the external world. On the other hand, interest payments and fees paid for the bank's services might be considered as transfers that occur internally in the bank. While it may be convenient to separate these two groups of transactions when analyzing an account, it is also true that a dollar deposited and a dollar of interest are indistinguishable once they are in the account. Similarly, in a chemical mass balance, a molecule of i that enters the system by physically crossing a system boundary is indistinguishable from one that is generated internally in the system by a reaction. Thus, if a molecule of i is found in the system at some time, is it neither necessary, nor in general is it possible, to decide how the molecule got there. All that is known about the molecule, and all that matters, is that it is there.

Once the steps listed above are completed, the system is fully defined, and it should be possible to write a detailed mass balance (in words) that characterizes i in the system. Such a mass balance will have terms that fit into the categories shown in the following statement, but which are more detailed and system-specific.

$$
\begin{array}{l}
\text{Rate of change} \\
\text{of the amount of} \\
i \text{ stored within} \\
\text{the system}
\end{array}
=
\begin{array}{l}
\text{Net rate} \\
\text{(in}-\text{out) at} \\
\text{which } i \text{ enters} \\
\text{by advection}
\end{array}
$$

$$
+
\begin{array}{l}
\text{Net rate} \\
\text{(in}-\text{out) at which } i \\
\text{enters by diffusion} \\
\text{and dispersion}
\end{array}
+
\begin{array}{l}
\text{Net rate} \\
\text{(formation}-\text{destruction)} \\
\text{at which } i \text{ is created by} \\
\text{chemical reaction}
\end{array}
$$

For instance, the flow scheme shown in Figure 1-1a might be used in a water softening process, in which soluble calcium (all of which we assume to be Ca^{2+}) is removed from solution as a $CaCO_3(s)$ precipitate. A mass balance on Ca^{2+} in such a system, with system boundaries chosen to enclose only the precipitation reactor, might be expressed as follows:

$$
\begin{array}{l}
\text{Rate of} \\
\text{change of} \\
\text{mass of} \\
Ca^{2+} \text{in the} \\
\text{reactor}
\end{array}
=
\begin{array}{l}
\text{Rate at which} \\
Ca^{2+} \text{enters into} \\
\text{the mixed} \\
\text{influent/} \\
\text{recycle stream}
\end{array}
-
\begin{array}{l}
\text{Rate at which} \\
Ca^{2+} \text{leaves in} \\
\text{the effluent} \\
\text{from the} \\
\text{reactor}
\end{array}
$$

$$
+
\begin{array}{l}
\text{Rate at which } Ca^{2+} \\
\text{enters the reactor by} \\
\text{diffusion and dispersion} \\
\text{at the points where the} \\
\text{inlet and outlet pipes} \\
\text{connect to the reactor}
\end{array}
-
\begin{array}{l}
\text{Rate at which} \\
Ca^{2+} \text{precipitates} \\
\text{to form } CaCO_3(s) \\
\text{in the reactor}
\end{array}
$$

In some systems, it is useful to write two or more mass balances with different system boundaries. In many such cases, an input term for one set of boundaries is an output term for another. For instance, in a system where volatile organic compounds (VOCs) are being stripped from solution by a gas, the rate at which VOCs leave the liquid equals the rate at which they enter the gas, so terms representing this transfer have the same magnitude but different signs in mass balances on the two phases.

Although the qualitative mass balances described above are of some value, to be truly useful they must be converted into quantitative mathematical expressions and solved, so that we can compute the concentration of i explicitly as a function of time and/or location. The steps needed to carry out this conversion are detailed in the remainder of the chapter, where mathematical expressions are derived for each of the terms in the mass balance. With the aid of these expressions, it is possible to identify the physical/chemical factors that control a given process, evaluate these factors in an existing system, and/or use the information to design a process to accomplish a desired goal.

A Note on Dimensions. Since mass balances for the systems of interest describe rates at which material enters or leaves the system, the appropriate dimensions for all terms in the mass balance are mass/time. By using these dimensions, mass balances can be written even for systems in which the volume, pressure, temperature, or shape are variable. In some cases, it is convenient to divide all terms in the mass balance by the system volume, so that they have dimensions of mass per unit volume per time or, equivalently, concentration per time. In this book, we refer to the mass balances written in the latter way as *volume-normalized mass balances*.

In a few cases, an equation essentially identical to a mass balance is written on a basis other than mass. The most common such equations represent an accounting based on numbers, such as the number of particles in a suspension. The dimensions for these equations are specific to the item of interest; for example, for a particle number balance, the dimensions of each term are time^{-1}, or, for a volume-normalized number balance, (volume $\times$ time)$^{-1}$.

■   **EXAMPLE 1-1.** A common approach to soften water is to adjust the chemistry of the solution to cause $CaCO_3(s)$ to precipitate. As noted previously, such processes often utilize a flow scheme like that shown in Figure 1-1. New solids are generated in the main reaction tank, and then the solids are separated from solution in a settling tank. However, rather than discarding all of the solids, a fraction of the settled sludge is returned to the reaction tank to provide seed crystals onto which more solid can precipitate. The advantages of this operating scheme are discussed in Chapter 9. The relevant reaction is
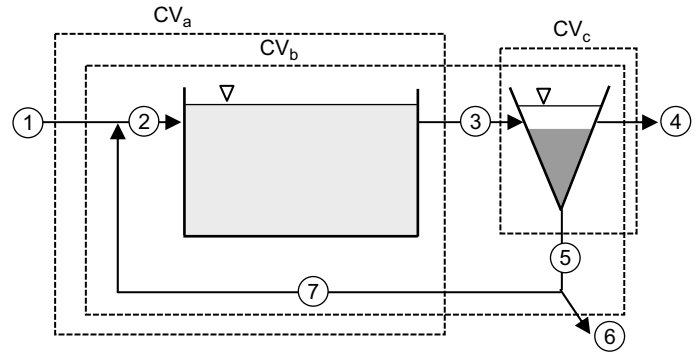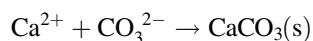
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s)$$

FIGURE 1-2.   Various control volumes for mass balances that are useful for solving the example problem.

A proposed water softening process will treat a flow of $3.0\,\text{m}^3/\text{s}$. The objective is to induce precipitation of $CaCO_3(s)$ to reduce the dissolved Ca^{2+} concentration from 150 to 40 mg/L. The influent contains no $CaCO_3(s)$. The settling step is expected to be very efficient, so the $CaCO_3(s)$ concentration in the treated effluent is negligible. Figure 1-2, which is a specific version of the more general Figure 1-1, shows some flow streams labeled and some potentially useful control volume (CV) boundaries identified. The flow rates at the indicated points are as follows:

$$Q_1 = 3000\,\text{L/s}, \quad Q_2 = 3240\,\text{L/s}, \quad Q_3 = 3240\,\text{L/s},$$
$$Q_4 = 2916\,\text{L/s}, \ Q_5 = 324\,\text{L/s}, \ Q_6 = 84\,\text{L/s}, \ Q_7 = 240\,\text{L/s}$$

Assuming that the water volumes in the various tanks, the water flow rates, and the concentrations of all the chemicals in the system are steady over time, write mass balances using appropriate CVs to determine the concentration of $CaCO_3(s)$ solids (mg/L) in the pipe between the main reactor and the settling basin (pipe 3), the pipe leading to the sludge processing facility (pipe 6), and the pipe conveying recycled solids to the main reaction vessel (pipe 7). Assume also that the precipitation reaction occurs only in the reactor, and not in the settling tank.

Solution. The $CaCO_3(s)$ concentrations (which we represent as c_s) at locations 1 and 4 are given as zero. Given this information, the location of interest where it is easiest to calculate c_s is point 6, based on a mass balance on $CaCO_3(s)$ in control volume CV_b (because only one of the three streams crossing the boundary of CV_b contains $CaCO_3(s)$).

The mass balance states that the rate of change of the mass of $CaCO_3(s)$ stored in the CV equals the rate at which $CaCO_3(s)$ enters the CV, minus the rate at which it exits the CV, plus the rate at which it is generated inside the CV. In this case, the rate at which $CaCO_3(s)$ enters or leaves in any stream i can be expressed as $Q_i c_{s,i}$. Because the system is specified to be operating with steady volumes and

concentrations throughout, the mass of $CaCO_3(s)$ in the CV is not changing, so the mass balance on $CaCO_3(s)$ in CV_b can be written as follows:

$$\begin{pmatrix} \text{Rate of change of mass} \\ \text{of } CaCO_3(s) \text{ stored in CV}_b \end{pmatrix}$$

$$= Q_1 c_{s,1} - Q_4 c_{s,4} - Q_6 c_{s,6} + \begin{pmatrix} \text{Rate of } CaCO_3(s) \\ \text{generation in CV}_b \end{pmatrix}$$

$$Q_6 c_{s,6} = \begin{pmatrix} \text{Rate of } CaCO_3(s) \\ \text{generation in CV}_b \end{pmatrix}$$

By our assumption, the only place where $CaCO_3(s)$ is generated by chemical precipitation in CV_b is the main reaction tank. Because we have information about the rates at which Ca^{2+} enters and leaves CV_b, and because we can relate the loss of Ca^{2+} to the production of $CaCO_3(s)$ via the reaction stoichiometry, it is convenient to proceed by writing a mass balance on Ca^{2+} in CV_b, as follows:

$$\begin{pmatrix} \text{Rate of change of} \\ \text{mass of } Ca^{2+} \text{ in CV}_b \end{pmatrix} = Q_1 c_{Ca^{2+},1} - Q_4 c_{Ca^{2+},4} - Q_6 c_{Ca^{2+},6}$$

$$+ \begin{pmatrix} \text{Rate of appearance of } Ca^{2+} \\ \text{in CV}_b \text{ by precipitation} \end{pmatrix}$$

The mass of Ca^{2+} stored in the reactor is not changing over time, so the term on the left is zero. Furthermore, all the Q and c terms on the right are given in the problem statement. (Because no chemical reaction occurs in the settling basin, the concentration of Ca^{2+} in both streams leaving that basin is the target concentration of 40 mg/L.) Also, because we know that Ca^{2+} is removed from solution by the precipitation reaction, it is convenient to write the final term in the previous equation as a subtraction of the rate of loss of Ca^{2+} in the CV. Making this change and substituting the known values into the previous equation, we obtain

$$0 = (3000\,\text{L/s})(150\,\text{mg/L}) - (2916\,\text{L/s})(40\,\text{mg/L})$$

$$- (84\,\text{L/s})(40\,\text{mg/L}) - \begin{pmatrix} \text{Rate of loss of } Ca^{2+} \text{ in} \\ \text{CV}_b \text{ by precipitation} \end{pmatrix}$$

$$\begin{pmatrix} \text{Rate of loss of } Ca^{2+} \text{ in} \\ \text{CV}_b \text{ by precipitation} \end{pmatrix} = 330,000\,\text{mg/s} = 330\,\text{g/s}$$

Noting that the molecular weights of Ca^{2+} and $CaCO_3(s)$ are 40 and 100, respectively, we compute the rate of $CaCO_3(s)$ generation as follows:

$$\text{Rate of } CaCO_3(s) \text{ generation} = \left(330\,\text{g/s Ca}^{2+}\right) \frac{100\,\text{g } CaCO_3(s)}{40\,\text{g Ca}^{2+}}$$

$$= 825\,\text{g/s } CaCO_3(s) \text{ generated}$$

Inserting this value into the mass balance on $CaCO_3(s)$ derived previously, we can find $c_{s,6}$ as

$$Q_6 c_{s,6} = \begin{pmatrix} \text{Rate of } CaCO_3(s) \\ \text{generation in CV}_b \end{pmatrix}$$

$$c_{s,6} = \frac{825\,\text{g/s}}{84\,\text{L/s}} = 9.82\,\text{g/L}$$

We can find $c_{s,3}$ by a mass balance on $CaCO_3(s)$ using CV_c, as follows:

$$\begin{pmatrix} \text{Rate of change of mass} \\ \text{of } CaCO_3(s) \text{ in CV}_c \end{pmatrix} = Q_3 c_{s,3} - Q_4 c_{s,4} - Q_5 c_{s,5}$$

$$+ \begin{pmatrix} \text{Rate of generation of } CaCO_3(s) \\ \text{in CV}_c \text{ by precipitation} \end{pmatrix}$$

Because the splitting of the flow stream at the junction of points 5, 6, and 7 does not involve any redistribution of solids, the solid concentrations in all three of these streams are the same; that is, $c_{s,5} = c_{s,6} = c_{s,7} = 9.82\,\text{g/L}$. Substituting these equalities into the mass balance, we find

$$0 = (3240\,\text{L/s})c_{s,3} - (2916\,\text{L/s})(0.0\,\text{g/L})$$

$$- (324\,\text{L/s})(9.82\,\text{g/L}) + 0$$

$$c_{s,3} = 0.982\,\text{g/L} = 982\,\text{mg/L} \qquad \blacksquare$$

1.2   THE MASS BALANCE FOR A SYSTEM WITH UNIDIRECTIONAL FLOW AND CONCENTRATION GRADIENT

In this section, we derive a mathematical expression for a mass balance on a substance i in a CV with only one inlet and one outlet through which water flows directly into or out of the system, as shown schematically in Figure 1-3.
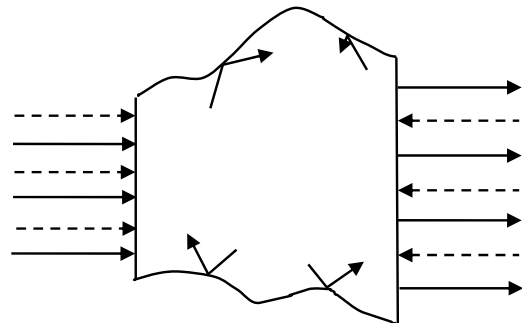

FIGURE 1-3. Schematic representation of the control volume, flow pattern (solid arrows), and concentration gradients (dashed arrows) in a hypothetical system in which the flow and the concentration gradients are perpendicular to the boundaries at the inlet and outlet.

Furthermore, the water is assumed to be well-mixed in the direction perpendicular to the flow as it crosses the system boundary; for example, if the flow is in the $+x$ direction, the concentration of i may vary in the x direction, but not in the $y-z$ plane at the inlet or outlet. These assumptions are reasonable for many real systems, such as a mixed-tank reactor with inflow and outflow through pipes, a tubular reactor with no internal axial mixing (a *plug flow reactor*), or a section of a river. No constraints are placed on the geometrical shape of the system or on the gradients that might exist inside it, as long as the gradients at the boundaries are exclusively in the direction of bulk flow.

