

Chapter 2

Conservation of Mass

In this chapter we start the quantitative development of thermodynamics using one of the qualitative observations of the previous chapter, that mass is conserved. Here we begin by developing the balance equations for the total mass of a system (a piece of equipment, a defined volume in space, or whatever is convenient for the problem at hand) by considering systems of only a single component. In this case, mass of the single species being considered is also the total mass, which is conserved, and we can write the balance equation either based on mass or by dividing by the molecular weight, on the number of moles. We develop two forms of these mass balance equations—one for computing the rate at which mass in a system changes with time, and the second set, obtained by integrating these rate equations over an interval of time, to compute only the change in mass (or number of moles) in that time interval.

We next consider the mass balances for a mixture. In this case while total mass is conserved, there will be a change of mass of each species if one or more chemical reactions occur. For this case, it is more convenient to develop the mass balance for mixtures on a molar basis, as chemical reaction stoichiometry is much easier to write on a molar basis than on a mass basis. In this chapter we will consider only the case of a single chemical reaction; in later chapters the more general case of several chemical reactions occurring simultaneously will be considered.

The most important goals of this chapter are for the student to understand when to use the rate-of-change form of the mass balance equation and when to use the difference form, and how to use these equations to solve problems. Mastering the use of the mass balance equations here will make it easier to use the more complicated energy and other balance equations that will be introduced in the following two chapters.

INSTRUCTIONAL OBJECTIVES FOR CHAPTER 2

The goals of this chapter are for the student to:

- Be able to use the rate-of-change form of the pure component mass balance in problem solving (Sec. 2.2)
- Be able to use the difference form of the pure component mass balance in problem solving (Sec. 2.2)
- Be able to use the rate-of-change form of the multicomponent mass balance in problem solving (Sec. 2.3)
- Be able to use the difference form of the multicomponent mass balance in problem solving (Sec. 2.3)
- Be able to solve mass balance problems involving a single chemical reaction (Sec. 2.3)

IMPORTANT NOTATION INTRODUCED IN THIS CHAPTER

M_i	Mass of species i (g)
\dot{M}	Mass flow rate (g/s)
\dot{M}_i	Mass flow rate of species i (g/s)
N_i	Moles of species i (mol)
\dot{N}	Molar flow rate of species i (mol/s)
\dot{N}_i	Molar flow rate (mol/s)
t	Time (s)
v	Velocity (m/s)
\mathbf{v}	Velocity vector (m/s)
\underline{x}	Set of mole fractions of all species x_1, x_2, x_3, \dots
X	Molar extent of reaction (mol)
ν_i	Stoichiometric coefficient of species i

2.1 A GENERAL BALANCE EQUATION AND CONSERVED QUANTITIES

The balance equations used in thermodynamics are conceptually simple. Each is obtained by choosing a system, either a quantity of mass or a region of space (e.g., the contents of a tank), and equating the change of some property of this system to the amounts of the property that have entered and left the system and that have been produced within it. We are interested both in the change of a system property over a time interval and in its instantaneous rate of change; therefore, we will formulate equations of change for both. Which of the two formulations of the equations of change is used for the description of a particular physical situation will largely depend on the type of information desired or available.

To illustrate the two types of descriptions and the relationship between them, as well as the idea of using balance equations, consider the problem of studying the total mass of water in Lake Mead (the lake behind Hoover Dam on the Colorado River). If you were interested in determining, at any instant, whether the water level in this lake was rising or falling, you would have to ascertain whether the water flows into the lake were greater or less than the flows of water out of the lake. That is, at some instant you would determine the rates at which water was entering the lake (due to the flow of the Colorado River and rainfall) and leaving it (due to flow across the dam, evaporation from the lake surface, and seepage through the canyon walls), and then use the equation

$$\left(\begin{array}{c} \text{Rate of change of} \\ \text{amount of water} \\ \text{in the lake} \end{array} \right) = \left(\begin{array}{c} \text{Rate at which} \\ \text{water flows} \\ \text{into the lake} \end{array} \right) - \left(\begin{array}{c} \text{Rate at which} \\ \text{water flows out} \\ \text{of the lake} \end{array} \right) \quad (2.1-1)$$

to determine the precise rate of change of the amount of water in the lake.

If, on the other hand, you were interested in determining the change in the amount of water for some period of time, say the month of January, you could use a balance equation in terms of the total amounts of water that entered and left the lake during this time:

$$\left(\begin{array}{c} \text{Change in amount} \\ \text{of water in the} \\ \text{lake during the} \\ \text{month of January} \end{array} \right) = \left(\begin{array}{c} \text{Amount of water that} \\ \text{flowed into the lake} \\ \text{during the month of} \\ \text{January} \end{array} \right) - \left(\begin{array}{c} \text{Amount of water that} \\ \text{flowed out of} \\ \text{the lake during the} \\ \text{month of January} \end{array} \right) \quad (2.1-2)$$

Notice that Eq. 2.1-1 is concerned with an instantaneous rate of change, and it requires data on the rates at which flows occur. Equation 2.1-2, on the other hand, is for computing the total change that has occurred and requires data only on the total flows over the time interval. These two equations, one for the instantaneous rate of change of a system property (here the amount of water) and the other for the change over an interval of time, illustrate the two types of change-of-state problems that are of interest in this book and the forms of the balance equations that are used in their solution.

There is, of course, an interrelationship between the two balance equations. If you had information on each water flow rate at each instant of time for the whole month of January, you could integrate Eq. 2.1-1 over that period of time to obtain the same answer for the total change in the amount of water as would be obtained directly from Eq. 2.1-2 using the much less detailed information on the total flows for the month.

The example used here to illustrate the balance equation concept is artificial in that although water flows into and out of a lake are difficult to measure, the amount of water in the lake can be determined directly from the water level. Thus, Eqs. 2.1-1 and 2.1-2 are not likely to be used. However, the system properties of interest in thermodynamics and, indeed, in most areas of engineering are frequently much more difficult to measure than flow rates of mass and energy, so that the balance equation approach may be the only practical way to proceed.

While our interest here is specifically in the mass balance, to avoid having to repeat the analysis leading to equation 2.1-4, which follows, for other properties, such as energy (see next chapter), we will develop a general balance equation for any extensive property θ . We will then replace θ with the total mass. In the next section θ will be the mass of only one of the species (which may undergo chemical reaction), and in the next chapter θ will be replaced by the total energy. In the remainder of this section, the balance equations for an unspecified extensive property θ of a thermodynamic system are developed.

With the balance equations formulated in a general manner, they will be applicable (by appropriate simplification) to all systems studied in this book. In this way it will not be necessary to rederive the balance equations for each new problem; we will merely simplify the general equations. Specific choices for θ , such as total mass, mass (or number of moles) of a single species, and energy, are considered in Sec. 2.2, 2.3, and 3.2, respectively.

We consider a general system that may be moving or stationary, in which mass and energy may flow across its boundaries at one or more places, and the boundaries of which may distort. Since we are concerned with equating the total change within the system to flows across its boundaries, the details of the internal structure of the system will be left unspecified. This “black-box” system is illustrated in Fig. 2.1-1, and characteristics of this system are

1. Mass may flow into one, several, all, or none of the K entry ports labeled 1, 2, . . . , K (i.e., the system may be either open or closed to the flow of mass). Since we are concerned with pure fluids here, only one molecular species will be involved, although its temperature and pressure may be different at each entry port. The

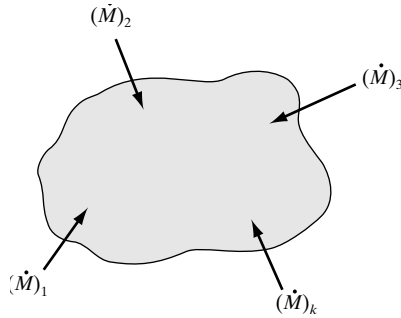


Figure 2.1-1 A single-component system with several mass flows.

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mass flow rate *into* the system at the k th entry port will be $(\dot{M})_k$, so that $(\dot{M})_k > 0$ for flow into the system, and $(\dot{M})_k < 0$ for flow out of the system.

2. The boundaries of the black-box system may be stationary or moving. If the system boundaries are moving, it can be either because the system is expanding or contracting, or because the system as a whole is moving, or both.

The following two characteristics are important for the energy balance.

3. Energy in the form of heat may enter or leave the system across the system boundaries.
4. Energy in the form of work (mechanical shaft motion, electrical energy, etc.) may enter or leave the system across the system boundaries.

Throughout this book we will use the convention that a flow into the system, whether it be a mass flow or an energy flow, is positive and a flow out of the system is negative.

The balance equation for the total amount of any extensive quantity θ in this system is obtained by equating the change in the amount of θ in the system between times t and $t + \Delta t$ to the flows of θ into and out of the system, and the generation of θ within the system, in the time interval Δt . Thus,

$$\begin{aligned} \left(\text{Amount of } \theta \text{ in the system at time } t + \Delta t \right) - \left(\text{Amount of } \theta \text{ in the system at time } t \right) = & \left(\text{Amount of } \theta \text{ that entered the system across} \right. \\ & \left. \text{system boundaries between } t \text{ and } t + \Delta t \right) \\ & - \left(\text{Amount of } \theta \text{ that left the system across} \right. \\ & \left. \text{system boundaries between } t \text{ and } t + \Delta t \right) \\ & + \left(\text{Amount of } \theta \text{ generated within the} \right. \\ & \left. \text{system between } t \text{ and } t + \Delta t \right) \quad (2.1-3) \end{aligned}$$

The meaning of the first two terms on the right side of this equation is clear, but the last term deserves some discussion. If the extensive property θ is equal to the total mass, total energy, or total momentum, quantities that are conserved (experimental observations 1 to 3 of Sec. 1.7), then the internal generation of θ is equal to zero. This is easily seen as follows for the special case of a system isolated from its environment (so that the flow terms across the system boundaries vanish); here Eq. 2.1-3 reduces to

$$\left(\text{Amount of } \theta \text{ in the system at time } t + \Delta t \right) - \left(\text{Amount of } \theta \text{ in the system at time } t \right) = \left(\text{Amount of } \theta \text{ generated within the system between } t \text{ and } t + \Delta t \right) \quad (2.1-3a)$$

Since neither total mass, total momentum, nor total energy can be spontaneously produced, if θ is any of these quantities, the internal generation term must be zero. If,

however, θ is some other quantity, the internal generation term may be positive (if θ is produced within the system), negative (if θ is consumed within the system), or zero. For example, suppose the black-box system in Fig. 2.1-1 is a closed (batch) chemical reactor in which cyclohexane is partially dehydrogenated to benzene and hydrogen according to the reaction



If θ is set equal to the total mass, then, by the principle of conservation of mass, the internal generation term in Eq. 2.1-3a would be zero. If, however, θ is taken to be the mass of benzene in the system, the internal generation term for benzene would be positive, since benzene is produced by the chemical reaction. Conversely, if θ is taken to be the mass of cyclohexane in the system, the internal generation term would be negative. In either case the magnitude of the internal generation term would depend on the rate of reaction.

The balance equation (Eq. 2.1-3) is useful for computing the change in the extensive property θ over the time interval Δt . We can also obtain an equation for computing the instantaneous rate of change of θ by letting the time interval Δt go to zero. This is done as follows. First we use the symbol $\theta(t)$ to represent the amount of θ in the system at time t , and we recognize that for a very small time interval Δt (over which the flows into and out of the system are constant) we can write

$$\left(\begin{array}{c} \text{Amount of } \theta \text{ that enters the} \\ \text{system across system boundaries} \\ \text{between } t \text{ and } t + \Delta t \end{array} \right) \text{ as } \left(\begin{array}{c} \text{Rate at which } \theta \text{ enters} \\ \text{the system across system} \\ \text{boundaries} \end{array} \right) \Delta t$$

with similar expressions for the outflow and generation terms. Next we rewrite Eq. 2.1-3 as

$$\begin{aligned} \frac{\theta(t + \Delta t) - \theta(t)}{\Delta t} &= \left(\begin{array}{c} \text{Rate at which } \theta \text{ enters the system} \\ \text{across system boundaries} \end{array} \right) \\ &\quad - \left(\begin{array}{c} \text{Rate at which } \theta \text{ leaves the system} \\ \text{across system boundaries} \end{array} \right) \\ &\quad + \left(\begin{array}{c} \text{Rate at which } \theta \text{ is generated} \\ \text{within the system} \end{array} \right) \end{aligned}$$

Finally, taking the limit as $\Delta t \rightarrow 0$ and using the definition of the derivative from calculus,

$$\frac{d\theta}{dt} = \lim_{\Delta t \rightarrow 0} \frac{\theta(t + \Delta t) - \theta(t)}{\Delta t}$$

we obtain

$$\begin{aligned} \frac{d\theta}{dt} = \left(\begin{array}{c} \text{Rate of change of} \\ \theta \text{ in the system} \end{array} \right) &= \left(\begin{array}{c} \text{Rate at which } \theta \text{ enters the} \\ \text{system across system boundaries} \end{array} \right) \\ &\quad - \left(\begin{array}{c} \text{Rate at which } \theta \text{ leaves the} \\ \text{system across system boundaries} \end{array} \right) \\ &\quad + \left(\begin{array}{c} \text{Rate at which } \theta \text{ is generated} \\ \text{within the system} \end{array} \right) \end{aligned} \quad (2.1-4)$$

Balance equation 2.1-4 is general and applicable to conserved and nonconserved quantities. There is, however, the important advantage in dealing with conserved quantities that the internal generation term is zero. For example, to use the total mass balance to compute the rate of change of mass in the system, we need know only the mass flows into and out of the system. On the other hand, to compute the rate of change of the mass of cyclohexane undergoing a dehydrogenation reaction in a chemical reactor, we also need data on the rate of reaction in the system, which may be a function of concentration, temperature, catalyst activity, and internal characteristics of the system. Thus, much other information may be needed to use the balance equation for the mass of cyclohexane, and, more generally, for any nonconserved quantity. The applications of thermodynamics sometimes require the use of balance equations for nonconserved quantities.

2.2 CONSERVATION OF MASS

The first balance equation of interest in thermodynamics is the conservation equation for total mass. If θ is taken to be the total mass in the system, designated by the symbol M , we have, from Eq. 2.1-3

$$M(t + \Delta t) - M(t) = \left(\begin{array}{c} \text{Amount of mass that} \\ \text{entered the system} \\ \text{across the system} \\ \text{boundaries between} \\ t \text{ and } t + \Delta t \end{array} \right) - \left(\begin{array}{c} \text{Amount of mass} \\ \text{that left the system} \\ \text{across the system} \\ \text{boundaries between} \\ t \text{ and } t + \Delta t \end{array} \right) \quad (2.2-1a)$$

where we have recognized that the total mass is a conserved quantity and that the only mechanism by which mass enters a system is by a mass flow. Using $(\dot{M})_k$ to represent the mass flow rate into the system at the k th entry point, we have, from Eq. 2.1-4, the equation for the instantaneous rate of change of mass in the system:

**Rate-of-change mass
balance**

$$\frac{dM}{dt} = \sum_{k=1}^K (\dot{M})_k \quad (2.2-1b)$$

Equations 2.2-1 are general and valid regardless of the details of the system and whether the system is stationary or moving.

Since we are interested only in pure fluids here, we can divide Eqs. 2.2-1 by the molecular weight of the fluid and use the fact that N , the number of moles in the system, is equal to M/mw , where mw is the molecular weight, and $(\dot{N})_k$, the molar flow rate into the system at the k th entry port, is $(\dot{M})_k/\text{mw}$, to obtain instead of Eq. 2.2-1a a similar equation in which the term *moles* replaces the word *mass* and, instead of Eq. 2.2-1b,

**Rate-of-change mass
balance: molar basis**

$$\frac{dN}{dt} = \sum_{k=1}^K (\dot{N})_k \quad (2.2-2)$$

We introduce this equation here because it is frequently convenient to do calculations on a molar rather than on a mass basis.