The Storage Term

The mass of i present (stored) in any differentially small volume element dV ($=dx dy dz$) within the system equals the product of the concentration of i in that volume element and the volume, or $c dV$.[1] To determine the total mass of i in the entire CV, it is necessary to sum the mass of i in all these differential volumes; that is, to integrate this term over the entire volume

$$\text{Mass of } i \text{ in volume } V = \int c\, dV \qquad (1\text{-}1)$$

The derivative of this quantity with respect to time gives the rate of change of the amount of i stored in volume V. Thus, the storage term in the mass balance can be represented as

$$\text{Rate of change of mass of } i \text{ in volume } V = \frac{\partial}{\partial t} \int c\, dV$$

$$(1\text{-}2)$$

In both engineered reactors and natural systems, conditions are often encountered in which one of two simplifications applies to the storage term. First, in many systems, the concentration of the substance of interest is approximately uniform throughout the CV; such systems are sometimes referred to as *well-mixed*, although the condition can sometimes be met without physical mixing. Examples include tanks where concentrated chemical reagents (e.g., acids or bases, alum in coagulation processes, or hypochlorite species in disinfection processes) are added to and, ideally, dispersed rapidly throughout the solution by intensive, mechanically induced mixing. In other cases, the water in a tank is thoroughly mixed by rising gas bubbles when air or another gas (e.g., pure oxygen, ozone, or carbon dioxide) is

injected to dissolve the injected gas or strip a volatile contaminant from the solution. In such systems, the right side of Equation 1-2 can be written as $V(dc/dt) + c(dV/dt)$. Furthermore, in many such cases, the volume of the system is constant, in which case the expression simplifies to $V(dc/dt)$. (If the system volume is constant but the concentration varies from one location to the next, the integral can be written as $\int (\partial c/\partial t) dV$, but this modification does not substantially ease the evaluation of the term.)

Second, many systems operate under conditions in which their composition and volume are approximately invariant over time (although the composition might vary as a function of location). In these systems, which are referred to as being at *steady state*, the storage term (i.e., the term describing the rate of change of the mass of i in the CV) is zero. The form of the storage term in the general case and for various simplifications is shown in Table 1-1.

■ **EXAMPLE 1-2.** Downstream of the point where wastewater is discharged into a small river, a contaminant decays in such a way that its concentration can be approximated by the equation $c(x) = c(0)/(1 + kc(0)x)$, where c is the contaminant concentration, x is the distance downstream, and k is a constant characterizing the reactivity of the contaminant. If the contaminant concentration in the river at the discharge point is 2 mg/L and $k = 3(\text{mg/L})^{-1}$ km^{-1}, how much contaminant is stored in the 5-km segment of the river downstream of the plant? Over this stretch, the river has an approximately uniform cross-sectional area of $A = 24\,\text{m}^2$.

Solution. To determine the mass of contaminant stored in the river, we can define a CV that is bounded by the cross-section of the river and a distance dx in the direction of flow. The volume of water in this differential section is therefore $A dx$, and the mass of contaminant stored in the section is $c(x) A dx$. Designating the concentration at the upstream end of

TABLE 1-1. Expressions for the Storage Term in Mass Balance Equations

Rate of Change of Mass of i in Volume $V =$	
General case	$\dfrac{\partial}{\partial t} \int c\, dV$
Concentration independent of location (well-mixed)	$V \dfrac{dc}{dt} + c \dfrac{dV}{dt}$
Concentration independent of location, and system volume fixed	$V \dfrac{dc}{dt}$
Concentration and volume constant over time (steady state)	0

---

[1] Throughout this chapter, mass balances are written for an arbitrary constituent of interest, i. To minimize clutter, the concentration of this constituent is written simply as c, rather than c_i; a similar convention applies to other parameters characterizing i.

the region of interest (i.e., $c(0)$) as c_o, the mass of contaminant in the entire 5-km segment can be computed by integrating this function over the length of the segment; that is

$$M = \int_{x=0}^{5\,\text{km}} c(x) A \, dx$$

$$= A \int_{x=0}^{5\,\text{km}} \frac{c_o}{1 + kc_o x} \, dx$$

$$= \frac{A}{k} \ln[1 + kc_o x]_0^{5\,\text{km}}$$

$$= \frac{A}{k} \ln \frac{1 + kc_o(5\,\text{km})}{1 + kc_o(0\,\text{km})} = \frac{A}{k} \ln\{1 + kc_o(5\,\text{km})\}$$

Inserting the known values of A, k, and c_o, and several conversion factors

$$M = \frac{24\,\text{m}^2}{3(\text{mg/L})^{-1}\text{km}^{-1}} \frac{10^3\,\text{m}}{\text{km}} \frac{10^3\,\text{L}}{\text{m}^3} \frac{1\,\text{kg}}{10^6\,\text{mg}}$$

$$\ln\left[1 + \left(3(\text{mg/L})^{-1}\text{km}^{-1}\right)(2\,\text{mg/L})(5\,\text{km})\right] = 27.5\,\text{kg} \quad \blacksquare$$

■ **EXAMPLE 1-3.** The first step in many water and wastewater treatment processes often involves nothing more than mixing the incoming water thoroughly with water that arrived earlier in a large mixing tank. This process, known as *equalization*, mitigates temporal variations in the composition of the water that enters downstream reactors and thereby eases process control.

(a) Consider an equalization tank in an industrial waste-water treatment plant that contains $500\,\text{m}^3$ of water with a Cu^{2+} concentration of 65 mg/L. One of the process lines feeding the tank is online, so that the incoming water contains 125 mg/L Cu^{2+}. If the flow rate into and out of the tank is $6\,\text{m}^3/\text{min}$, what is the rate of change of the mass of Cu^{2+} stored in the tank; that is, what would be the value of the storage term in a mass balance on Cu^{2+} in the equalization tank at the given time?

(b) The tank is intended to prevent the Cu^{2+} concentration in the exiting water from fluctuating at a rate greater than 1 mg/L-min. Is it achieving this objective at the instant in question?

Solution.
(a) We can compute the desired values by writing a mass balance on Cu^{2+}, using the space occupied by all the water in the tank as the CV:

| Rate of change of mass of Cu^{2+} in the tank | = | Rate at which Cu^{2+} enters in the influent to the tank | − | Rate at which Cu^{2+} leaves in the tank effluent |

| | + | Rate at which Cu^{2+} enters the reactor by diffusion and dispersion across the inlet and outlet pipes | + | Rate at which Cu^{2+} is generated by reactions in the tank |

Because the flow rates into and out of the tank are equal and the Cu^{2+} concentration is uniform throughout the tank (because the water is thoroughly mixed), we can use the simplification shown in the third row of Table 1-1 to represent the storage term, as follows:

$$\text{Rate of change of mass of } Cu^{2+} \text{ in tank} = V\frac{dc_{Cu^{2+}}}{dt}$$

In the system of interest, Cu^{2+} does not participate in any chemical reaction, and the mass rates at which it enters and leaves the tank by advection are $Qc_{Cu^{2+},\text{in}}$ and $Qc_{Cu^{2+},\text{out}}$, respectively. The mass balance can therefore be written in a mathematical form as follows:

$$V\frac{dc_{Cu^{2+}}}{dt} = Qc_{Cu^{2+},\text{in}} - Qc_{Cu^{2+},\text{out}} = Q(c_{Cu^{2+},\text{in}} - c_{Cu^{2+},\text{out}})$$

$$= 6\,\text{m}^3/\text{min}(125\,\text{mg/L} - 65\,\text{mg/L})$$

$$\times \left(\frac{1000\,\text{L}}{\text{m}^3}\right)\left(\frac{1\,\text{kg}}{10^6\,\text{mg}}\right) = 0.36\,\text{kg/min}$$

The value of the storage term (i.e., the term on the left of the above equation) is therefore

$$\left(\begin{array}{c}\text{Rate of change of}\\ \text{mass of } Cu^{2+} \text{ in tank}\end{array}\right) = V\frac{dc_{Cu^{2+}}}{dt} = 0.36\,\text{kg/min}$$

(b) The rate of change of the Cu^{2+} concentration is computed by dividing the storage term in the mass balance by the liquid volume as

$$\frac{dc_{Cu^{2+}}}{dt} = \frac{V\dfrac{dc_{Cu^{2+}}}{dt}}{V}$$

$$= \frac{3.6 \times 10^5\,\text{mg/min}}{500\,\text{m}^3} \frac{1\,\text{m}^3}{1000\,\text{L}}$$

$$= 0.72\,\text{mg/L-min}$$

The result indicates that the equalization process is working well: even though the influent contains 60 mg/L more Cu^{2+} than the water in the tank, the Cu^{2+} concentration in the water leaving the tank and entering the downstream treatment processes is changing at a rate of <1 mg/L-min; that is, it is meeting the equalization objective.   ■

The Advective Term

Whereas the storage term in the mass balance describes changes inside the control volume, the terms for physical transport (advection, diffusion, and dispersion) describe processes at the boundaries. As noted previously, movement of fluid inside the CV does not transport i into or out of the CV and is therefore not reflected in the physical transport terms of the mass balance.

The volumetric rate (Q, volume/time) at which fluid crosses a boundary is given by the product of the velocity component perpendicular to the boundary ($v_\perp$) and the area (A) of the boundary. In the simplified system in which the flow is perpendicular to the boundary, the volumetric flow rates into and out of the system are $Q_{in} = v_{in}A_{in}$ and $Q_{out} = v_{out}A_{out}$, respectively. The rate at which a substance i that is dissolved or suspended in the water crosses the boundary by advection is the product of the volumetric flow rate and the concentration of i in the water; that is, $v_{in}A_{in}c_{in}$ or $Q_{in}c_{in}$ at the inlet, and $v_{out}A_{out}c_{out}$ or $Q_{out}c_{out}$ at the outlet. (Recall that, in the simplified case, c_{in} and c_{out} are assumed to be uniform across the areas A_{in} and A_{out}, respectively. This assumption is implicit in the preceding expressions.) Note that the products vAc and Qc have the desired dimensions of mass per time. The net advective term in the mass balance for the simplified case is therefore

Net rate of transport of i into CV by advection

$$= v_{in}A_{in}c_{in} - v_{out}A_{out}c_{out} \qquad (1\text{-}3)$$

$$= Q_{in}c_{in} - Q_{out}c_{out} \qquad (1\text{-}4)$$

The product cv is called the advective flux, often designated J_{adv}.[2] The advective flux represents the mass of i being advected in the direction of interest (in this case, the direction of bulk flow) per unit cross-sectional area per unit time. That is, if an imaginary flat surface of unit area were placed perpendicular to the direction of interest, the advective flux would indicate the mass of i passing through that surface per unit time as a result of the flow.

This result can be extended to a system containing multiple inlets and outlets by including an additional, similar term in the expression for each advective input or output.

Net rate of transport of i into CV by advection

$$= \sum_{\text{inlets}} Q_{in}c_{in} - \sum_{\text{outlets}} Q_{out}c_{out} \qquad (1\text{-}5)$$

It is worth noting that advection can affect the amount of i stored in the CV only if the mass rates of inflow and outflow

FIGURE 1-4. Schematic diagram for the junction of two streams.

of i differ. That is, substance i might be entering and leaving at very large rates, but unless these rates are different, there is no net effect on the amount of i in the system.

In many applications, advection is the only process that has a significant effect on the mass of a substance stored in the CV, such as at the junction of two pipes or channels, or when a single stream is divided into components. In such cases, the advective term is the only one that appears on the right side of the mass balance.

Consider, for example, a CV that encloses the junction of two pipes, as shown in Figure 1-4. The CV, indicated in the figure by the dotted box, includes the entire zone where the two streams mix, as well as a small portion of each pipe outside the mixing zone. We will evaluate the mass balances on water and on a conservative (nonreactive) substance i in the water, assuming that the system is at steady state over the time frame of the analysis.

The mass balance for water in this control region contains no dispersion or reaction terms, since these terms are unimportant for water.[3] By the assumption of steady state, the mass of water in the CV is constant, so the storage term in the mass balance is also zero, leaving only the advective terms in the mass balance. Formally, the mass balance for water is written as follows:

$$\begin{bmatrix} \text{Rate of change} \\ \text{of mass of water} \\ \text{stored in the} \\ \text{CV} \end{bmatrix} = \begin{bmatrix} \text{Rate at which water} \\ \text{enters the CV} \\ \text{by advection in} \\ \text{both influent streams} \end{bmatrix}$$

$$- \begin{bmatrix} \text{Rate at which water} \\ \text{leaves the CV} \\ \text{by advection in} \\ \text{the effluent stream} \end{bmatrix}$$

$$\int_V \frac{\partial \rho}{\partial t}\, dV = 0 = \rho Q_1 + \rho Q_2 - \rho Q_3 \qquad (1\text{-}6)$$

---

[2] Formally, both the velocity and flux are vectors, related by $J_{adv} = cv$. However, since we are considering only flow in a single direction in this analysis, the direction is accounted for most simply by the signs on the terms (plus sign for input, and minus sign for output).

[3] The reaction term is unimportant, because the water undergoes no reaction that significantly affects the mass of water in the system. Similarly, dispersion is unimportant, since no gradient exists in the concentration of water. Thus, even though dispersive mixing of the water might be substantial, it has no effect on the concentration of water anywhere in the system.

(This equation is based on the assumption that the volumetric flow rate of the entire solution can be equated with the volumetric flow rate of the water; that is, that water molecules account for essentially 100% of the volume of the solution. This assumption is virtually always valid for the systems of interest in environmental engineering.) Canceling the density of water from all terms, the equation reduces to the simple and fully expected result:

$$Q_3 = Q_1 + Q_2 \tag{1-7}$$

Consider next the mass balance on i. Because i is stipulated to be nonreactive, the reaction term in the mass balance is zero. While some dispersion certainly occurs at the junction, the net transport of i across the boundaries of the CV by dispersion is likely to be negligible in comparison to that by advection, so the dispersion term in the mass balance can be ignored. Finally, since the system is at steady state, the storage term is also zero. Under these conditions, the mass balance on i can be written as follows:

$$
\begin{bmatrix}
\text{Rate of change} \\
\text{of mass of } i \\
\text{stored in the} \\
\text{CV}
\end{bmatrix}
=
\begin{bmatrix}
\text{Rate at which } i \\
\text{enters the CV} \\
\text{by advection in} \\
\text{both influent streams}
\end{bmatrix}
$$

$$
-
\begin{bmatrix}
\text{Rate at which } i \\
\text{leaves the CV} \\
\text{by advection in} \\
\text{the effluent stream}
\end{bmatrix}
$$

$$\int_V \frac{\partial c}{\partial t} dV = 0 = Q_1 c_1 + Q_2 c_2 - Q_3 c_3 \tag{1-8}$$

$$c_3 = \frac{Q_1 c_1 + Q_2 c_2}{Q_3} = \frac{Q_1 c_1 + Q_2 c_2}{Q_1 + Q_2} \tag{1-9}$$

This result is likely to be familiar. The idea is, in fact, no different from what is used to describe mixing problems in elementary school mathematics, such as finding the cost of mixed nuts when the cost and proportion of each component are known. What is valuable here is to see that this well-known result can be obtained formally using the mass balance tool. The discussion also makes clear the assumptions that have to be met for the result to be valid, namely that the reaction, dispersion, and storage terms in the mass balance are all negligibly small in comparison to the advection term. These assumptions are not necessarily met in all cases of a junction of two streams, so we must be careful when applying Equation 1-9. For example, when free chlorine is used to disinfect a potable water or wastewater, a portion of the chlorine reacts almost instantaneously with some constituents of the water. As a result, the mass rate at which chlorine exits the mixing zone is less than the rate at

which it is added, even if the water remains in the mixing zone for only an extremely short time.