In Sec. 2.1 it was indicated that the equation for the change of an extensive state variable of a system in the time interval Δt could be obtained by integration over the time interval of the equation for the rate of change of that variable. Here we demonstrate how this integration is accomplished. For convenience, t_1 represents the beginning of the time interval and t_2 represents the end of the time interval, so that $\Delta t = t_2 - t_1$. Integrating Eq. 2.2-1b between t_1 and t_2 yields

$$\int_{t_1}^{t_2} \frac{dM}{dt} dt = \sum_{k=1}^K \int_{t_1}^{t_2} (\dot{M})_k dt \quad (2.2-3)$$

The left side of the equation is treated as follows:

$$\int_{t_1}^{t_2} \frac{dM}{dt} dt = \int_{M(t_1)}^{M(t_2)} dM = M(t_2) - M(t_1) = \left(\begin{array}{c} \text{Change in total mass} \\ \text{of system between} \\ t_1 \text{ and } t_2 \end{array} \right)$$

where $M(t)$ is the mass in the system at time t . The term on the right side of the equation may be simplified by observing that

$$\int_{t_1}^{t_2} (\dot{M})_k dt = \left(\begin{array}{c} \text{Mass that entered the} \\ \text{system at the } k\text{th entry} \\ \text{port between } t_1 \text{ and } t_2 \end{array} \right) \equiv (\Delta M)_k$$

Thus

Integral mass balance

$$\boxed{M(t_2) - M(t_1) = \sum_{k=1}^K (\Delta M)_k} \quad (2.2-4)$$

This is the symbolic form of Eq. 2.2-1a.

Equation 2.2-4 may be written in a simpler form when the mass flow rates are steady, that is, independent of time. For this case

$$\int_{t_1}^{t_2} (\dot{M})_k dt = (\dot{M})_k \int_{t_1}^{t_2} dt = (\dot{M})_k \Delta t$$

so that

$$M(t_2) - M(t_1) = \sum_{k=1}^K (\dot{M})_k \Delta t \quad (\text{steady flows}) \quad (2.2-5)$$

The equations of this section that will be used throughout this book are listed in Table 2.2-1.

ILLUSTRATION 2.2-1

Use of the Difference Form of the Mass Balance

A tank of volume 25 m^3 contains $1.5 \times 10^4 \text{ kg}$ of water. Over a two-day period the inlet to the tank delivers $2.0 \times 10^3 \text{ kg}$, $1.3 \times 10^3 \text{ kg}$ leaves the tank through the outlet port, and 50 kg of

Table 2.2-1 The Mass Conservation Equation

	Mass Basis	Molar Basis
<i>Rate-of-change form of the mass balance</i>		
General equation	$\frac{dM}{dt} = \sum_{k=1}^K (\dot{M})_k$	$\frac{dN}{dt} = \sum_{k=1}^K (\dot{N})_k$
Special case:		
Closed system	$\frac{dM}{dt} = 0$ $M = \text{constant}$	$\frac{dN}{dt} = 0$ $N = \text{constant}$
<i>Difference form of the mass balance*</i>		
General equation	$M_2 - M_1 = \sum_{k=1}^K (\Delta M)_k$	$N_2 - N_1 = \sum_{k=1}^K (\Delta N)_k$
Special cases:		
Closed system	$M_2 = M_1$	$N_2 = N_1$
Steady flow	$M_2 - M_1 = \left(\frac{dN_1}{dt}\right)_{\text{rxn}} \sum_{k=1}^K (\dot{N})_k \Delta t + (\dot{M})_k \Delta t$	$N_2 - N_1 = \sum_{k=1}^K (\dot{N})_k \Delta t$

*Here we have used the abbreviated notation $M_i = M(t_i)$ and $N_i = N(t_i)$.

water leaves the tank by evaporation. How much water is in the tank at the end of the two-day period?

SOLUTION

Since we are interested only in the change in the mass of water in the tank over the two-day period, and not in the rate of change, we will use the difference form of the mass balance over the period from the initial time (which we take to be $t = 0$) until two days later ($t = 2$ days). We use Eq. 2.2-4, recognizing that we have three flow terms: $(\Delta M)_1$ (flow into the tank) = $+2.0 \times 10^3$ kg, $(\Delta M)_2$ (flow from the tank) = -1.3×10^3 kg, and $(\Delta M)_3$ (evaporation) = -50 kg. (Remember, in our notation the + sign is for flow into the system—the tank—and the – sign is for flow out of the system.)

Therefore,

$$\begin{aligned} M(t = 2 \text{ days}) - M(t = 0) &= (\Delta M)_1 + (\Delta M)_2 + (\Delta M)_3 \\ M(t = 2 \text{ days}) - 1.5 \times 10^4 \text{ kg} &= 2.0 \times 10^3 - 1.3 \times 10^3 - 50 \\ M(t = 2 \text{ days}) &= 1.5 \times 10^4 + 2.0 \times 10^3 - 1.3 \times 10^3 - 50 \\ &= 1.565 \times 10^4 \text{ kg} \end{aligned}$$

■¹

ILLUSTRATION 2.2-2

Use of the Rate-of-Change Form of the Mass Balance

A storage tank is being used in a chemical plant to dampen fluctuations in the flow to a downstream chemical reactor. The exit flow from this tank will be kept constant at 1.5 kg/s; if the instantaneous flow into the tank exceeds this, the level in the tank will rise, while if the instantaneous flow is less, the level in the tank will drop. If the instantaneous flow into the storage tank is 1.2 kg/s, what is the rate of change of mass in the tank?

¹Throughout this text the symbol ■ will be used to indicate the end of an illustration.

SOLUTION

Since we are interested in the rate of change of mass, here we use the rate-of-change form of the mass balance (Eq. 2.2-1b):

$$\frac{dM}{dt} = \sum_k (\dot{M})_k$$

or, in this case,

$$\frac{dM}{dt} = -1.5 + 1.2 = -0.3 \frac{\text{kg}}{\text{s}}$$

Thus, at the instant the measurements were made, the amount of liquid in the tank was decreasing by 0.3 kg/s or 300 g/s.

COMMENT

Remember, if we are interested in the rate of change of mass, as we are here, we use the rate-of-change form of the mass balance, Eq. 2.2-1b. However, if we are interested only in the change of total mass over a period of time, we use Eq. 2.2-4. ■

ILLUSTRATION 2.2-3

Use of the Rate-of-Change Form of the Mass Balance

Gas is being removed from a high-pressure storage tank through a device that removes 1 percent of the current contents of the tank each minute. If the tank initially contains 1000 mols of gas, how much will remain at the end of 20 minutes?

SOLUTION

Since 1 percent of the gas is removed at any time, the rate at which gas leaves the tank will change with time. For example, initially gas is leaving at the rate of $0.01 \times 1000 \text{ mol/min} = 10 \text{ mol/min}$. However, later when only 900 mol of gas remain in the tank, the exiting flow rate will be $0.01 \times 900 \text{ mol/min} = 9 \text{ mol/min}$. In fact, the exiting flow rate is continuously changing with time. Therefore, we have to use the rate-of-change or differential form of the mass (mole) balance. Starting from the rate-of-change form of the mass balance (Eq. 2.2-1b) around the tank that has only a single flow term, we have

$$\frac{dN}{dt} = \dot{N} \quad \text{where} \quad \dot{N} = -0.01 \times N \quad \text{so that} \quad \frac{d \ln N}{dt} = -0.01$$

The solution to this first-order differential equation is

$$\ln \left(\frac{N(t)}{N(t=0)} \right) = -0.01t \quad \text{or} \quad N(t) = N(t=0)e^{-0.01t}$$

Therefore,

$$N(t=20) = N(t=0)e^{-0.01 \times 20} = 1000e^{-0.2} = 818.7 \text{ mol}$$

Note that if we had merely (and incorrectly) used the initial rate of 10 mol/min we would have obtained the incorrect answer of 800 mol remaining in the tank.