Note that this analysis does not require the concentration to be the same everywhere in the CV for the result to be valid; indeed, the inclusion in the CV of a small portion of the water upstream of the mixing zone in pipes 1 and 2 ensures that this condition is not met. The only requirement is that the mixing of the streams be negligible before the water crosses the influent planes (points 1 and 2 in the figure), and complete before the water crosses the effluent plane (point 3).

■ **EXAMPLE 1-4.** A suspension flowing at $0.5 \text{ m}^3/\text{s}$ is to be dosed with a polymeric coagulant to induce large numbers of small, suspended particles to grow into fewer, larger ones. The coagulant is present in a stock solution at a concentration of 1000 mg/L, and it is to be dosed at a rate that yields a concentration of 0.3 mg/L in the mixed solution. What flow rate of stock solution is required?

Solution. The mixing process is, in effect, mixing at a junction, and hence can be analyzed using Equation 1-8. Referring to the water undergoing treatment as stream 1, the coagulant stock solution as stream 2, and the mixed solution as stream 3, the mass balance on coagulant is

$$0 = Q_1 c_1 + Q_2 c_2 - Q_3 c_3 = Q_1 c_1 + Q_2 c_2 - (Q_1 + Q_2)c_3$$

In this case, Q_2 is expected to be much less than Q_1; hence we can make the approximation that $Q_1 + Q_2 \approx Q_1$. Substituting the approximation and the given values and rearranging, we obtain

$$
\begin{aligned}
Q_2 &= \frac{Q_1(c_3 - c_1)}{c_2} \\
&= \frac{(0.5 \text{ m}^3/\text{s})((0.3 - 0.0) \text{ mg/L})}{1000 \text{ mg/L}} \\
&= 0.15 \times 10^{-3} \text{ m}^3/\text{s} = 0.15 \text{ L/s}
\end{aligned}
$$

Note that the assumption that Q_2 is negligible in comparison to Q_1 is valid. ■

The Diffusion and Dispersion Terms

Diffusion occurs because, even in a fluid that is stagnant at the macroscopic level, motion occurs at the molecular level. Molecules of water and all solutes in the water are in constant (small-scale) motion. The concentration of water molecules is essentially the same at all locations in the solution, so the small-scale motion of these molecules tends to be equal in all directions and to have no noticeable effect on the solution composition at any point. However, the concentration of a solute might be different at different locations. If the solute concentration differs in adjacent packets of fluid, random motion of these molecules is likely to cause more of them to move from the high-concentration

to the low-concentration packet than vice versa, leading to a net movement of solute toward the low-concentration region. Over time, this motion tends to diminish differences in the solute concentration throughout the solution.

Similarly, in a flowing fluid, different molecules of fluid (and solute) flow at different rates, even if on a larger scale the fluid flow is uniform and steady. As noted previously, in laminar flow, fluid velocity tends to vary spatially across a plane perpendicular to the net flow, and this variation causes mass transport to be different from that described by the average advection. Turbulence also causes different molecules in the same solution to move at different velocities, in this case because of temporal variations of velocity around the mean at any point (or plane). In all these situations, the mass transport that is not captured by the average advective term is described by dispersion. Both time averaging (in the case of turbulence) and spatial averaging (in laminar flow) of the microscopic motions across a plane often lead to terms that are identical in form to those that describe molecular diffusion; here, we do not distinguish among the various phenomena that lead to this dispersion. The classic work of Taylor (1953, 1954) defined the dispersion in both laminar and turbulent flow. A succinct description of these phenomena is given by Holley[4] (1969), while a more thorough analysis and application to flow through porous media is given by Bear (1972, 1979).

Similar to advection, transport of i by diffusion and dispersion is described in terms of fluxes. According to *Fick's law*, the diffusive flux of a substance in any direction equals the negative product of the local concentration gradient of that substance and a *diffusion coefficient* or *diffusivity*, D.[5] By analogy, the dispersive flux in any given direction equals the negative product of the concentration gradient and a *dispersion coefficient* or *dispersivity*, ϵ. Both D and ϵ have dimensions of length squared per time. Except in very quiescent systems (e.g., the bottom of a quiet lake, the stagnant fluid in biofilms, or the pores inside granular activated carbon particles), the dispersion coefficient, ϵ, is generally much greater than the diffusion coefficient, D.

The diffusion coefficient depends on the particular substance being considered, and, in general, would be written as D_i. On the other hand, ϵ depends on the hydrodynamic characteristics of the system and applies equally to all substances in the water. However, because the intensity of dispersion might be different in different directions, ϵ

depends on the direction of interest. For this simplified analysis, we are assuming that a concentration gradient exists only in the x direction, as shown schematically in Figure 1-5. For such a case, we can write[6]

$$\text{Flux in } +x \text{ direction due to diffusion} \equiv J_{\text{diff},x} = -D\frac{\partial c}{\partial x}$$
$$(1\text{-}10)$$

$$\text{Flux in } +x \text{ direction due to dispersion} \equiv J_{\text{disp},x} = -\epsilon_x\frac{\partial c}{\partial x}$$
$$(1\text{-}11)$$

Flux in $+x$ direction due to combined diffusion and

$$\text{dispersion} \equiv J_{\text{diff},x} + J_{\text{disp},x} \equiv J_{\mathbf{D},x} = -(D+\epsilon_x)\frac{\partial c}{\partial x}$$
$$(1\text{-}12)$$

where $J_{\mathbf{D},x}$ is the combined diffusive and dispersive flux in the x direction.

The concentration gradient $\partial c/\partial x$ is positive if the concentration increases in the $+x$ direction. Similarly, flux is defined as positive if material moves in the $+x$ direction. The negative sign in Equations 1-10–1-12 indicates that the direction of the diffusive and dispersive fluxes is opposite to the direction of the concentration gradient; that is, concentration increasing in the downstream $(+x)$ direction leads to net diffusion and dispersion in the upstream $(-x)$ direction.

The mass rate of input of i into the CV by diffusion and dispersion is the product of the flux and the appropriate area

Net rate of transport of i into CV via diffusion/dispersion

$$= \left[J_{\mathbf{D},x}A\right]_{\text{inlet}} - \left[J_{\mathbf{D},x}A\right]_{\text{outlet}} \qquad (1\text{-}13a)$$

$$= -\left\{\left((D+\epsilon_x)\frac{\partial c}{\partial x}A\right)_{\text{inlet}} - \left((D+\epsilon_x)\frac{\partial c}{\partial x}A\right)_{\text{outlet}}\right\}$$
$$(1\text{-}13b)$$

$$= -(D+\epsilon_x)\left\{\left(\frac{\partial c}{\partial x}A\right)_{\text{inlet}} - \left(\frac{\partial c}{\partial x}A\right)_{\text{outlet}}\right\} \qquad (1\text{-}13c)$$

$$= (D+\epsilon_x)\left\{\left(\frac{\partial c}{\partial x}A\right)_{\text{outlet}} - \left(\frac{\partial c}{\partial x}A\right)_{\text{inlet}}\right\} \qquad (1\text{-}13d)$$

Note that the equality of Equations 1-13b and 1-13c relies on the assumption that the diffusion and dispersion coefficients are the same at the outlet as at the inlet. This assumption might be acceptable for flow through engineered systems with similar inlet and outlet structures, but many other situations exist in which the assumption does not apply.

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[4] Holley reserves the term diffusion for time-averaged processes and the term dispersion for spatially averaged processes, but this distinction is not used universally. In this book, we reserve the word diffusion to refer to molecular diffusion of any chemical in water, and dispersion to refer to any process related to fluid motion that causes transport down a concentration gradient.

[5] When considering solutes, this statement assumes that the direction of decreasing concentration is also the direction of decreasing chemical activity, which is almost always true in aqueous systems.

[6] Although the dispersivity ϵ_x could vary with location (e.g., as a function of x in a reactor with flow in the x direction), we assume here that it is constant.
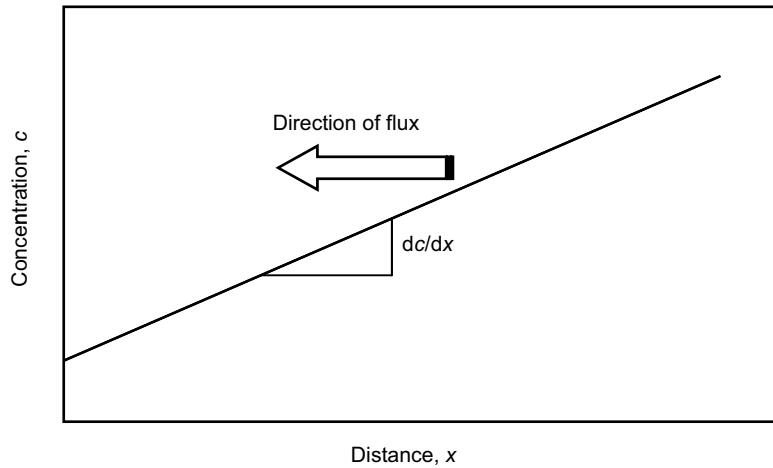
FIGURE 1-5. Schematic showing a (positive) concentration gradient ($dc/dx > 0$), leading to flux in the $-x$ direction.

Equation 1-13 indicates that the net transport of i into the CV by diffusion and dispersion equals the diffusive/dispersive transport in the $+x$ direction at the inlet minus that in the $+x$ direction at the outlet. Note that this statement does not imply that diffusion and dispersion must be into the CV at the inlet and out of it at the outlet. It is entirely possible for $\partial c/\partial x$ to be positive at the inlet point, in which case the diffusion/dispersion term would be negative; that is, out of the CV. Thus, the words inlet and outlet in Equation 1-13 describe locations where the bulk flow enters or leaves and where the area and concentration gradient must be evaluated to determine the diffusive/dispersive flux; they do not imply that diffusive/dispersive transport must be in any particular direction.

In many situations, we are interested in a CV that is differentially thick in the x direction and that has equal areas bounding it at its two ends (in the y–z plane). In such a case, Equation 1-13d can be rewritten as follows:

Net rate of transport of i into the CV via diffusion/

$$\text{dispersion} = (D + \epsilon_x)A\left\{\left(\frac{\partial c}{\partial x}\right)_{x+dx} - \left(\frac{\partial c}{\partial x}\right)_x\right\} \quad (1\text{-}14)$$

From the definition of the derivative, $(\partial c/\partial x)_{x+dx} - (\partial c/\partial x)_x = (\partial/\partial x)(\partial c/\partial x)dx = (\partial^2 c/\partial x^2)dx$, so that

Net rate of transport of i into the CV via diffusion/

$$\text{dispersion} = (D + \epsilon_x)A\frac{\partial^2 c}{\partial x^2}dx \quad (1\text{-}15)$$

■ **EXAMPLE 1-5.** Assume that, at the bottom of a deep lake, the sediment surface is flat and the water is quiescent. This region of the lake has become anaerobic, and phosphate species are being released from the sediment as a result of microbial activity. The pH of the lake is 8.8, causing almost all the phosphate to be present as the species HPO_4^{2-}. Assume that the concentration of this species at the sediment surface is approximately steady at 1.0 mg/L as P.[7] Under the ambient conditions, the diffusion coefficient of HPO_4^{2-} is 1.2×10^{-5} cm^2/s. Assuming that the HPO_4^{2-} does not participate in any chemical reactions in the water near the sediment, and that c_P in the water column is negligible at time $t = 0$, compute the concentration of HPO_4^{2-} and the flux of this species into the water thereafter, as a function of location and time. The water column can be considered deep enough that the phosphate species do not reach the top of the stagnant zone in the time frame of interest.

Solution. Choosing a CV that is differentially thick in the vertical direction (which we define as the x direction for this problem), a mass balance on the total dissolved phosphate includes only the diffusive term on the right, because the phosphate species are nonreactive and are not brought into or out of the CV by flow. Dropping the subscript on c, and noting that $A\,dx = dV$, the mass balance can be written and simplified as follows:

$$dV\frac{\partial c}{\partial t} = AD\frac{\partial^2 c}{\partial x^2}dx \quad (1\text{-}16)$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \quad (1\text{-}17)$$

Equation 1-17 describes how the changes in the concentration of a nonreactive material over distance and time are related in a stagnant solution. Because the differential equation is first order in time and second order in space, we need an initial condition and two boundary conditions to

_____

[7] This terminology indicates that the concentration of HPO_4^{2-} molecules in the water is such that the water contains 1.0 mg/L of P.

solve it. For this problem, these equations are written as

Initial condition: $c(x, 0) = 0$

Boundary conditions: $c(0, t > 0) = c_o = 1.0\,\text{mg/L}$

$$c(\infty, t) = 0$$

Even with the simplifying assumptions that the water is stagnant and the phosphate is nonreactive, this is not an easy problem to solve. The solution, which is developed in many textbooks on differential equations (see, e.g., Kreyszig, 1993), can be expressed as follows:

$$c(x, t) = c_o\left(1 - \text{erf}\left\{\frac{x}{\sqrt{4Dt}}\right\}\right) = c_o\,\text{erfc}\left\{\frac{x}{\sqrt{4Dt}}\right\}$$

$$(1\text{-}18)$$

where $\text{erf}(z) \equiv (2/\sqrt{\pi}) \int_0^z e^{-u^2}\,du$ and $\text{erfc}(z) \equiv 1 - \text{erf}(z)$.