COMMENT

To solve any problem in which the mass (or molar) flow rate changes with time, we need to use the differential or rate-of-change form of the mass balance. For problems in which all of the flow terms are constant, we can use the general difference form of the mass balance (which has been obtained from the rate-of-change form by integration over time), or we can use the rate-of-change form and then integrate over time. However, it is important to emphasize that if one (or more) flow rates are changing with time, the rate-of-change form must be used. ■

ILLUSTRATION 2.2-4

Another Problem Using the Rate-of-Change Form of the Mass Balance

An open cylindrical tank with a base area of 1 m^2 and a height of 10 m contains 5 m^3 of water. As a result of corrosion, the tank develops a leak at its bottom. The rate at which water leaves the tank through the leak is

$$\text{Leak rate} \left(\frac{\text{m}^3}{\text{s}} \right) = 0.5\sqrt{\Delta P}$$

where ΔP is the pressure difference in bar between the fluid at the base of the tank and the atmosphere. (You will learn about the origin of this equation in a course in fluid flow.)

Determine the amount of water in the tank at any time.

SOLUTION

Note that the pressure at the bottom of the tank is equal to the atmosphere pressure plus the hydrostatic pressure due to the water above the leak; that is, $P = 1.013 \text{ bar} + \rho h$, where ρ is the density of water and h is the height of water above the leak. Therefore, $\Delta P = (1.013 + \rho h) - 1.013 = \rho h$ and

$$\Delta P = 10^3 \frac{\text{kg}}{\text{m}^3} \times h \text{ m} \times 9.807 \frac{\text{m}}{\text{s}^2} \times 1 \frac{\text{Pa m s}}{\text{kg}} \times 10^5 \frac{\text{bar}}{\text{Pa}} = 0.09807h \text{ bar}$$

Since the height of fluid in the tank is changing with time, the flow rate of the leak will change with time. Therefore, to solve the problem, we must use the rate-of-change form of the mass balance. The mass of water in the tank at any time is

$$M(t) = \rho A h(t) = 10^3 \frac{\text{kg}}{\text{m}^3} \cdot 1 \text{ m}^2 \cdot h(t) \text{ m} = 10^3 h(t) \text{ kg}$$

The mass balance on the contents of the tank at any time is

$$\frac{dM(t)}{dt} = 10^3 \frac{dh(t)}{dt} = \dot{M} = -0.5\sqrt{0.09807h(t)} = -0.1566\sqrt{h(t)}$$

where the negative sign arises because the flow is out of the tank. Integrating this equation between $t = 0$ and any later time t yields

$$2\sqrt{h(t)} - 2\sqrt{h(0)} = 2\sqrt{h(t)} - 2\sqrt{5} = -0.1566 \times 10^{-3}t$$

or

$$\sqrt{h(t)} = \sqrt{5} - \left(\frac{0.1566}{2} \right) \times 10^{-3}t$$

which can be rearranged to

$$h(t) = \left(\sqrt{5} - 0.7829 \times 10^{-4}t\right)^2 \quad \text{and} \quad M(t) = \left(\sqrt{5} - 0.7829 \times 10^{-4}t\right)^2 \times 10^3 \text{ kg}$$

From this equation, one finds that the tank will be completely drained in 28 580 s or 7.938 hr.

COMMENT

Since the rate of flow of water out of the tank depends on the hydrostatic pressure due to the water column above the leak, and since the height of this column changes with time, again we must use the rate-of-change form of the mass balance to solve the problem.

It is important in any problem to be able to recognize whether the flows are steady, in which case the difference form of the mass balance can be used, or the flows vary with time, as is the case here, in which case the rate-of-change form of the mass balance must be used. ■

2.3 THE MASS BALANCE EQUATIONS FOR A MULTICOMPONENT SYSTEM WITH A CHEMICAL REACTION

When chemical reactions occur, the mass (or mole) balance for each species is somewhat more complicated since the amount of the species can increase or decrease as a result of the reactions. Here we will consider mass balances when there is only a single chemical reaction; in Chapter 8 and later chapters the more general case of several chemical reactions occurring simultaneously is considered. Also, we will write the mass balances using number of moles only, since the stoichiometry of chemical reactions is usually written in terms of the number of moles of each species that undergoes chemical reaction rather than the mass of each species that reacts. Using the notation $(\dot{N}_i)_k$ for the rate at which moles of species i enter (if positive) or leave (if negative) in flow stream k , we have the differential or rate-of-change form of the mass balance on species i as

Rate-of-change mass balance with chemical reaction on a molar basis

$$\frac{dN_i}{dt} = \sum_{k=1}^K (\dot{N}_i)_k + \left(\frac{dN_i}{dt}\right)_{\text{rxn}} \quad (2.3-1)$$

where the last term is new and describes the rate at which species i is produced (if positive) or consumed (if negative) within the system by chemical reaction. The difference form of this equation, obtained by integrating over the time period from t_1 to t_2 , is

Difference form of the mass balance

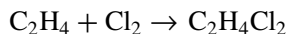
$$N_i(t_2) - N_i(t_1) = \sum_{k=1}^K \int_{t_1}^{t_2} (\dot{N}_i)_k dt + (\Delta N_i)_{\text{rxn}} = \sum_{k=1}^K (\Delta N_i)_k + (\Delta N_i)_{\text{rxn}} \quad (2.3-2)$$

where the summation terms after the equal signs are the changes in the number of moles of the species due to the flow streams, and the second terms are the result of the chemical reaction. Note that only if the flow rate of a stream is steady (i.e., $(\dot{N}_i)_k$ is constant), then

If a flow rate is steady

$$(\Delta N_i)_k = (\dot{N}_i)_k \Delta t$$

Now consider the mass (mole) balances for a reactor in which the following chemical reaction occurs



but in which neither ethylene nor chlorine is completely consumed. The mass balances for these species, in which stream 1 is pure ethylene and stream 2 is pure chlorine, are

$$\begin{aligned} \text{C}_2\text{H}_4: \quad \left(\frac{dN_{\text{C}_2\text{H}_4}}{dt}\right) &= (\dot{N}_{\text{C}_2\text{H}_4})_1 + (\dot{N}_{\text{C}_2\text{H}_4})_3 + \left(\frac{dN_{\text{C}_2\text{H}_4}}{dt}\right)_{\text{rxn}} \\ \text{Cl}_2: \quad \left(\frac{dN_{\text{Cl}_2}}{dt}\right) &= (\dot{N}_{\text{Cl}_2})_2 + (\dot{N}_{\text{Cl}_2})_3 + \left(\frac{dN_{\text{Cl}_2}}{dt}\right)_{\text{rxn}} \\ \text{C}_2\text{H}_4\text{Cl}_2: \quad \left(\frac{dN_{\text{C}_2\text{H}_4\text{Cl}_2}}{dt}\right) &= (\dot{N}_{\text{C}_2\text{H}_4\text{Cl}_2})_3 + \left(\frac{dN_{\text{C}_2\text{H}_4\text{Cl}_2}}{dt}\right)_{\text{rxn}} \end{aligned} \quad (2.3-3)$$

where all the exit streams [i.e., $(\dots)_3$] will be negative in value.

From the stoichiometry of this reaction, all the reaction rate terms are interrelated. In the case here, the rate at which ethylene chloride is created, that is, the number of moles per second, is equal to the rate at which ethylene is consumed, which is also equal to the rate at which chlorine is consumed. That is,

$$\left(\frac{dN_{\text{C}_2\text{H}_4\text{Cl}_2}}{dt}\right)_{\text{rxn}} = -\left(\frac{dN_{\text{C}_2\text{H}_4}}{dt}\right)_{\text{rxn}} = -\left(\frac{dN_{\text{Cl}_2}}{dt}\right)_{\text{rxn}}$$

so we can simplify Eqs. 2.3-3 by replacing the three different reaction rates with a single one.

We can generalize this discussion of the interrelationships between reaction rates by introducing the following convenient notation for the description of chemical reactions. Throughout this book the chemical reaction



where α, β, \dots , are the molar stoichiometric coefficients, will be written as

$$\rho R + \dots - \alpha A - \beta B - \dots = 0$$

or

$$\sum_i v_i I = 0 \quad (2.3-4)$$

Here v_i is the **stoichiometric coefficient** of species I , defined so that v_i is positive for reaction products, negative for reactants, and equal to zero for inert species. In this notation the reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$ is written as $\text{H}_2\text{O} - \text{H}_2 - \frac{1}{2}\text{O}_2 = 0$, so that $v_{\text{H}_2\text{O}} = +1$, $v_{\text{H}_2} = -1$, and $v_{\text{O}_2} = -\frac{1}{2}$.

We will use N_i to represent the number of moles of species i in the system at any time t and $N_{i,0}$ to be the initial number of moles of species i . However, N_i and $N_{i,0}$ are related through the reaction variable X , called the **molar extent of reaction**, and the

stoichiometric coefficient ν_i by the equation

Molar extent of reaction

$$N_i = N_{i,0} + \nu_i X \quad (2.3-5a)$$

or

$$X = \frac{N_i - N_{i,0}}{\nu_i} \quad (2.3-5b)$$

An important characteristic of the reaction variable X defined in this way is that it has the same value for each molecular species involved in a reaction; this is illustrated in the following example. Thus, given the initial mole numbers of all species and X (or the number of moles of one species from which the molar extent of reaction X can be calculated) at time t , one can easily compute all other mole numbers in the system. In this way the complete progress of a chemical reaction (i.e., the change in mole numbers of all the species involved in the reaction) is given by the value of the single variable X .

ILLUSTRATION 2.3-1

Using the Molar Extent of Reaction Notation

The electrolytic decomposition of water to form hydrogen and oxygen occurs as follows: $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$. Initially, only 3.0 mol of water are present in a closed system. At some later time it is found that 1.2 mol of H_2 and 1.8 mol of H_2O are present.

- Show that the molar extents of reaction based on H_2 and H_2O are equal.
- Compute the number of moles of O_2 in the system.

SOLUTION

- The reaction $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$ is rewritten as

$$\text{H}_2 + \frac{1}{2}\text{O}_2 - \text{H}_2\text{O} = 0$$

so that

$$\nu_{\text{H}_2\text{O}} = -1 \quad \nu_{\text{H}_2} = +1 \quad \text{and} \quad \nu_{\text{O}_2} = +\frac{1}{2}$$

From the H_2 data,

$$X = \frac{1.2 - 0.0}{+1} = +1.2 \text{ mol}$$

From the H_2O data,

$$X = \frac{1.8 - 3.0}{-1} = +1.2 \text{ mol}$$

- Starting from $N_i = N_{i,0} + \nu_i X$, we have

$$N_{\text{O}_2} = 0 + (+\frac{1}{2})(1.2) = 0.6 \text{ mol}$$

COMMENT

Note that the molar extent of reaction is *not* a fractional conversion variable, and therefore its value is *not* restricted to lie between 0 and 1. As defined here X , which has units of number

of moles, is the number of moles of a species that has reacted divided by the stoichiometric coefficient for the species. In fact, X may be negative if the reaction proceeds in the reverse direction to that indicated (e.g., if hydrogen and oxygen react to form water). ■

The rate of change of the number of the moles of species i resulting from a chemical reaction is

$$\left(\frac{dN_i}{dt}\right)_{\text{rxn}} = v_i \dot{X} \quad (2.3-6)$$

where the subscript rxn indicates that this is the rate of change of the number of moles of species i due to chemical reaction alone, and \dot{X} is the rate of change of the molar extent of reaction. Using this notation, the balance equation for species i is

Rate-of-change form of the mass balance with chemical reaction: molar basis

$$\frac{dN_i}{dt} = \sum_{k=1}^K (\dot{N}_i)_k + v_i \frac{dX}{dt} \quad (2.3-7)$$

The difference form of this equation, obtained by integrating over the time period from t_1 to t_2 , is

Difference form of mass balance with chemical reaction

$$N_i(t_2) - N_i(t_1) = \sum_{k=1}^K \int_{t_1}^{t_2} (\dot{N}_i)_k dt + (\Delta N_i)_{\text{rxn}} = \sum_{k=1}^K (\Delta N_i)_k + v_i \Delta X \quad (2.3-8)$$

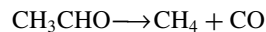
Using this notation for the description of the production of ethylene dichloride considered earlier, we have

$$\begin{aligned} \text{C}_2\text{H}_4: \quad \left(\frac{dN_{\text{C}_2\text{H}_4}}{dt}\right) &= (\dot{N}_{\text{C}_2\text{H}_4})_1 + (\dot{N}_{\text{C}_2\text{H}_4})_3 - \frac{dX}{dt} \\ \text{Cl}_2: \quad \left(\frac{dN_{\text{Cl}_2}}{dt}\right) &= (\dot{N}_{\text{Cl}_2})_2 + (\dot{N}_{\text{Cl}_2})_3 - \frac{dX}{dt} \\ \text{C}_2\text{H}_4\text{Cl}_2: \quad \left(\frac{dN_{\text{C}_2\text{H}_4\text{Cl}_2}}{dt}\right) &= (\dot{N}_{\text{C}_2\text{H}_4\text{Cl}_2})_3 + \frac{dX}{dt} \end{aligned} \quad (2.3-9)$$

ILLUSTRATION 2.3-2

Mass Balance for a Mixture with Chemical Reaction

At high temperatures acetaldehyde (CH_3CHO) dissociates into methane and carbon monoxide by the following reaction



At 520°C the rate at which acetaldehyde dissociates is

$$\frac{dC_{\text{CH}_3\text{CHO}}}{dt} = -0.48 C_{\text{CH}_3\text{CHO}}^2 \frac{\text{m}^3}{\text{kmol s}}$$

2.3 The Mass Balance Equations for a Multicomponent System with a Chemical Reaction 39

where C is concentration in kmol/m^3 . The reaction occurs in a constant-volume, 1-L vessel, and the initial concentration of acetaldehyde is 10 kmol/m^3 .

- If 5 mols of the acetaldehyde reacts, how much methane and carbon monoxide is produced?
- Develop expressions for the amounts of acetaldehyde, methane, and carbon monoxide present at any time, and determine how long it would take for 5 mol of acetaldehyde to have reacted.

SOLUTION

First we must determine the initial amount of acetaldehyde present. Since the initial concentration is

$$C_{\text{CH}_3\text{CHO}} = 10 \frac{\text{mol}}{\text{L}} = 10 \frac{\text{kmol}}{\text{m}^3}$$

it follows that initially

$$N_{\text{CH}_3\text{CHO}} = 10 \frac{\text{mol}}{\text{L}} \times 1 \text{ L} = 10 \text{ mol}$$

Next we write the stoichiometry for the reaction in terms of the molar extent of reaction X as follows:

$$N_{\text{CH}_3\text{CHO}} = 10 - X \quad N_{\text{CH}_4} = X \quad \text{and} \quad N_{\text{CO}} = X \quad (\text{a})$$

- To determine the amounts of each species after a given amount of acetaldehyde has reacted, we can use the difference form of the mass balance for this system with no flows of species into or out of the reactor:

$$N_i(t) - N_i(t=0) = (\Delta N_i)_{\text{rxn}} = \nu_i \Delta X$$

Therefore, for acetaldehyde

$$N_{\text{CH}_3\text{CHO}}(t) - N_{\text{CH}_3\text{CHO}}(t=0) = 5 - 10 \text{ mol} = -5 \text{ mol} = -X \text{ mol}$$

so that $X = 5 \text{ mol}$. Then amounts of the other species are

$$N_{\text{CH}_4}(t) = X = 5 \text{ mol} \quad \text{and} \quad N_{\text{CO}}(t) = X = 5 \text{ mol}$$

- To determine the amount of each species as a function of time is more difficult and must be done using the rate-of-change form of the mass balance since the rate of reaction and therefore the value of X change with time. However, because the amounts of the species are always related by the stoichiometry of Eq. a, we can use the mass balance for one of the species to determine the time variation of X , and then can use the expression for $X(t)$ to obtain the compositions of all species in the reaction as a function of time. Since the rate expression is written for acetaldehyde, we will use this substance to determine the time dependence of X . Since there are no flows into or out of the reactor, Eq. 2.3-7 is

$$\frac{dN_{\text{CH}_3\text{CHO}}}{dt} = \left(\frac{dN_{\text{CH}_3\text{CHO}}}{dt} \right)_{\text{rxn}} = \nu_{\text{CH}_3\text{CHO}} \frac{dX}{dt} = -\frac{dX}{dt}$$