The function $\text{erf}(z)$ is known as the error function, the gaussian distribution, or the probability integral. The function $\text{erfc}(z)$ is known as the complementary error function and equals the same integral as $\text{erf}(z)$, except integrated from z to ∞, rather than from 0 to z. Values of these functions are widely tabulated and are available in many spreadsheet programs. Using such a program, we can determine for a given system (i.e., a given value of D) the concentration profile ($c(x)$) at a given time t, the concentration variation over time ($c(t)$) at a given location x, or $c(x, t)$ for selected values of x and t. Some results of such calculations are shown in Figure 1-6. The concentration gradient is steep at short times and distances, and it becomes flatter and extends farther into the water column at later times. Note that molecular diffusion is an extremely slow process for mixing

Concentration (mg/L) vs Distance from sediment surface (cm), with curves labeled Time = 1 y, 30 d, 1 d, 1 h.
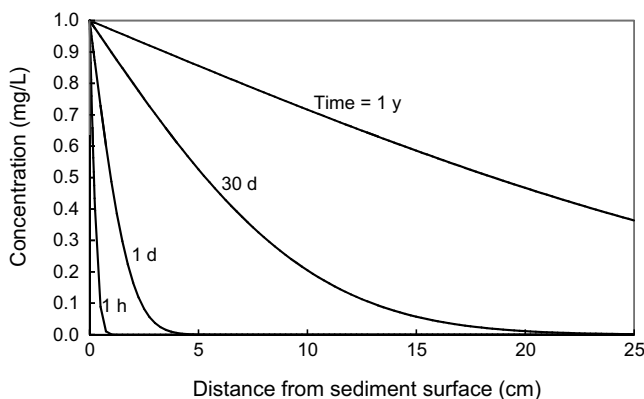
FIGURE 1-6. Concentration profile as a function of time and distance for unidirectional diffusion of a nonreactive contaminant (HPO_4^{2-}, in the current example) into stagnant water. The concentration of HPO_4^{2-} at the sediment surface is assumed to be constant at $1.0\,\text{mg/L}$.

a constituent into a solution. For example, even after 30 days, dissolved phosphate is barely detectable a mere 20 cm from its source.

The flux out of the sediment is given by the product of the diffusivity and the concentration gradient as

$$\text{Flux} = J_{\text{diff}} = -D\frac{dc}{dx} \tag{1-19}$$

$$= -Dc_o\frac{d}{dx}\left(1 - \text{erf}\left\{\frac{x}{\sqrt{4Dt}}\right\}\right)$$

$$= Dc_o\frac{d}{dx}\left(\text{erf}\left\{\frac{x}{\sqrt{4Dt}}\right\}\right) \tag{1-20a}$$

which is equivalent to

$$J_{\text{diff}} = Dc_o\frac{d}{dx}\left(\frac{2}{\sqrt{\pi}}\int_0^{x/\sqrt{4Dt}} \exp\{-u^2\}\,du\right) \tag{1-20b}$$

Using Leibniz's rule for differentiating an integral,[8] we can rewrite Equation 1-20b as

$$J_{\text{diff}} = Dc_0\frac{2}{\sqrt{\pi}}\exp\left(-\frac{x^2}{4Dt}\right)\frac{d}{dx}\left(\frac{x}{\sqrt{4Dt}}\right) \tag{1-21}$$

and, at $x = 0$,

$$J_{\text{diff},x=0} = Dc_0\frac{2}{\sqrt{\pi}}(1.0)\left(\frac{1}{\sqrt{4Dt}}\right) = c_0\sqrt{\frac{D}{\pi t}} \tag{1-22}$$

Inserting values into this expression, we find the following fluxes at the interface at times corresponding to the four curves in the plot:

Time	Flux at $x = 0$ (mg/m^2 d)
1 h	28.14
1 d	5.74
30 d	1.05
1 y	0.30

∎

Diffusion and dispersion are extremely important in many natural and engineered environmental processes. In particular, diffusion controls the behavior of solutes in systems, or parts of systems, where advection is minimal, such as in the

[8] This rule is given by Beyer (1987) as $\partial \int_{a(y)}^{b(y)} (f(z, y)\,dz)/\partial y = \int_{a(y)}^{b(y)} (\partial f(z, y)/\partial y)\,dz + f(b(y), y)(\partial a/\partial y) - f(a(y), y)(\partial b/\partial y)$. For the application here, we define $\eta \equiv x/\sqrt{4Dt}$, and use Leibniz's rule with $y = \eta$, $z = u$, and the limits of integration $a(y) = 0$ and $b(y) = \eta$.

deep sediments of lakes and in the interior of porous particles (e.g., granules of activated carbon, which is used to collect many contaminants from solution via adsorption). Similarly, dispersion can control the spreading of solutes upstream and downstream along the length of a river and in reactors that have nearly uniform flow in one direction. Reactors that are designed to be *plug flow reactors* (with exactly uniform flow in the axial direction) often do not achieve that ideal, in which case dispersion can control the longitudinal mixing in the reactor. Such reactors include packed beds that are used to carry out adsorption of solutes and filtration of particles, and tanks used for water disinfection.

In many other commonly encountered situations, on the other hand, diffusion and dispersion are negligible. In particular, in CVs that are large and that connect with regions outside the system across relatively little surface area, the diffusion/dispersion term can often be ignored. The most common such systems are large tanks receiving influent and discharging effluent through pipes in which the water velocity is rapid. In some systems, these flows are not even continuous with the water in the tank (e.g., if the influent enters by being discharged from a free flowing pipe above the water level). In such cases, advection carries molecules across the system boundaries much more rapidly than diffusion and dispersion do; as a result, diffusion and dispersion can be ignored.

The Chemical Reaction Term

The final term in the mass balance represents the net rate of change of i due to chemical reactions in the CV. Contrary to advection, diffusion, and dispersion, chemical reactions affect the mass balance only if they occur inside the CV, rather than across its boundaries.

Conventionally, the rate of a reaction in a homogeneous phase is normalized to the volume and is given as r_V, the amount of i being formed per unit volume per time. Thus, in any differentially small region dV of the CV, the rate of formation of i by reaction is $r_V dV$. If i is being destroyed by chemical reaction, then r is negative. The rate at which the mass of i changes in the entire CV as a result of homogeneous chemical reactions is obtained by summing the rates applicable in all the dV-sized regions within the volume; that is, by integrating over the entire CV

Net rate of change of mass of i in CV by homogeneous

$$\text{reactions} = \int r_V dV \qquad (1\text{-}23)$$

Many reactions that are important for water quality occur at the interface between two phases. Examples of such reactions include the transfer of gases into and out of

solution, precipitation and dissolution of solid phases, corrosion of water distribution pipes, and the adsorption from solution of trace compounds onto the surfaces of activated carbon or minerals. Depending on the geometry and other characteristics of the system, the interfacial surfaces at which reactions occur might all be at the boundary of the CV or distributed throughout the CV. The former case would apply, for instance, if we chose a single droplet of water as the CV for the analysis of gas transfer in a spray aeration system (a system in which water droplets are sprayed into the air to enhance transfer of oxygen into the water). On the other hand, when analyzing the adsorption of pesticides onto powdered activated carbon in a well-mixed, batch system, the most appropriate CV might be a portion of fluid with a representative amount of activated carbon dispersed in it, in which case the interfacial area is distributed throughout the CV.

When interfacial reactions are important in a mass balance analysis, it is often convenient to normalize their rates to the amount of surface area in the system, rather than to the system volume. That is, the rate of a reaction occurring at a surface might be quantified by a term $r_{i,\sigma}$, indicating the rate at which i is being created per unit amount of surface area present. Thus, $r_{i,\sigma}$ would have dimensions of mass per area per time. The corresponding term in the mass balance would then be $r_{i,\sigma} a\, dV$, where a is the surface area concentration in the system (surface area per unit volume).

Writing the terms for homogeneous and interfacial reactions individually, the net rate of formation of i by chemical reactions in the CV is

Net rate of change of mass of i in CV by chemical

$$\text{reactions} = \int (r_V + r_\sigma a) dV \qquad (1\text{-}24)$$

Recall that a system in which the composition is uniform throughout the CV is referred to as being well-mixed. Since the rates of chemical reactions depend on the system composition, the reaction rate is also spatially uniform in well-mixed systems; that is, it does not depend on the location. In such cases, the reaction terms can be taken out of the integral, leading to the following simpler form:

Net rate of change of mass of i in a well-mixed CV by

$$\text{chemical reactions} = (r_V + r_\sigma a) V \qquad (1\text{-}25)$$

Each term in Equations 1-24 and 1-25 might be a composite of several others, each of which represents the rate of a single reaction by which i is generated or destroyed within the CV. For example, in a given CV, oxygen might be consumed by a chemical reaction with ferrous iron and by a biochemical reaction with degradable organic matter

(mediated by organisms), and it might simultaneously enter the solution by transfer from injected air bubbles. Each of these reactions would be included individually in the mass balance on oxygen, as a component of the term shown generically above as the (single) reaction term.

The symbol r is used as a generic descriptor of the overall reaction rate of i in mass balances. However, the rate of each reaction that is occurring in the system is characterized by a distinct dependence on the concentrations of the reactants, solution temperature, pH, and other parameters. An example of such a relationship, and how it can be used in a mass balance, is provided below. Reaction rate expressions are the major focus of Chapter 3.

■ **EXAMPLE 1-6.** When drinking water is disinfected with chlorine-containing compounds (especially hypochlorous acid and hypochlorite ion [HOCl and OCl$^-$, respectively]), chlorinated organic compounds such as chloroform ($CHCl_3$) and chloro-acetic acid ($CH_xCl_{3-x}COOH$) are generated. The organic reactants in this process comprise a diverse collection of molecules referred to as natural organic matter (NOM), and the chlorinated products of the reaction are referred to as disinfection byproducts (DBPs).

The kinetics of DBP formation is complex, both because of the diversity of the NOM molecules and because the disinfectant can simultaneously participate in many other reactions that do not form DBPs. Nevertheless, a number of mathematical models have been proposed to describe the kinetics, especially for the formation of $CHCl_3$. One such model suggests that the rate of $CHCl_3$ formation can be approximated by a function of the form $r_{CHCl_3} = k(NOM)(HOCl)^3$, where (NOM) and (HOCl) are the concentrations of NOM and HOCl, respectively, and k is an empirical constant. Chloroform is essentially inert in water.

The following data have been collected in a batch treatment test, under conditions where k is estimated to have a value of $3.0 \times 10^{-6} (mg/L)^{-3} min^{-1}$. Estimate the $CHCl_3$ concentration in the solution at $t = 1\,h$.

t (min)	0	5	10	20	30	40	50	60
NOM (mg/L)	5.2	5.0	4.9	4.9	4.9	4.9	4.9	4.9
HOCl (mg/L)	7.0	5.1	4.8	4.4	4.0	3.7	3.4	3.2

Solution. The data for the NOM and HOCl concentrations are plotted in Figure 1-7a, and the corresponding rate of formation of $CHCl_3$ at each time (computed from the given expression for r_{CHCl_3}) is plotted in Figure 1-7b.

Since the only process that is affecting the $CHCl_3$ concentration in solution is the reaction, and since that

(a)

(b)
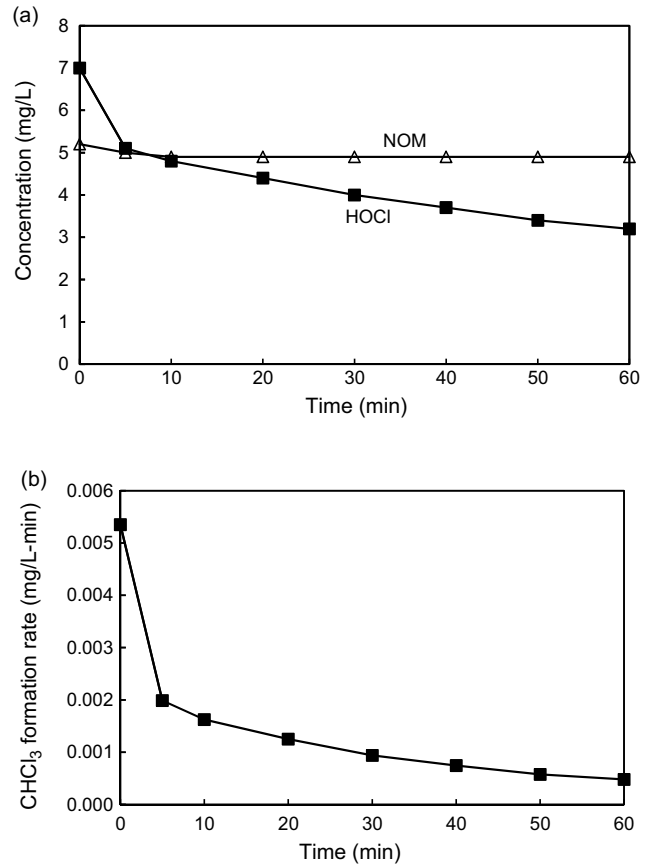
FIGURE 1-7. Conditions in an example, batch system undergoing chlorination. (a) Reactant concentrations; (b) the rate of chloroform formation, calculated as $k(NOM)(HOCl)^3$.

concentration is uniform throughout the solution, the mass balance on $CHCl_3$ can be expressed as follows:

$$V \frac{dc_{CHCl_3}}{dt} = V r_{CHCl_3}$$

$$\int_{c_0}^{c_{60\,min}} dc_{CHCl_3} = \int_{0}^{60\,min} r_{CHCl_3} dt$$

$$c_{CHCl_3,\,60\,min} = \int_{0}^{60\,min} r_{CHCl_3} dt$$

Thus, the concentration of $CHCl_3$ in the solution at $t = 60\,min$ can be computed as the time integral of the formation rate over the period from 0 to 60 min. Although this integral cannot be evaluated analytically, it can be evaluated as the area under the curve in Figure 1-7b. The result is that, at $t = 60\,min$, $c_{CHCl_3} = 0.073\,mg/L = 73\,\mu g/L$. ■

Combining the Terms into the Overall Mass Balance

The overall mass balance for a system with unidirectional flow, a concentration gradient only in the direction of flow, and only one inlet and one outlet can be written by combining the terms described in the preceding sections for the individual processes as

$$\frac{\partial}{\partial t}\int c\,dV = Q_{in}c_{in} - Q_{out}c_{out} + (D + \epsilon_x)\left\{\left[A\frac{\partial c}{\partial x}\right]_{outlet}\right.$$
$$\left. -\left[A\frac{\partial c}{\partial x}\right]_{inlet}\right\} + \int (r_V + r_\sigma a)dV \quad (1\text{-}26)$$

Although Equation 1-26 is applicable to any system with unidirectional flow, it is often quite daunting to use. Fortunately, the criteria for applying several of the simplifications described in the discussion of the individual terms are often met in systems of interest. Some mass balances in these cases are summarized in Table 1-2. (Note that, although the CVs for these equations are written as V, the equations might be applied to differential-sized CVs, dV.)

■ **EXAMPLE 1-7.** The amount of dissolved oxygen (DO) that would be consumed by microbial oxidation of the biodegradable organic matter in a solution is referred to as the biochemical oxygen demand of the solution and is commonly symbolized by the letter L. Note that, although L is a measure of the concentration of organics in the water, it is expressed in terms of the concentration of oxygen that would be consumed if the organics decayed. Over time, if the organics in solution are actually degraded, and if no biodegradable inputs enter the solution, the biochemical oxygen demand remaining in the solution declines; that is, L decreases over time. The rate of this decline is commonly represented as follows:

$$r_L = -k_d L$$

Consider a well-mixed lake (no concentration gradients in the lake) with volume 5×10^8 L that is fed by a stream

flowing at 2.4×10^7 L/d. The stream contains 8 mg/L of DO and an amount of biodegradable organic matter that corresponds to $L = 10$ mg/L. Waste from a small municipality ($L = 95$ mg/L, DO $= 0$ mg/L) flows into the lake at a rate of 4.8×10^6 L/d. The value of k_d in the lake is $0.10\,d^{-1}$.

In addition to the input of oxygen via the stream, oxygen can enter the lake from the atmosphere at a rate given by the expression $r_{O_2} = k_r(DO^* - DO)$, where k_r is a constant known as the reaeration constant, and DO^* is the saturation (equilibrium) value of DO in the water. For the given system, $k_r = 0.05\,d^{-1}$ and $DO^* = 11.2$ mg/L. The values of DO and L in the lake are approximately constant over time, and diffusion and dispersion contribute negligibly to the transport of either substance into or out of the lake. The system is shown schematically in Figure 1-8.

(a) Write mass balances on biochemical oxygen demand and oxygen in the lake and determine the values of L and DO.

(b) Compute the rate (kg/d) at which each individual process (advection, reaeration, biological reaction) increases or decreases DO and L in the lake.

Known : $Q_1 = 2.4 \times 10^7$ L/d $Q_3 = Q_1 + Q_2 = 2.88 \times 10^7$ L/d
$\qquad\quad$ $DO_1 = 8$ mg/L $\qquad\qquad$ $DO_3 = ?$
$\qquad\quad$ $L_1 = 10$ mg/L $\qquad\qquad$ $L_3 = ?$
$\qquad\quad$ $Q_2 = 4.8 \times 10^6$ L/d $\qquad$ $V = 5 \times 10^8$ L
$\qquad\quad$ $DO_2 = 0$ mg/L $\qquad\qquad$ $k_d = 0.10\,d^{-1}$
$\qquad\quad$ $L_2 = 95$ mg/L $\qquad\qquad$ $DO^* = 11.2$ mg/L
$\qquad\qquad\qquad\qquad\qquad\quad$ $k_r = 0.05\,d^{-1}$
$\qquad\qquad\qquad$ $L_{in\ lake} = ?$
$\qquad\qquad\qquad$ $DO_{in\ lake} = ?$

Solution.

(a) This system is at steady state and is well-mixed, so it meets the criteria for using Equation 1-28. Substituting the appropriate expression for the reaction term, the mass balance on biochemical oxygen demand is

$$0 = Q_1L_1 + Q_2L_2 - Q_3L_3 - k_d V L_{in\ lake}$$

Note that the reaction is taking place *in* the lake, so the L that is used to compute r_L is the concentration

TABLE 1-2. Simplified Mass Balances Applicable to Many Systems of Interest

Well-mixed reactor with fixed volume
$$V\frac{dc}{dt} = Q(c_{in} - c_{out}) + (r_V + r_\sigma a)V \quad (1\text{-}27)$$

Well-mixed reactor with fixed volume, at steady state
$$0 = Q(c_{in} - c_{out}) + (r_V + r_\sigma a)V \quad (1\text{-}28)$$

Plug flow reactor (negligible axial diffusion), at steady state
$$0 = Q(c_{in} - c_{out}) + \int (r_V + r_\sigma a)dV \quad (1\text{-}29)$$

Well-mixed batch reactor (no flow) with fixed volume
$$V\frac{dc}{dt} = (r_V + r_\sigma a)V \quad (1\text{-}30)$$

FIGURE 1-8. Schematic showing the inflows and outflow from the lake in the example system.

in the lake. On the other hand, the advective terms describe processes at the inlets and outlet, so the concentrations used to compute these terms are the concentrations at the system boundaries. However, because the lake is well-mixed, L in the outlet stream (L_3) equals that in the lake ($L_{in\ lake}$). Using L_3 to represent both these quantities, we obtain

$$0 = (2.4 \times 10^7\ \text{L/d})(10\ \text{mg/L}) + (4.8 \times 10^6\ \text{L/d})(95\ \text{mg/L})$$
$$- (2.88 \times 10^7\ \text{L/d})L_3 - (0.10\,\text{d}^{-1})(5 \times 10^8\ \text{L})L_3$$

$$L_3 = \frac{(2.4 \times 10^7\ \text{L/d})(10\ \text{mg/L}) + (4.8 \times 10^6\ \text{L/d})(95\ \text{mg/L})}{(2.88 \times 10^7\ \text{L/d}) + (0.10\,\text{d}^{-1})(5 \times 10^8\ \text{L})}$$

$$L_3 = L_{in\ lake} = 8.83\ \text{mg/L}$$

The mass balance on oxygen is almost identical in form to the mass balance on L, except that the reaeration reaction provides a pathway for oxygen to enter the system (and therefore an additional term in the mass balance) that does not apply to L. Because of the definition of the oxygen demand, the term in the mass balance on DO that accounts for DO consumption by the biodegradation reaction is identical to the term in the mass balance on L for consumption of L. The mass balance on DO is therefore

$$\begin{matrix} \text{Rate of change} \\ \text{of mass of DO} \\ \text{stored in the lake} \end{matrix} = \begin{matrix} \text{Net rate (in-out)} \\ \text{at which oxygen} \\ \text{enters by advection} \end{matrix}$$

$$+ \begin{matrix} \text{Rate at which} \\ \text{oxygen is generated} \\ \text{by biochemical} \\ \text{reactions} (< 0) \end{matrix} + \begin{matrix} \text{Rate at which oxygen} \\ \text{transfers into lake water} \\ \text{from the air} (> 0) \end{matrix}$$

$$\frac{d}{dt}[(\text{DO}_{in\ lake})V] = Q_1(\text{DO}_1) + Q_2(\text{DO}_2) - Q_3(\text{DO}_3)$$
$$- k_d(L_{in\ lake})V + k_r(\text{DO}^* - \text{DO}_{in\ lake})V$$

Applying the assumptions of complete mixing ($\text{DO}_{in\ lake} = \text{DO}_3$) and steady state, the equation becomes

$$0 = Q_1(\text{DO}_1) + Q_2(\text{DO}_2) - Q_3(\text{DO}_3) - k_d(L_3)V$$
$$+ k_r(\text{DO}^* - \text{DO}_3)V$$

All the values in the above equation except DO_3 are known. Substituting these values and solving for DO_3, we obtain

$$0 = (2.4 \times 10^7\ \text{L/d})(8\ \text{mg/L}) + (4.8 \times 10^6\ \text{L/d})(0\ \text{mg/L})$$
$$- (2.88 \times 10^7\ \text{L/d})(\text{DO}_3)$$
$$- (0.1\,\text{d}^{-1})(8.83\ \text{mg/L})(5 \times 10^8\ \text{L})$$
$$+ (0.05\,\text{d}^{-1})(11.2\ \text{mg/L} - \text{DO}_3)(5 \times 10^8\ \text{L})$$

$$\text{DO}_3 = \text{DO}_{in\ lake} = 0.57\ \text{mg/L}$$

(b) The rates of the various terms in the mass balance are computed as follows:

Advective inflow of biochemical oxygen demand:

$$Q_1(L_1) + Q_2(L_2) = [(2.4 \times 10^7\ \text{L/d})(10\ \text{mg/L})$$
$$+ (4.8 \times 10^6\ \text{L/d})(95\ \text{mg/L})]\,[10^{-6}\ \text{kg/mg}]$$
$$= 240\ \text{kg/d} + 456\ \text{kg/d} = 696\ \text{kg/d}$$

Advective outflow of biochemical oxygen demand:

$$Q_3(L_3) = (2.88 \times 10^7\ \text{L/d})(8.83\ \text{mg/L})\,(10^{-6}\ \text{kg/mg})$$
$$= 254\ \text{kg/d}$$

Rate of L utilization (i.e., the rate of DO utilization by biochemical reactions). (Note that, because r_L is defined to be positive when L increases, the rate of utilization of biochemical oxygen demand is defined as $-r_L V$.):

$$-r_L V = k_d(L_{in\ lake})V$$
$$= (0.10\,\text{d}^{-1})\,(8.83\ \text{mg/L})\,(5 \times 10^8\ \text{L})$$
$$= 4.42 \times 10^8\ \text{mg/d} = 442\ \text{kg/d}$$

Advective inflow of O_2:

$$Q_1(\text{DO}_1) + Q_2(\text{DO}_2) = (2.4 \times 10^7\ \text{L/d})\,(8\ \text{mg/L})$$
$$(10^{-6}\ \text{kg/mg}) = 192\ \text{kg/d}$$

Advective outflow of O_2:

$$Q_3(\text{DO}_3) = (2.88 \times 10^7\ \text{L/d})\,(0.57\ \text{mg/L})(10^{-6}\ \text{kg/mg})$$
$$= 16\ \text{kg/d}$$

Rate of reaeration:

$$r_r V = k_r(\text{DO}^* - \text{DO})V$$
$$= (0.05\,\text{d}^{-1})(11.2 - 0.57\ \text{mg/L})(5 \times 10^8\ \text{L})$$
$$= 2.66 \times 10^8\ \text{mg/d} = 266\ \text{kg/d}$$

The terms in the mass balance equations for L and DO, in kg/d, are summarized schematically in Figure 1-9. ∎

The Differential Form of the One-Dimensional Mass Balance

The overall mass balance derived in the preceding sections is conceptually satisfying and is useful in many applications. However, in some systems, we are more interested in the rate of change of the concentration of i at a single location than in the rate of change of the mass of i stored in a specified volume. We can convert Equation 1-26 into a form that is applicable at a unique location by writing it for a CV that is of differential length, dx. In that case, the cross-sectional
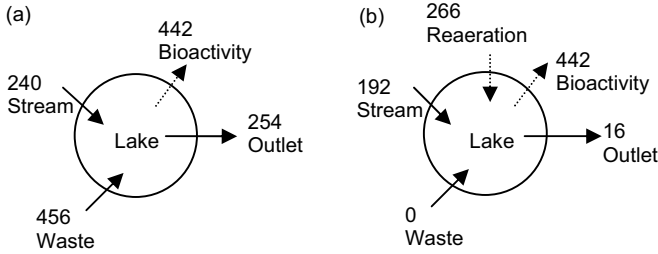
FIGURE 1-9. Contributions of various terms in the mass balance on (a) biochemical oxygen demand and (b) dissolved oxygen for the lake described in Example 1-7. Solid lines represent advective processes, and broken lines represent reactions. All numbers represent mass rates in kg/d.

areas at the inlet and outlet can be assumed to equal one another ($A_{inlet} = A_{outlet} = A$). Also, Q_{in} must equal Q_{out}, and we can write both as Av_x. Making these substitutions, writing dV as Adx, and dividing by A yields

$$\frac{\partial}{\partial t}\int c\,dx = v_x c_{in} - v_x c_{out} + (D + \epsilon_x)\left\{\left[\frac{\partial c}{\partial x}\right]_{outlet} - \left[\frac{\partial c}{\partial x}\right]_{inlet}\right\}$$
$$+ \int (r_V + r_\sigma a)dx \qquad (1\text{-}31)$$

Then, since the distance from the inlet to the outlet is dx, we can write $c_{in}-c_{out}$ as $-$dc or, equivalently, $-(\partial c/\partial x)$dx. Similarly, $\{[\partial c/\partial c]_{outlet} - [\partial c/\partial c]_{inlet}\}$ can be written as $(\partial/\partial x)[\partial c/\partial x]dx$, yielding

$$\frac{\partial}{\partial t}\int c\,dx = -v_x\frac{\partial c}{\partial x}dx + (D+\epsilon_x)\left\{\frac{\partial}{\partial x}\left[\frac{\partial c}{\partial x}\right]\right\}dx + \int (r_V + r_\sigma a)dx$$

$$\frac{\partial}{\partial t}\int c\,dx = -v_x\frac{\partial c}{\partial x}dx + (D+\epsilon_x)\frac{\partial^2 c}{\partial x^2}dx + \int (r_V + r_\sigma a)dx$$
$$(1\text{-}32)$$

Finally, differentiating both sides with respect to x, we obtain:

$$\frac{d}{dx}\left[\frac{\partial}{\partial t}\int c\,dx\right] = -v_x\frac{\partial c}{\partial x} + (D+\epsilon_x)\frac{\partial^2 c}{\partial x^2} + \frac{d}{dx}\int (r_V + r_\sigma a)dx$$
$$(1\text{-}33)$$

$$\frac{\partial c}{\partial t} = -v_x\frac{\partial c}{\partial x} + (D+\epsilon)\frac{\partial^2 c}{\partial x^2} + (r_V + r_\sigma a) \qquad (1\text{-}34)$$

Equation 1-34 is known as the *one-dimensional advective diffusion equation*. As suggested above, it is the mass balance on a differential volume in a system in which concentration varies in only one dimension, and for this reason it is sometimes referred to as the mass balance "at a point." The equation is often the most convenient starting point for analyzing systems with unidirectional flow. If the initial and boundary conditions of the system are known, the equation can be integrated over the length of the reactor

(x values from 0 to L) to determine the concentration profile as a function of location in the system.

■ **EXAMPLE 1-8.** Consider a plug flow reactor with uniform cross-section (i.e., one with flow in only one direction and negligible mixing in that direction), so that the solution has a uniform concentration perpendicular to the flow direction. A reaction is occurring in the solution at a rate given by $r_V = -kc$, and no surface reactions are occurring. Determine the relationship between the influent and effluent concentrations, if the system is at steady state.

Solution. To solve this problem, it is convenient to use Equation 1-34.