Next the reaction rate expression can be written as

$$\frac{d\left(\frac{N_{\text{CH}_3\text{CHO}}}{V}\right)}{dt} = \frac{1}{V} \frac{dN_{\text{CH}_3\text{CHO}}}{dt} = -0.48 C_{\text{CH}_3\text{CHO}}^2 = -0.48 \frac{N_{\text{CH}_3\text{CHO}}^2}{V^2} \frac{\text{m}^3}{\text{kmol s}}$$

which, after using $N_{\text{CH}_3\text{CHO}} = 10 - X$, becomes

$$\frac{dX}{dt} = \frac{0.48(10 - X)^2 \text{ mol}}{V \text{ L s}} = 0.48(10 - X)^2 \frac{\text{mol}}{\text{s}}$$

Now integrating from $t = 0$, at which $X = 0$, to some other time t gives

$$\frac{1}{10 - X(t)} - \frac{1}{10} = 0.48t \quad \text{or} \quad X(t) = 10 - \frac{1}{0.48t + 0.1} \text{ mol}$$

Therefore,

$$N_{\text{CH}_3\text{CHO}}(t) = \frac{1}{0.48t + 0.1} \quad \text{and} \quad N_{\text{CH}_4}(t) = N_{\text{CO}}(t) = 10 - \frac{1}{0.48t + 0.1}$$

Finally, solving this equation for $X(t) = 5 \text{ mol}$ gives $t = 0.208 \text{ s}$; that is, half of the acetaldehyde dissociates within approximately two-tenths of a second.

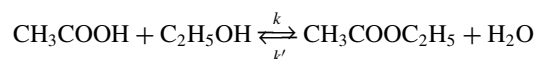
COMMENT

Notice again that solving the rate-of-change form of the mass balance requires more information (here the rate of reaction) and more effort than solving the difference form of the mass balance. However, we also get more information—the amount of each species present as a function of time. In Sec. 2.4, which is optional and more difficult, we consider another, even deeper level of description, where not only is time allowed to vary, but the system is not spatially homogeneous; that is, the composition in the reactor varies from point to point. However, this section is not for the faint-hearted and is best considered after a course in fluid mechanics. ■

ILLUSTRATION 2.3-3

Mass Balance for a Liquid Mixture with a Reversible Reaction

The ester ethyl acetate is produced by the reversible reaction



in the presence of a catalyst such as sulfuric or hydrochloric acid. The rate of ethyl acetate production has been found, from the analysis of chemical kinetics data, to be given by the following equation:

$$\frac{dC_{\text{EA}}}{dt} = kC_{\text{A}}C_{\text{E}} - k'C_{\text{EA}}C_{\text{W}}$$

where the subscripts EA, A, E, and W denote ethyl acetate, acetic acid, ethanol, and water, respectively, and the concentration of each species in units of kmol/m^3 . The values of the reaction rate constants at 100°C and the catalyst concentration of interest are

$$k = 4.76 \times 10^{-4} \text{ m}^3/\text{kmol min}$$

and

$$k' = 1.63 \times 10^{-4} \text{ m}^3/\text{kmol min}$$

Develop expressions for the number of moles of each species as a function of time if the feed to the reactor is 1 m^3 of an aqueous solution that initially contains 250 kg of acetic acid and 500 kg of ethyl alcohol. The density of the solution may be assumed to be constant and equal to 1040 kg/m^3 , and the reactor will be operated at a sufficiently high pressure that negligible amounts

2.3 The Mass Balance Equations for a Multicomponent System with a Chemical Reaction 41

of reactants or products vaporize. Compute the number of moles of each species present 100 minutes after the reaction has started, and at infinite time when the reaction will have stopped and the system is at equilibrium.

SOLUTION

Since the reaction rate expression is a function of the compositions, which are changing as a function of time, the mass balance for each species must be written in the rate-of-change form. Since the species mole numbers and concentrations are functions of the molar extent of reaction, X , we first determine how X varies with time by solving the mass balance for one species. We will use ethyl acetate since the reaction rate is given for that species. Once the amount of ethyl acetate is known, the other species mole numbers are easily computed as shown below.

The initial concentration of each species is

$$C_A = \frac{250 \text{ kg/m}^3}{60 \text{ g/mol}} = 4.17 \text{ kmol/m}^3$$

$$C_E = \frac{500 \text{ kg/m}^3}{46 \text{ g/mol}} = 10.9 \text{ kmol/m}^3$$

$$C_W = \frac{(1040 - 250 - 500) \text{ kg/m}^3}{18 \text{ g/mol}} = 16.1 \text{ kmol/m}^3$$

Since there is 1 m^3 of solution, the initial amount of each species is

$$N_A = 4.17 \text{ kmol}$$

$$N_E = 10.9 \text{ kmol}$$

$$N_W = 16.1 \text{ kmol}$$

$$N_{EA} = 0 \text{ kmol}$$

and by the reaction stoichiometry, the amount of each species present at any time (in kmol) and its concentration (since 1 m^3 of volume is being considered) is

$$N_A = 4.17 - X \quad C_A = 4.17 - X$$

$$N_E = 10.9 - X \quad C_E = 10.9 - X$$

$$N_W = 16.1 + X \quad C_W = 16.1 + X$$

and

$$N_{EA} = X \quad C_{EA} = X$$

Because the concentration of a species is equal to the number of moles N divided by the volume V , the chemical reaction rate equation can be written as

$$\frac{d}{dt} \left(\frac{N_{EA}}{V} \right) = k \frac{N_A}{V} \frac{N_E}{V} - k' \frac{N_{EA}}{V} \frac{N_W}{V}$$

Now using $V = 1 \text{ m}^3$ and the mole numbers, we have

$$\frac{d}{dt} X = k(4.17 - X)(10.9 - X) - k'X(16.1 + X)$$

or

$$\begin{aligned} \frac{dX}{dt} &= 4.76 \times 10^{-4}(4.17 - X)(10.9 - X) - 1.63 \times 10^{-4}(16.1 + X)X \\ &= 2.163 \times 10^{-2}(1 - 0.4528X - 0.01447X^2) \text{ kmol/m}^3 \text{ min} \end{aligned}$$

which can be rearranged to

$$2.163 \times 10^{-2} dt = \frac{dX}{1 - 0.4528X + 0.01447X^2}$$

Integrating this equation between $t = 0$ and time t yields²

$$2.163 \times 10^{-2} \int_0^t dt = 2.163 \times 10^{-2} \times t = \int_0^X \frac{dX}{1 - 0.4528X + 0.01447X^2}$$

or

$$\ln \left\{ \frac{0.02894X - 0.8364}{0.02894X - 0.0692} \right\} - \ln \left(\frac{0.8364}{0.0692} \right) = 0.8297 \times 10^{-2}t \quad (\text{c})$$

and on rearrangement

$$X(t) = 2.3911 \frac{e^{0.008297t} - 1}{e^{0.008297t} - 0.08274}$$

for t in minutes and X in kmol.

Therefore,

$$N_A(t) = C_A(t) = 4.17 - X = 4.17 - 2.3911 \frac{e^{0.008297t} - 1}{e^{0.008297t} - 0.08274}$$

$$N_E(t) = C_E(t) = 10.9 - X = 10.9 - 2.3911 \frac{e^{0.008297t} - 1}{e^{0.008297t} - 0.08274}$$

$$N_W(t) = C_W(t) = 16.1 + X = 16.1 + 2.3911 \frac{e^{0.008297t} - 1}{e^{0.008297t} - 0.08274}$$

and

$$N_{EA}(t) = C_{EA}(t) = X = 2.3911 \frac{e^{0.008297t} - 1}{e^{0.008297t} - 0.08274}$$

At 100 minutes, $X = 1.40$ kmol so that

$$N_A = 4.17 - X = 4.17 - 1.4 = 2.77 \quad N_E = 9.5, \quad N_W = 17.5, \quad N_{EA} = 1.4$$

Also, at infinite time $X = 2.39$ (actually 2.3911) and

$$N_A = 4.17 - X = 4.17 - 2.39 = 1.78, \quad N_E = 8.51, \quad N_W = 18.49, \quad N_{EA} = 2.39$$

■

ILLUSTRATION 2.3-4

Mass Balance Modeling of a Simple Environmental Problem

Water in a lake initially contains a pollutant at a parts-per-million concentration. This pollutant is no longer present in the water entering the lake. The rate of inflow of water to the lake from a creek is constant and equal to the rate of outflow, so the lake volume does not change.