$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + (D+\epsilon)\frac{\partial^2 c}{\partial x^2} + (r_V + r_\sigma a) \qquad (1\text{-}34)$$

where x is the direction of flow. Steady state indicates that $\partial c/\partial t = 0$, and the assumptions of plug flow and negligible axial diffusion indicate that the middle term on the right side of the equation is zero. Therefore, for the given situation, the equation can be simplified as follows:

$$0 = -v\frac{\partial c}{\partial x} - kc \qquad (1\text{-}35)$$

$$\frac{dc}{dx} = -\frac{k}{v}c \qquad (1\text{-}36)$$

The partial differential operator in Equation 1-35 has been converted into an ordinary differential in Equation 1-36, because c_i is a function of only one variable (x). Equation 1-36 can be rearranged and integrated between the inlet ($x = 0$), where the concentration is c_{in}, and the outlet ($x = L$), where the concentration is c_{out}

$$\int_{c_{in}}^{c_{out}} \frac{dc}{c} = -\frac{k}{v}\int_0^L dx \qquad (1\text{-}37)$$

$$\ln\frac{c_{out}}{c_{in}} = -\frac{k_1 L}{v} \qquad (1\text{-}38)$$

$$c_{out} = c_{in}\exp\left(-\frac{k_1 L}{v}\right) \qquad (1\text{-}39)$$

Multiplying the numerator and denominator of the exponential argument in Equation 1-39 by the cross-sectional area of the reactor, A, and noting that LA is the volume of the reactor (V), and vA is the volumetric flow rate (Q), we obtain

$$c_{out} = c_{in}\exp\left(-\frac{k_1 L}{v}\right) = c_{in}\exp\left(-\frac{kLA}{vA}\right) = c_{in}\exp\left(-\frac{kV}{Q}\right)$$

$$c_{out} = c_{in}\exp(-k\tau) \qquad (1\text{-}40)$$

where τ is the hydraulic detention time, V/Q, equal to the amount of time that the fluid resides in the reactor. The significance of this term is discussed in detail in Chapter 2.   ■

1.3   THE MASS BALANCE FOR A SYSTEM WITH FLOW AND CONCENTRATION GRADIENTS IN ARBITRARY DIRECTIONS

The Advection Term

We next consider how we can extend the preceding analysis to a system in which the flow can approach the surface at an arbitrary angle, and the concentration gradients causing diffusion and dispersive flux are not necessarily perpendicular to the boundary of the CV. Such a system is shown schematically in Figure 1-10. In this system, mass is capable of entering and leaving the CV across any point on its surface, and the bulk water flow is allowed to approach the CV from any angle. The analysis of such a system is broadly applicable, but the generality of the analysis unavoidably introduces greater mathematical complexity than is present in the case of unidirectional flow.

Consider first the advective flux in such a system. As in the simpler system, that flux is given by the product $v_\perp c$. However, in this system, it is possible that only a portion of the flow will be perpendicular to the system boundary; that is, $v_\perp$ might be less than v. To quantify the relationship between v and $v_\perp$, consider a differentially small region dA on the surface of the CV, and define the angle between the direction of flow (advection) and a line perpendicular to and directed into the surface as θ_{SAd}, as shown in Figure 1-11.

The velocity vector near dA can be divided into three orthogonal components, two of which are parallel to the boundary, while the third is perpendicular to it. The components of flow parallel to the boundary cannot cross it, so the only component that is relevant for the mass balance is the perpendicular component. Mathematically, the magnitude of
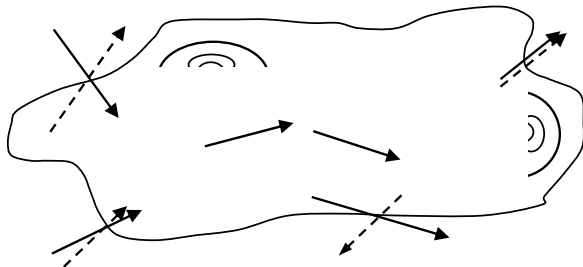

FIGURE 1-10.   Schematic representation of a control volume, flow pattern (solid arrows), and concentration gradients (dashed arrows) in a system with an arbitrary boundary shape and with the flow direction and the direction of the concentration gradient bearing no simple relationship with the shape of the surface.
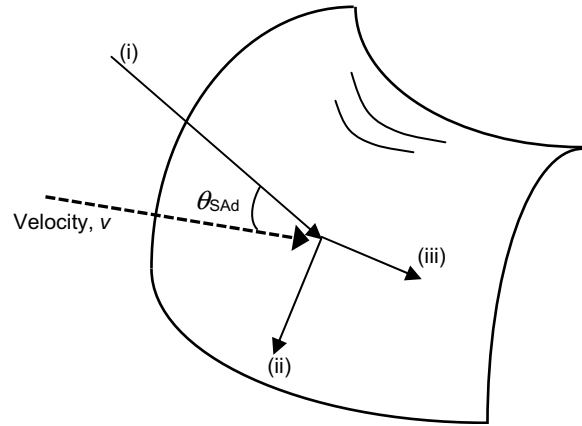

FIGURE 1-11.   Definition diagram for a system in which flow can approach the boundary of the control volume from arbitrary directions. The flow toward the surface (broken line) can be represented as a combination of a component perpendicular to the surface (i) and two components parallel to the surface (ii and iii).

this component equals the product of the magnitude of v and the cosine of the angle θ_{SAd}

$$v_\perp = v \cos\theta_{SAd} \qquad (1\text{-}41)$$

The volumetric flow rate crossing dA and entering the CV is the product of the velocity component perpendicular to and into the CV and the area dA; that is,

$$dQ_{in} = v \cos\theta_{SAd}\, dA \qquad (1\text{-}42)$$

Note that, if the actual bulk flow is perpendicular to dA, the angle θ_{SAd} is 0. In this case, $\cos\theta_{SAd}$ is 1.0, and the entire flow enters the CV. This situation applies to the simplified one-dimensional model discussed in Section 1-2. Similarly, if $\theta_{SAd} = 180°$, $\cos\theta_{SAd}$ equals -1.0; in that case, the magnitude of $v\cos\theta_{SAd}$ equals that of the bulk velocity, but the sign is negative, indicating that flow is directly out of the CV (this applies to the outflow in the simplified model). For any other value of θ_{SAd}, the component of the flow perpendicular to and therefore crossing the system boundary is less than the entire flow. Thus, the product $v\cos\theta_{SAd}dA$ yields a value that indicates both the magnitude of the flow that is crossing the boundary of the CV and the direction in which that fluid transfer is occurring.

As noted in the prior discussion of the simplified system, the rate at which a substance i enters the CV by advection across a patch dA is the product of the concentration of i in the water and the volumetric flow rate across that area. Thus, for the more general case under consideration here, the rate at which i enters the CV by advection is given by $cv\cos\theta_{SAd}dA$. Since c can never be negative, the direction of solute advection is always the same as the direction of

bulk fluid advection and is incorporated into the result by virtue of the sign of the computed value (positive for transfer into the CV, negative for transfer out of it).

To compute the overall rate of advective transport of i into the CV, the value of $cv\cos\theta_{\text{SAd}}\,dA$ must be computed for all patches of surface enclosing that volume, and summed (i.e., integrated), as follows:

Net rate of transport of i into CV by advection

$$= \oint cv\cos\theta_{\text{SAd}}\,dA \qquad (1\text{-}43)$$

$$= \oint J_{\text{adv}}\cos\theta_{\text{SAd}}\,dA \qquad (1\text{-}44)$$

The circle on the integral sign indicates that the integration is carried out around a surface that completely encloses the CV. The dimensions of c, v, and A are mass per volume, length per time, and area, respectively, giving a product with dimensions of mass per time, as required.

Equation 1-43 is often written in a slightly different form, using vector notation. To understand the alternative form, recall that a spatial vector A can be decomposed into the sum of components in the x, y, and z directions as: $A \equiv a_x\boldsymbol{i} + a_y\boldsymbol{j} + a_z\boldsymbol{k}$, where a_x, a_y, and a_z, are the magnitudes of the vector in the three directions, and $\boldsymbol{i}, \boldsymbol{j}$, and $\boldsymbol{k}$ are unit vectors in these directions. The magnitude of A can be computed as $A \equiv \sqrt{a_x^2 + a_y^2 + a_z^2}$.[9]

Recall also that the dot product of two vectors is a scalar whose value equals the product of the magnitudes of the two vectors and the cosine of the angle between them

$$A \cdot B = AB\cos\alpha \qquad (1\text{-}45)$$

If a vector $\boldsymbol{m}$ is defined whose magnitude is 1.0 and whose direction is perpendicular to and directed into the surface of the CV, the dot product of the velocity vector with $\boldsymbol{m}$ is

$$\boldsymbol{v} \cdot \boldsymbol{m} = v(1.0)\cos\theta_{\text{SAd}} = v\cos\theta_{\text{SAd}} \qquad (1\text{-}46)$$

Thus, Equation 1-43 could be written in vector form as

Net rate of transport of i into CV by advection $= \oint c\boldsymbol{v} \cdot \boldsymbol{m}\,dA$

$$\qquad (1\text{-}47)$$

By convention, however, the vector defining the perpendicular to the surface is assigned a magnitude of 1.0 and a direction *out* of the surface. It is called the *outwardly directed unit normal* and is designated $\boldsymbol{n}$. Since $\boldsymbol{m} = -\boldsymbol{n}$, $\boldsymbol{v} \cdot \boldsymbol{m} = -\boldsymbol{v} \cdot \boldsymbol{n}$, and the conventional way of writing the

[9] In this book, vectors are shown in bold, and the magnitude of a vector is shown as the same symbol in normal text.

advective term in the mass balance using vector notation is

Net rate of transport of i into CV by advection $= \oint c\boldsymbol{v} \cdot \boldsymbol{n}\,dA$

$$\qquad (1\text{-}48)$$

The product $c\boldsymbol{v}$ is the vector representation of the advective flux of i, $\boldsymbol{J}_{\text{adv}}$. $\boldsymbol{J}_{\text{adv}}$ characterizes the mass of i transported across a unit area per unit time in the direction of flow (i.e., the direction of $\boldsymbol{v}$). The product $\boldsymbol{n}dA$ is sometimes written as $d\boldsymbol{A}$, defined as a vector with magnitude equal to dA and direction perpendicular to and directed out of the surface. Thus, a few alternative forms of Equation 1-48 are as follows:

Net rate of transport of i into CV by advection

$$= \oint c\boldsymbol{v} \cdot d\boldsymbol{A} \qquad (1\text{-}49\text{a})$$

$$= -\oint \boldsymbol{J}_{\text{adv}} \cdot \boldsymbol{n}dA \qquad (1\text{-}49\text{b})$$

$$= -\oint \boldsymbol{J}_{\text{adv}} \cdot d\boldsymbol{A} \qquad (1\text{-}49\text{c})$$

The various forms for representing the advective term in mass balances, both for the general case and the simplified system with unidirectional flow, are summarized in Table 1-3.

The Diffusion and Dispersion Terms

Consider now the diffusive and dispersive fluxes for the general case represented in Figure 1-10. In this case, the concentration of i may vary in all directions, rather than just in the direction perpendicular to the boundary, so diffusion and dispersion can occur in all directions as well. Furthermore, whereas the diffusion coefficient is the same in all

TABLE 1-3. Summary of Equations Describing Advective Transport Into a Control Volume

Net rate of transport of i into control volume by advection =	
Arbitrary surface shape and flow pattern	*Flow directly into and out of control volume across a flat boundary*
Geometric or scalar representation	
$\oint cv\cos\theta_{\text{SAd}}\,dA \qquad (1\text{-}43)$	$\displaystyle\sum_{\text{inlets}} Q_{\text{in}}c_{\text{in}} - \sum_{\text{outlets}} Q_{\text{out}}c_{\text{out}} \quad (1\text{-}5)$
$\oint J_{\text{adv}}\cos\theta_{\text{SAd}}\,dA \qquad (1\text{-}44)$	
Vector representation	
$-\oint c\boldsymbol{v} \cdot \boldsymbol{n}dA \qquad (1\text{-}48)$	
$-\oint c\boldsymbol{v} \cdot dA \qquad (1\text{-}49\text{a})$	
$-\oint \boldsymbol{J}_{\text{adv}} \cdot \boldsymbol{n}dA \qquad (1\text{-}49\text{b})$	
$-\oint \boldsymbol{J}_{\text{adv}} \cdot dA \qquad (1\text{-}49\text{c})$	

directions, the dispersion coefficient is often different in different directions. As a result, the dispersive flux in a given direction depends on both the concentration gradient and the dispersion coefficient in that direction, and the maximum dispersive flux might not be in the direction of either the maximum concentration gradient or the maximum dispersivity; rather, it is always in the direction of the maximum product of these two terms.

The variation in ϵ with direction complicates the mathematics beyond the scope of this discussion. This mathematics is presented in many advanced fluid dynamics textbooks (e.g., Bear, 1972; Domenico and Schwartz, 1990). Here, we focus on two limiting cases: one in which dispersion is significant in only one direction (the situation analyzed previously, yielding the various forms of Equation 1-13), and the other for so-called *isotropic turbulence*, in which the dispersion coefficient is identical in all directions, and the directions of maximum diffusion and maximum dispersion are identical. In the latter case, the diffusive, dispersive, and combined fluxes in any given direction can be computed as follows:

$$J_{\text{diff},l} = -D\frac{\partial c}{\partial l} \tag{1-50}$$

$$J_{\text{disp},l} = -\epsilon\frac{\partial c}{\partial l} \tag{1-51}$$

$$J_{\mathbf{D},l} = -(D+\epsilon)\frac{\partial c}{\partial l} \tag{1-52}$$

where l is a measure of distance in the direction of interest. As is the case for the advective term, only the components of these fluxes that are perpendicular to the surface of the CV and therefore causing i to enter or leave the CV should be considered in the mass balance. That is, we are interested in the value of $\partial c/\partial l$ along a line normal to the surface of the CV, which we will refer to as $\partial c/\partial l_n$.

If we knew the concentration profile in all directions at a given location on the CV boundary, and if we knew the orientation of the surface at that location, we could compute $\partial c/\partial l_n$ and the corresponding flux across a differential patch of surface at the location. By carrying out this process repeatedly until we have considered the boundary of the entire CV, we could compute the transport of i into the CV as follows:

Net rate of transport of i into CV by diffusion and

$$\text{dispersion} = -\oint (D+\epsilon)\frac{\partial c}{\partial l_n}\mathrm{d}A \tag{1-53}$$

In some cases, the known information is the magnitude and direction of the maximum concentration gradient at various locations in the system, rather than the concentration gradient in the direction normal to the surface. In

such a case, we can represent the maximum concentration gradient as the vector sum of three components, much as we did for the velocity vector: two components parallel to the surface, and one perpendicular to it. The component of the concentration gradient that is perpendicular to the surface, and that therefore is responsible for all the diffusive and dispersive transport across the CV boundary, is

$$\frac{\partial c}{\partial l_n} = \frac{\partial c}{\partial l'}\cos\theta_{nl'} \tag{1-54}$$

where $\partial c/\partial l_n$ is the gradient at the point of interest in the direction perpendicular to the surface, $\partial c/\partial l'$ is the largest concentration gradient at that location, and $\theta_{nl'}$ is the angle between these two gradients.