²Note that

$$\int \frac{dX}{a + bX + cX^2} = \frac{1}{\sqrt{2}} \ln \left[\frac{2cX + b - \sqrt{-q}}{2cX + b + \sqrt{-q}} \right]$$

where $q = 4ac - b^2$.

- a. Assuming the water in the lake is well mixed, so its composition is uniform and the pollutant concentration in the exit stream is the same as in the lake, estimate the number of lake volumes of water that must be added to the lake and then leave in order for the concentration of the pollutant in the water to decrease to one-half of its initial concentration.
- b. How many lake volumes would it take for the concentration of the pollutant in the lake to decrease to one-tenth of its initial concentration?
- c. If the volume of water in the lake is equal to the inflow for a one-year period, assuming the inflow of water is uniform in time, how long would it take for the concentration of the pollutant in the lake to decrease to one-half and one-tenth of its initial concentration?

SOLUTION

- a. In writing the overall mass balance for the lake, which we take to be the system, we will use that the flow rates into and out of the lake are constant and equal, and that the concentration of the pollutant is so low that its change has a negligible effect on the total mass of the water in the lake. With these simplifications the mass balance is

$$\frac{dM}{dt} = 0 = (\dot{M})_1 + (\dot{M})_2, \quad \text{so that} \quad (\dot{M})_1 = -(\dot{M})_2 = \dot{M}$$

That is, the rate of mass flow out of the lake is equal in magnitude and opposite in sign to the rate of mass flow into the lake. The mass balance on the pollutant is

$$\frac{dM_p}{dt} = \frac{d(C_p M)}{dt} = M \frac{d(C_p)}{dt} = (\dot{M}_p)_2 = (\dot{M})_2 C_p = -(\dot{M})_1 C_p$$

where we have used the principle that the total amount of pollutant is equal to the product of its concentration per unit mass C_p and the total mass M of water in the lake. Therefore,

$$\frac{dC_p}{C_p} = -\frac{\dot{M}}{M} dt \quad \text{which has the solution} \quad C_p(t) = C_p(t=0) e^{-(\dot{M}/M)t}$$

$$\frac{C_p(t)}{C_p(t=0)} = 0.5 = \exp\left(-\frac{\dot{M}t}{M}\right) \quad \text{or} \quad \dot{M}t = 0.693M$$

Now $\dot{M}t = \Delta M$, which is the amount of water that entered the lake over the time interval from 0 to t . Therefore, when the amount of fresh water that has entered the lake $Mt = \Delta M$ equals 69.3 percent of the initial (polluted) water in the lake, the concentration of the pollutant in the lake will have decreased to half its initial value.

- b. We proceed as in part (a), except that we now have

$$\frac{C_p(t)}{C_p(t=0)} = 0.1 = \exp\left(-\frac{\dot{M}t}{M}\right) \quad \text{or} \quad \dot{M}t = 2.303M$$

so that when an amount of water enters that equals 2.303 times the initial volume of water in the lake, the concentration of pollutant will have decreased to one-tenth its initial value.

- c. It will take 0.693 years (253 days) and 2.303 years (840 days) for the concentration of the pollutant to decrease to 50 percent and 10 percent of its initial concentration, respectively. ■

2.4 THE MICROSCOPIC MASS BALANCE EQUATIONS IN THERMODYNAMICS AND FLUID MECHANICS³

The balance equations we have developed so far are those commonly used in engineering thermodynamics. An important characteristic of these equations is that they are

³This section is optional—only for graduate and advanced undergraduate students.

balances for large, black-box systems⁴ and therefore yield information only about the total mass or the rate of change of mass in the system. Frequently it is useful to have information not about the total mass, but about the mass density at each point in the system. To get a balance equation for mass density at any point in the system, we must start with a system of microscopic (or differential) size. There is some advantage to developing the microscopic balance equations here. First, it exposes the essential similarity between thermodynamics and fluid mechanics, and, second, these equations will be of use in the following chapters. However, since the formulation of these equations requires a greater degree of mathematical complexity than has been used heretofore, and since these equations are of only peripheral interest in our development of thermodynamics, you may wish to proceed directly to Chapter 3.

To obtain the microscopic equations of fluid mechanics and thermodynamics, we apply the general balance equation, Eq. 2.1-4, to the small stationary volume element of Fig 2.4-1. This volume element, of dimensions Δx , Δy , and Δz , is part of a much larger fluid system, so the boundaries are not physical boundaries and mass can flow across each of its faces. Finally, since this volume element is of infinitesimal size (our interest is in the case in which Δx , Δy , and Δz simultaneously go to zero), the properties within it can be assumed to be uniform. Thus the mass contained within the volume element is $\rho \Delta x \Delta y \Delta z$, where ρ is the mass density within the infinitesimal volume element. With this introduction we can now make the following identifications in Eq. 2.1-4:

$$\left(\begin{array}{l} \text{Rate of change of mass in} \\ \text{the volume element} \end{array} \right) = \Delta x \Delta y \Delta z \frac{\partial \rho}{\partial t} \quad (2.4-1a)$$

$$\left(\begin{array}{l} \text{Net rate at which} \\ \text{mass enters the} \\ \text{volume element} \end{array} \right) = \rho v_x \Delta y \Delta z|_x - \rho v_x \Delta y \Delta z|_{x+\Delta x} \\ + \rho v_y \Delta x \Delta z|_y - \rho v_y \Delta x \Delta z|_{y+\Delta y} \\ + \rho v_z \Delta x \Delta y|_z - \rho v_z \Delta x \Delta y|_{z+\Delta z} \quad (2.4-1b)$$

where x , y , and z are the rectangular coordinate directions and v_i is the fluid velocity in the i th coordinate direction. The interpretation of the terms in Eq. 2.4-1b is as

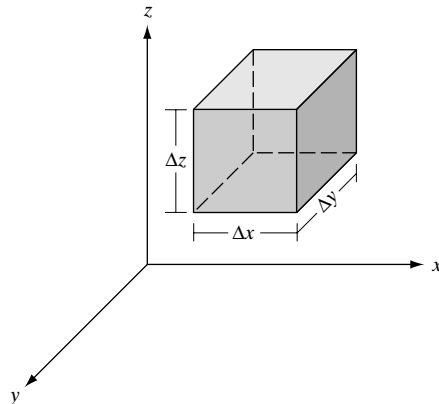


Figure 2.4-1 Volume element for a microscopic balance equation.

⁴Here the term *black box* is being used to indicate that we did not consider the exact details of what was inside the box or system for which we were writing the balance equation. That is, we were concerned only with the total mass in the system, not the details of how it was distributed within the system or the mass density at every point.

follows. The mass flow into the volume element across the face of the volume element perpendicular to the x -axis at x is

$$\rho v_x \Delta y \Delta z|_x$$

where $\Delta y \Delta z$ is the area of the face and ρv_x is the flow rate in the x direction per unit area. Similarly, the term

$$-\rho v_x \Delta y \Delta z|_{x+\Delta x}$$

is the mass flow out of the volume element at the face perpendicular to the x -axis at $x + \Delta x$ and therefore has a negative sign. The remaining terms in Eq. 2.4-1b represent the mass flows into and out of the other faces of the volume element.

Using Eqs. 2.4-1 in Eq. 2.1-4 yields

$$\Delta x \Delta y \Delta z \frac{\partial \rho}{\partial t} = \rho v_x \Delta y \Delta z|_x - \rho v_x \Delta y \Delta z|_{x+\Delta x} + \rho v_y \Delta x \Delta z|_y - \rho v_y \Delta x \Delta z|_{y+\Delta y} + \rho v_z \Delta x \Delta y|_z - \rho v_z \Delta x \Delta y|_{z+\Delta z}$$

Now, dividing by $\Delta x \Delta y \Delta z$ and taking the limit as Δx , Δy , and Δz go to zero gives

$$\frac{\partial \rho}{\partial t} = \lim_{\Delta x \rightarrow 0} \frac{\rho v_x|_x - \rho v_x|_{x+\Delta x}}{\Delta x} + \lim_{\Delta y \rightarrow 0} \frac{\rho v_y|_y - \rho v_y|_{y+\Delta y}}{\Delta y} + \lim_{\Delta z \rightarrow 0} \frac{\rho v_z|_z - \rho v_z|_{z+\Delta z}}{\Delta z} \quad (2.4-2)$$

Finally, using the definition of the partial derivative, that is,

$$\frac{\partial F(x, t)}{\partial x} = \lim_{\Delta x \rightarrow 0} \frac{F(x + \Delta x, t) - F(x, t)}{\Delta x} \quad (2.4-3)$$

we obtain

$$\frac{\partial \rho}{\partial t} = -\frac{\partial(\rho v_x)}{\partial x} - \frac{\partial(\rho v_y)}{\partial y} - \frac{\partial(\rho v_z)}{\partial z}$$

or, in vector notation,

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) \quad (2.4-4)$$

Continuity equation

Equation 2.4-4 is the mass conservation equation for a stationary differential volume element; in fluid mechanics it is called the **continuity equation**. This equation can be rearranged to yield

$$\frac{\partial \rho}{\partial t} = -\rho \nabla \cdot \mathbf{v} - \mathbf{v} \cdot \nabla \rho$$

or

$$\frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho \equiv \frac{D\rho}{Dt} = -\rho \nabla \cdot \mathbf{v} \quad (2.4-5)$$

Here we have introduced the notation $D/Dt = \partial/\partial t + \mathbf{v} \cdot \nabla$, where D/Dt is the convected derivative; it is the derivative with respect to time in a volume element moving with fluid velocity \mathbf{v} . To see this, consider the moving volume element shown in Fig. 2.4-2. The position vector of the center of this volume element is \mathbf{r} at time t , and

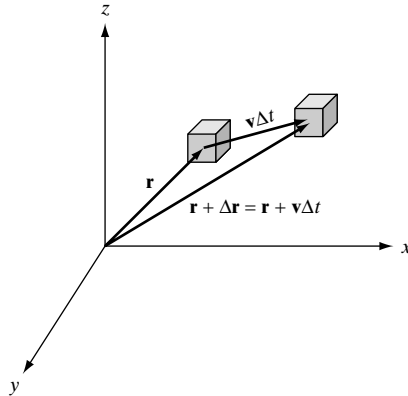


Figure 2.4-2 Positions of a moving volume element at t and at $t + \Delta t$.

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$\mathbf{r} + \Delta \mathbf{r}$ at time $t + \Delta t$, where $\Delta \mathbf{r} = \mathbf{v} \Delta t$. The time derivative of any function F taken in this moving differential volume, DF/Dt , is defined, in analogy with Eq. 2.4-3, as

$$\begin{aligned} \frac{DF}{Dt} &= \lim_{\Delta t \rightarrow 0} \left\{ \frac{F(\mathbf{r} + \Delta \mathbf{r}, t + \Delta t) - F(\mathbf{r}, t)}{\Delta t} \right\} \\ &= \lim_{\Delta t \rightarrow 0} \left\{ \frac{F(\mathbf{r} + \Delta \mathbf{r}, t + \Delta t) - F(\mathbf{r} + \Delta \mathbf{r}, t)}{\Delta t} + \frac{F(\mathbf{r} + \Delta \mathbf{r}, t) - F(\mathbf{r}, t)}{\Delta t} \right\} \\ &= \lim_{\Delta t \rightarrow 0} \left\{ \frac{F(\mathbf{r} + \Delta \mathbf{r}, t + \Delta t) - F(\mathbf{r} + \Delta \mathbf{r}, t)}{\Delta t} + \frac{\Delta \mathbf{r}}{\Delta t} \cdot \frac{F(\mathbf{r} + \Delta \mathbf{r}, t) - F(\mathbf{r}, t)}{\Delta \mathbf{r}} \right\} \end{aligned}$$

or

$$\frac{DF}{Dt} = \frac{\partial F}{\partial t} + \mathbf{v} \cdot \nabla F \quad (2.4-6)$$

where we have used the fact that $\lim_{\Delta t \rightarrow 0} \Delta \mathbf{r} / \Delta t = \mathbf{v}$, and $\Delta \mathbf{r} \rightarrow 0$ as $\Delta t \rightarrow 0$.

Equation 2.4-4 can be integrated over a finite volume element to obtain Eq. 2.2-1b. Since this requires the use of certain mathematical theorems that may be unfamiliar to you, this integration will not be pursued here except to point out that for a stationary system ($v = 0$) we can integrate the left side of Eq. 2.4-4 over the volume V to obtain

$$\int \frac{\partial \rho}{\partial t} dV = \frac{d}{dt} \int \rho dV = \frac{dM}{dt}$$

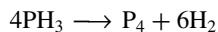
which is equal to the left side of Eq. 2.2-1b. A similar correspondence exists between the right sides of Eqs. 2.2-1b and 2.4-4, but this is more difficult to prove. This analysis does establish a very important general relationship; the black-box thermodynamic equations developed in Sec. 2.2 can be obtained by an integration over volume of the more detailed microscopic equations.

At this point, it is useful to reflect on the three levels of description used in this book. The microscopic equations, of which the mass conservation equation developed here is only the first, require detailed information about the internal structure and internal flows in any macroscopic system in order to be of use. Next, by integration over a finite volume element these microscopic equations result in an equation for the time rate of change for the black-box description of the system. For these equations to be of use, only information about flow rates into and out of the system as a function of time is needed. Finally, by integration over time of the time rate-of-change equations,

we obtain equations for the change over an interval of time of various properties of the black-box system. For these last equations to be useful, one merely needs information about the total flows into and out of the system over the time interval, and not a history of how these flow rates varied with time.

PROBLEMS

- 2.1** As a result of a chemical spill, benzene is evaporating at the rate of 1 gram per minute into a room that is 6 m × 6 m × 3 m in size and has a ventilation rate of 10 m³/min.
- Compute the steady-state concentration of benzene in the room.
 - Assuming the air in the room is initially free of benzene, compute the time necessary for benzene to reach 95 percent of the steady-state concentration.
- 2.2** The insecticide DDT has a half-life in the human body of approximately 7 years. That is, in 7 years its concentration decreases to half its initial concentration. Although DDT is no longer in general use in the United States, it was estimated that 25 years ago the average farm worker had a body DDT concentration of 22 ppm (parts per million by weight). Estimate what the farm worker's present concentration would be.
- 2.3** At high temperatures phosphine (PH₃) dissociates into phosphorus and hydrogen by the following reaction:

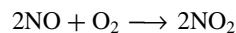


At 800°C the rate at which phosphine dissociates is

$$\frac{dC_{\text{PH}_3}}{dt} = -3.715 \times 10^{-6} C_{\text{PH}_3}$$

for t in seconds. The reaction occurs in a constant-volume, 2-L vessel, and the initial concentration of phosphine is 5 kmol/m³

- If 3 mol of the phosphine reacts, how much phosphorus and hydrogen is produced?
 - Develop expressions for the number of moles of phosphine, phosphorus, and hydrogen present at any time, and determine how long it would take for 3 mol of phosphine to have reacted.
- 2.4** The following reaction occurs in air:



At 20°C the rate of this reaction is

$$\frac{dC_{\text{NO}}}{dt} = -1.4 \times 10^{-4} C_{\text{NO}}^2 C_{\text{O}_2}$$

for t in seconds and concentrations in kmol/m³. The reaction occurs in a constant-volume, 2-L vessel, and the initial concentration of NO is 1 kmol/m³ and that of O₂ is 3 kmol/m³

- If 0.5 mol of NO reacts, how much NO₂ is produced?
- Determine how long it would take for 0.5 mol of NO to have reacted.