Then, substituting Equation 1-54 into Equation 1-53:

Net rate of transport of i into CV by diffusion and

$$\text{dispersion} = -\oint (D+\epsilon)\frac{\partial c}{\partial l'}\cos\theta_{nl'}\mathrm{d}A \tag{1-55}$$

For consistency with the notation used in the equations derived earlier for advective flux, we subsequently refer to the angle between the normal to the surface and the steepest concentration gradient ($\theta_{nl'}$) as $\theta_{S\mathbf{D}}$; that is

Net rate of transport of i into CV by diffusion and

$$\text{dispersion} = -\oint (D+\epsilon)\frac{\partial c}{\partial l'}\cos\theta_{S\mathbf{D}}\mathrm{d}A \tag{1-56}$$

$$= \oint J_{\mathbf{D},\max}\cos\theta_{S\mathbf{D}}\mathrm{d}A \tag{1-57}$$

where $J_{\mathbf{D},\max}$ is the maximum diffusive and dispersive flux in any direction at the location where the integral is being evaluated.

The steepest gradient in some property (e.g., concentration, temperature, or electrical potential) is of interest in a number of engineering contexts and can be represented conveniently using vector notation. Specifically, for a property P, the vector characterizing the magnitude and direction of the steepest gradient in P is given the symbol ∇P and can be computed as

$$\nabla P = \frac{\partial P}{\partial x}\mathbf{i} + \frac{\partial P}{\partial y}\mathbf{j} + \frac{\partial P}{\partial z}\mathbf{k} \tag{1-58}$$

In this context, the vector of interest is ∇c, which has the magnitude and direction of $\partial c/\partial l'$. The vector $\mathbf{n}$ has a magnitude of unity and a direction perpendicular to the

surface. Therefore, the dot product of ∇c and $-\boldsymbol{n}$ is

$$\nabla c \cdot (-\boldsymbol{n}) = \frac{\partial c}{\partial l'} \cos\theta_{\text{SD}} \qquad (1\text{-}59)$$

Substituting this equality into Equation 1-56, we obtain

Net rate of transport of i into CV by diffusion and

$$\text{dispersion} = \oint (D + \epsilon)\nabla c \cdot \boldsymbol{n} dA \qquad (1\text{-}60)$$

The product $(D + \epsilon)\nabla c$ is the flux in the direction of the steepest gradient in concentration. Representing this term as $J_{\text{D,max}}$, we can write Equation 1-60 in the following alternative form:

Net rate of transport of i into CV by diffusion

$$= -\oint J_{\text{D,max}} \cdot \boldsymbol{n} dA \qquad (1\text{-}61)$$

Several equations derived above for the diffusive and dispersive terms in the mass balance equation are summarized in Table 1-4.

The Storage and Reaction Terms

Because the storage and reaction terms in the mass balance describe processes that occur inside the CV rather than at its boundary, these terms are identical regardless of whether the direction of flow and the direction of the concentration gradient are perpendicular to the boundary or not; that is, they have the same form for the systems as shown in both Figure 1-3a and 1-3b.

The Overall Mass Balance

The overall mass balance for the system with arbitrary flow and boundary characteristics, but constant volume and isotropic turbulence, can therefore be written by combining the expressions for advective and diffusive/dispersive flux with those derived earlier for storage and reaction. Two equivalent forms of the resulting equation are as follows:

$$\int \frac{\partial c}{\partial t} dV = \oint (-c\boldsymbol{v} + (D + \epsilon)\nabla c) \cdot \boldsymbol{n} dA + \int_V (r_{\text{V}} + r_\sigma a)\, dV$$
$$(1\text{-}66)$$

$$\int \frac{\partial c}{\partial t} dV = -\oint \{J_{\text{adv}} + J_{\text{D,max}}\} \cdot \boldsymbol{n} dA + \int_V (r_{\text{V}} + r_\sigma a) dV$$
$$(1\text{-}67)$$

The two types of integrals in Equations 1-66 and 1-67 reflect the distinction between the terms in the mass balance that account for changes *within* the CV (the storage and reaction terms) and those that account for transport of molecules *across the boundaries* of the CV (the advection and dispersion terms). The idea of the volume integrals (for the storage and reaction terms) is that one moves through the CV and, in each differential element of volume evaluates $(\partial c/\partial t) dV$ or $r dV$. All these differential terms are then summed to get the values of the corresponding integrals. The idea of the surface integrals (for the advective and dispersion terms) is that one moves around the surface that encloses the CV, considering one differential area after another, and at each area evaluates the local concentration of i, the gradient of i, and the magnitude and direction of flow. The appropriate differential terms are then computed and summed to determine the value of the corresponding integrated terms.

The equations for the advective and dispersive fluxes of i in the simplified case can all be derived from these for the more general case by making appropriate substitutions for θ_{SAd} and θ_{SD} and assuming that the velocity and concentration are uniform across the cross-sections of the inlet and outlet; that is, in the y and z directions.

TABLE 1-4.   Summary of Equations Describing Diffusive and Dispersive Transport Into a Control Volume

Net rate of transport of i into control volume by diffusion and dispersion $=$

Arbitrary surface shape and flow pattern, but isotropic turbulence	*Flow directly into and out of control volume across a flat boundary*
Geometric or scalar representation	
$-\oint (D + \epsilon)\dfrac{\partial c}{\partial l'} \cos\theta_{\text{SD}} dA$ (1-62)	$[J_{\text{D}}A]_{\text{inlet}} - [J_{\text{D}}A]_{\text{outlet}}$ (1-13)
$\oint J_{\text{D,max}}\cos\theta_{\text{SD}} dA$ (1-63)	$-(D + \epsilon_x)\left\{\left[\dfrac{\partial c}{\partial x}A\right]_{\text{inlet}} - \left[\dfrac{\partial c}{\partial x}A\right]_{\text{outlet}}\right\}$ (1-13)^a
Vector representation	
$\oint (D + \epsilon)\nabla c \cdot \boldsymbol{n} dA$ (1-64)	
$-\oint J_{\text{D,max}} \cdot \boldsymbol{n} dA$ (1-65)	

^{a}Assumes $(D + \epsilon)_{\text{inlet}} = (D + \epsilon)_{\text{outlet}}$

1.4   THE DIFFERENTIAL FORM OF THE THREE-DIMENSIONAL MASS BALANCE

As is the case for the one-dimensional mass balance, it is sometimes of interest to shrink the CV to differential dimensions for mass balances in three-dimensional space. Equations 1-66 and 1-67 can be converted into such a form by using a mathematical equality known as the divergence theorem, which provides a means for relating phenomena at the boundaries of a surface to quantities in the space that the surface encloses. This theorem states that, for any vector X

$$\oint X \cdot n \, dA = \int \nabla \cdot X dV \qquad (1\text{-}68)$$

The symbol $\nabla \cdot X$ is a scalar referred to as the divergence of X and defined as

$$\nabla \cdot X = i \cdot \frac{\partial X}{\partial x} + j \cdot \frac{\partial X}{\partial y} + k \cdot \frac{\partial X}{\partial z} \qquad (1\text{-}69a)$$

$$= \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} \qquad (1\text{-}69b)$$

where X_x is the x-component of X, and so on. The divergence operation is, in a way, analogous to the gradient operation: the gradient operation is applied to a scalar and yields a vector with the magnitude and direction of the steepest change in that scalar, whereas the divergence operation is applied to a vector and yields a scalar with the magnitude of the steepest change in that vector (and, of course, no direction, since it is a scalar).[10]

In essence, the divergence theorem states that any material that crosses the boundary enclosing a space (the area integral on the left side of the equation) can be expressed in terms of the increase in the amount of material inside the boundary (the volume integral on the right side). Applying this theorem to the right side of Equation 1-66, the mass balance can be rewritten as follows:

$$\int \frac{\partial c}{\partial t} dV = \oint \left(-cv + (D+\epsilon)\nabla c \right) \cdot n dA + \int (r_V + r_\sigma \sigma) dV \qquad (1\text{-}66)$$

$$\int \frac{\partial c}{\partial t} dV = \int [\nabla \cdot \{-cv + (D+\epsilon)\nabla c\} + (r_V + r_\sigma a)] dV \qquad (1\text{-}70)$$

The terms on the right side of Equation 1-70 are the same terms that appear in the mass balances derived previously, except that now the advective and diffusive/dispersive fluxes have been converted into a volume basis.

[10] See Schey (1973) for a thorough and readable discussion of these mathematical operations.

The first term on the right side of Equation 1-70 can be expanded based on the chain rule, as follows:

$$\nabla \cdot (-cv) = -\left(\frac{\partial(cv_x)}{\partial x} + \frac{\partial(cv_y)}{\partial y} + \frac{\partial(cv_z)}{\partial z} \right) \qquad (1\text{-}71)$$

$$= -c\left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) - \left(v_x \frac{\partial c}{\partial x} + v_y \frac{\partial c}{\partial y} + v_z \frac{\partial c}{\partial z} \right) \qquad (1\text{-}72)$$

$$= -c(\nabla \cdot v) - v(\nabla c) \qquad (1\text{-}73)$$

According to the continuity equation, $\nabla \cdot v$ is zero for any incompressible fluid, such as water, so Equation 1-73 indicates that, for any constituent in an aqueous system[11]

$$\nabla \cdot (-cv) = -v \cdot \nabla v \qquad (1\text{-}74)$$

Furthermore, since we are assuming that ϵ is independent of direction (i.e., we are assuming isotropic dispersion), the term accounting for transport by diffusion and dispersion in Equation 1-70 can be written as follows:

$$\nabla \cdot \{(D+\epsilon)\nabla c\} = (D+\epsilon)\nabla \cdot \nabla c \qquad (1\text{-}75)$$

$$= (D+\epsilon)\nabla^2 c \qquad (1\text{-}76)$$

where $\nabla^2 c$ is a scalar known as the Laplacian of c. This symbol is a short-hand expression for the following summation:

$$\nabla^2 c \equiv \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \qquad (1\text{-}77)$$

Substituting Equations 1-74 and 1-76 into Equation 1-70, we obtain

$$\int \frac{\partial c}{\partial t} dV = \int \left(-v \cdot \nabla c + (D+\epsilon)\nabla^2 c + (r_V + r_\sigma a) \right) dV \qquad (1\text{-}78)$$

By differentiating both sides of Equation 1-78 with respect to volume, the equation becomes a mass balance on a differential volume

$$\frac{\partial c}{\partial t} dV = \left(-v \cdot \nabla c + (D+\epsilon)\nabla^2 c + (r_V + r_\sigma a) \right) dV \qquad (1\text{-}79)$$

[11] The continuity equation is a mass balance applied to the fluid (in our case, water) in a differential control volume of fixed dimensions. The equation indicates that, since water is incompressible, it cannot accumulate in the control volume, so it must enter and exit at the same rate. Any decrease in its velocity in one direction must therefore be compensated by an increase in its velocity in a different direction. The equation is derived formally in most texts dealing with fluid mechanics and/or environmental transport processes; see, for example, Clark (2009).

Finally, dividing by dV, we obtain a version of the volume-normalized mass balance (i.e., an equation for the rate of change of concentration in a differential CV) that is commonly referred to as the mass balance at a point.

$$\frac{\partial c}{\partial t} = -\boldsymbol{v} \cdot \boldsymbol{\nabla} c + (D + \epsilon)\nabla^2 c + (r_V + r_\sigma a) \qquad (1\text{-}80)$$

As shown in Equation 1-72, the term $\boldsymbol{v} \cdot \boldsymbol{\nabla} c$ in Equation 1-80 is a scalar equal to $v_x(\partial c/\partial x) + v_y(\partial c/\partial y) + v_z(\partial c/\partial z)$. This term is very frequently represented as $v\nabla c$, with the implicit understanding that v is a vector and that the product is a dot product. Equation 1-80 is the advective diffusion equation written for a system in which parameters can vary in all three spatial dimensions. Similar to Equation 1-34, Equation 1-80 is sometimes referred to as a mass balance at a point.

■ **EXAMPLE 1-9.** The HOCl concentration in drinking water decays as the water flows through the distribution system, due to reactions with NOM (as described in Example 1-6) and with the pipe walls (HOCl can react with both the metal and attached biomass). Assume that, in a given system, the overall decay rate accounting for reactions both in solution and on the surface (i.e., $r_V + r_\sigma a$) can be characterized by the expression $r_{HOCl} = -kc_{HOCl}$, where k has a value of $0.1\,h^{-1}$.

Compare the magnitudes of the net advection and reaction terms in the mass balance for a 5-km long section of 1-m diameter pipe in which the flow rate is $1.5\,m^3/s$. The concentration of HOCl entering this section of pipe is 3 mg/L. Assume that the pipe section can be characterized by plug flow and that the system is operating at steady state.

Solution. The most general form of the mass balance on HOCl for this system is given by Equation 1-26

$$\frac{\partial}{\partial t}\int_V c\,dV = Q_{in}c_{in} - Q_{out}c_{out} + (D + \epsilon_x)\left\{\left[A\frac{\partial c}{\partial x}\right]_{outlet} \right. $$
$$\left. -\left[A\frac{\partial c}{\partial x}\right]_{inlet}\right\} + \int_V (r_V + r_\sigma a)\,dV$$

However, since the system is at steady state, the rate of change of HOCl stored in the system (the term on the left hand side of the mass balance) is zero, and since the system is characterized by plug flow, the middle term on the right is zero as well. Noting that $Q_{in} = Q_{out} = Q$, the mass balance can therefore be simplified as follows:

$$0 = Qc_{in} - Qc_{out} + \int_V (r_V + r_\sigma a)\,dV \qquad (1\text{-}81)$$

The difference $Qc_{in} - Qc_{out}$ is the net advective term in the mass balance, and the volume integral is the net reaction term. Since the pipe behaves as a plug flow reactor and the

reaction rate is directly proportional to the HOCl concentration, we can use the result from Example 1-8 (specifically, Equation 1-40) to compute c_{out}. To do so, we need to first find the hydraulic residence time, τ. This value is

$$\tau = \frac{V}{Q} = \frac{(\pi d^2/4)L}{Q} = \frac{(\pi(1\,m)^2/4)(5000\,m)}{1.5\,m^3/s}\left(\frac{1\,h}{3600\,s}\right) = 0.73\,h$$

Therefore, c_{out} can be computed as follows:

$$c_{out} = c_{in}\exp(-k\tau)$$
$$= (3.0\,mg/L)\exp\left[-(0.1\,h^{-1})(0.73\,h)\right] = 2.79\,mg/L$$

The net advective term in the mass balance is therefore

$$\text{Net advective term} = Q(c_{in} - c_{out})$$
$$= (1.5\,m^3/s)(10^3\,L/m^3)((3.0 - 2.79)\,mg/L)$$
$$= 316\,mg/s$$

The net reaction term could be computed formally by substituting the reaction rate expression ($-kc_{HOCl}$) for $r_V + r_\sigma a$ and then integrating throughout the pipe volume. However, Equation 1-81 indicates that the reaction term is just the opposite of the advection term. This must be the case, since the system is at steady state (so no HOCl is accumulating in the CV), and the only factors that affect the HOCl concentration in the CV are advection and reaction. Therefore, the net reaction term in the CV must be $-316\,mg/s$. The negative sign indicates that the reaction removes HOCl from the system. ■

1.5 SUMMARY

Mass balances are accounting tools that can be used to identify the relative importance of different processes occurring in a reactor and to predict how the system behaves under any conditions. The critical steps in writing a mass balance are identifying the substance for which the balance is to be written, defining the system boundaries, and establishing all the ways that the substance can enter or exit the CV or be created or destroyed within it.

The overall mass balance states that the rate of change of the mass of i stored in the CV is a function of the flow rates into and out of the CV, the concentration gradient at the boundary of the CV, the reaction rate within the CV, and several physical variables describing the system (D, ϵ, V). In most cases, the initial condition of the system is known, and many of the parameters in the equation relating to the physical properties of the system are known. Techniques for estimating some of the physical parameters that are not known in advance are presented in Chapter 2. Similarly, explicit expressions describing the reaction rate (r) as a function of concentration are presented and discussed in Chapter 3.

TABLE 1-5.   Summary of Mass Balance Equations Derived in this Chapter

Storage term	=	Net advection term	+	Net diffusion/dispersion term	+	Net chemical reaction term	Eq. no.

Equation describing the rate of change of mass of i in a control volume for one-dimensional flow:

$$\frac{\partial}{\partial t}\int c\,dV \quad = \quad Q_{in}c_{in} - Q_{out}c_{out} \quad + \quad (D + \epsilon_x)\left\{\left[A\frac{\partial c}{\partial x}\right]_{outlet} - \left[A\frac{\partial c}{\partial x}\right]_{inlet}\right\} \quad + \quad \int (r_V + r_\sigma a)\,dV \qquad (1\text{-}26)$$

Equation describing the rate of change of concentration of i (i.e., the volume-normalized mass balance) at a point for one-dimensional flow:

$$\frac{\partial c}{\partial t} \quad = \quad -v_x\frac{\partial c}{\partial x} \quad + \quad (D + \epsilon_x)\frac{\partial^2 c}{\partial x^2} \quad + \quad (r_V + r_\sigma a) \qquad (1\text{-}34)$$

Equations describing the rate of change of mass of i in a control volume for an arbitrary flow pattern:

$$\frac{\partial}{\partial t}\int c\,dV \quad = \quad \oint\{-c\mathbf{v} + (D + \epsilon)\nabla c\}\cdot \mathbf{n}\,dA \quad + \quad \int (r_V + r_\sigma a)\,dV \qquad (1\text{-}66)$$

$$\frac{\partial}{\partial t}\int c\,dV \quad = \quad -\oint(\mathbf{J}_{adv} + \mathbf{J}_{\mathbf{D},max})\cdot \mathbf{n}\,dA \quad + \quad \int (r_V + r_\sigma a)\,dV \qquad (1\text{-}67)$$

Equation describing the rate of change of concentration of i (i.e., the volume-normalized mass balance) at a point for an arbitrary flow pattern:

$$\frac{\partial c}{\partial t} \quad = \quad -\mathbf{v}\cdot\nabla c \quad + \quad (D + \epsilon)\nabla^2 c \quad + \quad (r_V + r_\sigma a) \qquad (1\text{-}80)$$

Equation describing the rate of change of mass of i in a well-mixed reactor with continuous flow, but with fixed volume:

$$V\frac{dc}{dt} \quad = \quad Q(c_{in} - c_{out}) \quad + \quad (r_V + r_\sigma a)V \qquad (1\text{-}27)$$

Equation describing the rate of change of concentration of i in a well-mixed batch (no flow) reactor:

$$\frac{dc}{dt} \quad = \quad r_V + r_\sigma\sigma \qquad (1\text{-}30)$$

Equation describing the rate of change of mass of i in a well-mixed reactor with continuous flow at steady state:

$$0 \quad = \quad Q(c_{in} - c_{out}) \quad + \quad (r_V + r_\sigma a)V \qquad (1\text{-}28)$$

In theory, if all the physical parameters and the reaction rates are characterized, the mass balance equation can be solved for the concentration of i at any given time and location. However, even for relatively simple geometries and reaction rates, solving the mass balance equation can be formidable, especially if all the terms are significant. The equation becomes much easier to solve if additional simplifying assumptions can be made. For instance, in many cases the flows into and out of the reactor are equal, or the system composition is approximately invariant over time ($\partial c/\partial t = 0$). Sometimes, systems are set up in which several of the terms in the mass balance are designed to be negligible, to make it easier to evaluate those that remain. For example, reactors are conveniently evaluated by passing nonreactive constituents (tracers) through them, so that the chemical reaction term is zero ($r_V = r_\sigma = 0$). In other cases, chemical reactions are conveniently studied in well-mixed batch systems, where there is no flow and no concentration gradient, so the net advective, diffusive, and dispersive terms are all zero. These types of systems are discussed in Chapters 2 and 3, after which the problem of predicting the behavior of systems in which all the processes are occurring is addressed in Chapter 4.

The various forms of the mass balance equation derived throughout the chapter are summarized in Table 1-5.

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PROBLEMS

1-1. The raw water supply for a community contains 18 mg/L total particulate matter. It is to be treated by addition of 60 mg alum ($Al_2(SO_4)_3 \cdot 14H_2O$) per liter of water treated. Essentially, all the added alum precipitates represented by the following reaction:

$$Al_2(SO_4)_3 \cdot 14H_2O \rightarrow 2\,Al(OH)_3(s) + 3SO_4^{2-}$$
$$+ 6H^+ + 8H_2O$$
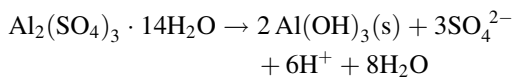
For a total flow of 7500 m³/d, compute the daily alum requirement, the total concentration of suspended solids in the water following alum addition, and the daily load of particulate solids requiring disposal (including both those initially present and those formed during treatment).

1-2. Manufacturing of electronic chips or wafers requires ultrapure water (UPW) in substantial quantities; the primary use of this water is to clean the wafers after various manufacturing steps. As a result, wafer fabrication plants have a UPW production plant to supply this water to the manufacturing plant. Typically, the UPW plant takes municipal tap water and treats it further to remove a substantial fraction of the solutes. The UPW then flows into the manufacturing plant, where it is contaminated as it is used to clean the wafers. The typical situation, in which the contaminated water is collected and discharged without any reuse, is shown schematically in Figure 1-Pr2a. If the manufacturing process continuously adds a specific contaminant into the UPW at a rate $\dot{X}$ (mass per time), the key flows can be represented as in Figure 1-Pr2b.

It is very expensive to make UPW, and the contamination levels in the manufacturing process are quite low. Therefore, it makes sense to consider recycling some of the wastewater back to the start of the UPW production plant. Under these circumstances, the schematic would be as shown in Figure 1-Pr2c. Note that the flow rate of water supplied to the manufacturing plant (Q) remains the same, but the use of municipal water is decreased (to $Q - Q_R$).

(a) Unfortunately, some contaminants that are added to the water in the chip manufacturing process are
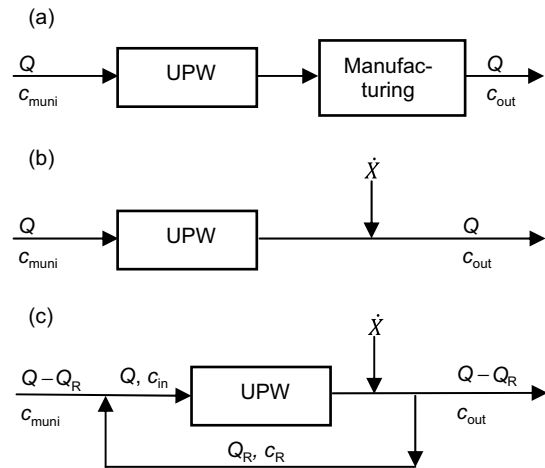

FIGURE 1-Pr2. Water and contaminant flows in a hypothetical electronic chip production plant with internal production of ultrapure water. (a) Generic flow diagram; (b) flow diagram assuming a continuous input of contaminant from the chip manufacturing process; (c) flow diagram from (b), modified to account for recycle of a portion of the contaminated water back to the inlet of the UPW production process.

not removed at all in the UPW production plant. As a result, they accumulate in the system with recycle until a steady-state condition is achieved. If the particular chemical that is added at the rate $\dot{X}$ is not removed at all in the UPW treatment, and if it is also not present at all in the influent (municipal water), what is the steady-state concentration in the effluent (c_{out}) in terms of $\dot{X}$ and the flow rates indicated? (Note: We are *not* concerned in this problem with the gradual rise of concentration until this concentration is reached, only with the ultimate steady-state condition.)

(b) Problems arise if the contaminant concentration in the influent to the manufacturing step rises above a critical acceptable level (c_{acc}). Again, assuming that the contaminant concentration in the municipal water is zero and that the UPW system does not remove any of this contaminant, develop an expression relating the recycle ratio ($R = Q_R/Q$) to the known quantities Q, c_{acc}, and $\dot{X}$. (Hint: Develop an expression relating Q_R, Q, c_{acc}, and $\dot{X}$ first, and then change it to include R.)

(c) If the water used in the manufacturing process is 2500 L/min, $\dot{X}$ is 300 mg/min, and c_{acc} is 0.2 mg/L, what flow rate of municipal water would have to be supplied?

1-3. A settling tank has a single influent flow and two effluent flows, as indicated in Figure 1-Pr3. The
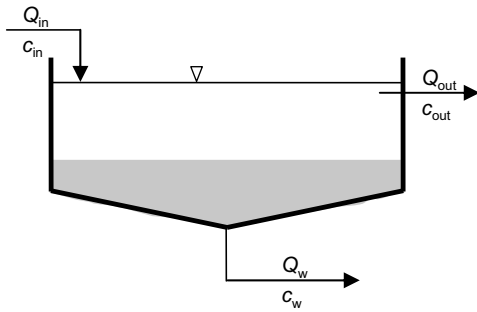
FIGURE 1-Pr3. A settling tank for separating and concentrating solids, and generating an effluent liquid stream with low solids concentration.

objective of sedimentation is to make c_{out} be much less than c_{in}, while making c_w much greater than c_{in}. A primary settling tank in a wastewater treatment plant is operating under steady-state conditions and has an influent concentration of 220 mg/L of suspended solids, an effluent concentration (c_{out}) of 45 mg/L, and a waste concentration (c_w) of 10,000 mg/L. Assume that no reactions involving these solids occur in the reactor.

(a) If the influent flow rate is $450\,m^3/h$, what is the waste flow rate (Q_w)?

(b) What percentage of the influent flow is the waste flow?

1-4. Water flows into and out of a well-mixed, 1.6×10^5-L tank at a rate of 1000 L/min. The dissolved oxygen (DO) concentration in the influent is 1.0 mg/L. In the tank, bacteria use the oxygen for metabolism in proportion to the amount of oxygen present; that is, they use it at a rate $k_1(DO)$, where $k_1 = 2 \times 10^{-3}\,min^{-1}$. Oxygen is dissolving into the water at a rate proportional to the degree of undersaturation; that is, at a rate given by $k_2(DO^* - DO)$, where DO^* is 10 mg/L and $k_2 = 4 \times 10^{-3}\,min^{-1}$. Write a mass balance for DO in the solution, and find the steady-state concentration of DO.

1-5. A pond of volume 10^6 L receives influent stream water containing 75 mg/L soluble organic carbon and 6 mg/L inorganic carbon (H_2CO_3, HCO_3^-, and CO_3^{2-}) at a rate of $0.01\,m^3/s$. Advection is much more important than diffusion or dispersion as a mechanism for transporting material into and out of the pond. In the pond, 75% of the incoming organic matter is consumed by

microorganisms, which convert 30% of the ingested organic carbon into new cellular material and release 70% as CO_2 after respiration. The CO_2 combines immediately with water to form H_2CO_3 and then rapidly becomes distributed among the three inorganic carbon species listed above, with the distribution dependent on solution pH. Assume that 50% of the cellular mass is carbon. The entire system is at steady state.

(a) Write mass balances on total organic carbon (TOC), dissolved organic carbon (DOC), and total inorganic carbon (TIC), and compute the steady-state concentrations of these species.

(b) How much biomass is created per liter of influent?

1-6. In a biological waste treatment system, solids may enter in the influent, be created or destroyed by biological growth or decay, and may leave in the effluent. Consider a waste treatment plant treating $1\,m^3/s$ of an influent containing 55 mg/L of degradable organic solids. The wastewater also contains 180 mg/L of dissolved organic carbon (DOC), which may be degraded. For every gram of dissolved organic matter that is degraded, the overall reaction converts a portion of the material into CO_2 and H_2O, and another portion into 0.4 g of new biomass. Analytically, this biomass and the degradable solids in the influent are both quantified as volatile suspended solids (VSS); that is, the degradable solids in the influent and the new biomass that grows in the reactor are indistinguishable from one another.

(a) In a particular system, the dissolved organic matter (i.e., the substrate, S) is removed from solution at an overall rate (including both the conversion into CO_2 and into new cells) given by $r_S = -k_1 S^2 X/(S^2 + K_s)$, where X is the VSS concentration in the reactor. The values of k_1, K_s, and X in the reactor of interest are 8 mg DOC/mg VSS d, $110\,(mg\,DOC/L)^2$, and 120 mg VSS/L, respectively. Write a mass balance and compute the hydraulic detention time, τ (i.e., the average amount of time that water resides in the reactor, equal to V_L/Q_L) necessary to reduce the concentration of substrate to 3 mg DOC/L in a complete mix reactor operating at steady state.

(b) Solids decay in the reactor at a rate equal to $k_d X$, where k_d is the decay rate constant. Write a mass balance on VSS and compute the value of k_d.