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## Mass and Energy Balances

One of the fundamental laws of physics states that mass can neither be produced nor destroyed---that is, mass is conserved. Equally fundamental is the law of conservation of energy. Although energy can change in *form*, it can not be created or destroyed. These two laws of physics provide the basis for two tools which are used routinely in environmental engineering and science---the mass balance and the energy balance. This portion of the course deals with these tools. Mass balances are developed and applied in some detail in the following section, after which the concept of the energy balance is presented and applied.

### Mass Balance

This principle of conservation of mass is extremely useful. It means that if the amount of a pollutant somewhere (say, in a lake) increases, then that increase cannot be the result of some "magical" formation out of nowhere. The pollutant must have been either carried into the lake from elsewhere or produced via chemical reaction from other compounds that were already in the lake. And, if chemical reactions produced the mass increase in our pollutant, they must also have caused a corresponding decrease in the mass of some other compounds. Thus, conservation of mass allows us to compile a budget of the mass of our pollutant in the lake. This budget keeps track of the amounts of pollutant entering the lake, leaving the lake, and the amount formed or destroyed by chemical reaction. This budget can be balanced for a given time period, similar to the way you might balance your checkbook:

$$\begin{aligned} \left( \begin{array}{c} \text{mass at} \\ \text{time } t + \Delta t \end{array} \right) &= \left( \begin{array}{c} \text{mass at} \\ \text{time } t \end{array} \right) + \left( \begin{array}{c} \text{mass that} \\ \text{entered} \\ \text{from } t \text{ to} \\ t + \Delta t \end{array} \right) - \left( \begin{array}{c} \text{mass that} \\ \text{exited} \\ \text{from } t \text{ to} \\ t + \Delta t \end{array} \right) \\ &+ \left( \begin{array}{c} \text{net mass of pollutant produced from} \\ \text{other compounds by chemical} \\ \text{reactions between } t \text{ and } t + \Delta t \end{array} \right) \quad (12) \end{aligned}$$

Note that each term of this equation has units of mass. This form of balance is most useful when there is a clear beginning and end to the balance period, so that  $\Delta t$  is meaningful. For example, in a checkbook balance  $\Delta t$  is usually one month. In environmental problems, however, it is usually more convenient to work with values of mass *flux*---the *rate* at which mass enters or leaves a system. To develop an equation in terms of mass flux, the mass balance equation is divided by  $\Delta t$  to produce an equation with units of mass per unit time. Dividing equation 12 by  $\Delta t$  and moving the first term on the right (mass at time  $t$ ) to the left hand side yields the following equation.

$$\begin{aligned} \frac{\left( \begin{array}{c} \text{mass at} \\ \text{time } t + \Delta t \end{array} \right) - \left( \begin{array}{c} \text{mass at} \\ \text{time } t \end{array} \right)}{\Delta t} &= \frac{\left( \begin{array}{c} \text{mass} \\ \text{entering} \\ \text{from } t \text{ to} \\ t + \Delta t \end{array} \right)}{\Delta t} - \frac{\left( \begin{array}{c} \text{mass} \\ \text{exiting} \\ \text{from } t \text{ to} \\ t + \Delta t \end{array} \right)}{\Delta t} \\ &+ \frac{\left( \begin{array}{c} \text{net} \\ \text{chemical} \\ \text{production} \\ \text{between } t \\ \text{and } t + \Delta t \end{array} \right)}{\Delta t} \quad (13) \end{aligned}$$

Note that each term in this equation has units of mass/time. The left hand side of equation 13 is equal to  $\Delta m / \Delta t$ . In the limit as  $\Delta t \rightarrow 0$ , this becomes  $dm/dt$ , the rate of change of pollutant mass in the lake. We will refer to  $dm/dt$  as the *accumulation rate* of the pollutant. As  $\Delta t \rightarrow 0$ , the first two terms on the right side of equation 13 become the mass flux into the lake and the mass flux out of the lake. The last term of equation 13 is the *rate* of chemical production or loss. To stress the fact that each

term in the new equation refers to a *flux* or *rate*, we will use the symbol  $\dot{m}$  to refer to a mass flux with units of mass/time. The equation for mass balances is then

$$\left( \begin{array}{c} \text{mass accu-} \\ \text{mulation} \\ \text{rate} \end{array} \right) = \left( \begin{array}{c} \text{mass flux} \\ \text{in} \end{array} \right) - \left( \begin{array}{c} \text{mass flux} \\ \text{out} \end{array} \right) + \left( \begin{array}{c} \text{net rate of} \\ \text{chemical} \\ \text{production} \end{array} \right) \text{ or,}$$

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{reaction} \quad (14)$$

Equation 14 is the governing equation for the mass balances we will work with in this course.

In the remainder of this section, we will examine the importance of carefully defining the region over which the mass balance is applied and discuss the terms of equation 14. We will then present examples of the main types of situations for which mass balances are useful.

## The Control Volume

A mass balance is only meaningful in terms of a specific region of space, which has boundaries across which the terms  $\dot{m}_{in}$  and  $\dot{m}_{out}$  are determined. This region is called the **control volume**. In our derivation of the mass balance equation, we have referred to the mass of pollutant in a lake and the fluxes of pollutant into and out of the lake---that is, we have used a lake as our control volume. Theoretically, any volume of any shape and location can be used. Realistically, however, certain control volumes are more useful than others. *The most important attribute of a control volume is that it have boundaries over which you can calculate  $\dot{m}_{in}$  and  $\dot{m}_{out}$ .*

## Terms of the Mass Balance Equation for a CSTR

A well-mixed tank is an analogue for many control volumes used in environmental engineering. For example, in our lake example it might be reasonable to assume that pollutants dumped into the lake are rapidly mixed throughout the entire lake. In environmental engineering and chemical engineering, the term *Continuously Stirred Tank Reactor*, or *CSTR* is used for such a system. An example of a CSTR is shown in Figure 1. We will use a mass balance for a control volume which encloses the CSTR in Figure 1 as an example to describe the meaning of each term in equation 14.

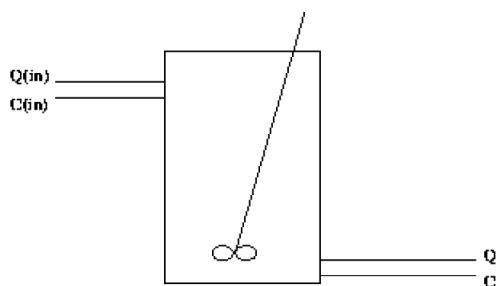


Figure 1: Schematic diagram of a CSTR

### Mass Accumulation Rate, .

The mass accumulation rate is, by definition,  $\frac{dm}{dt}$ , or  $\frac{\Delta m}{\Delta t}$ . The total mass in the CSTR cannot usually be measured. For example, if the CSTR represented an entire lake, measuring the total pollutant mass would require analyzing all of the water in the lake. However, our assumption that the CSTR is well-mixed means that this is not necessary. If the tank is well-mixed, then the concentration of our pollutant is the same everywhere in the tank, and we need only to measure the concentration in a sampling from the tank. Using concentration units of (mass)/(volume), the total pollutant mass in the tank is equal to  $C \cdot V$ , where  $V$  is the volume of the CSTR. Thus, the accumulation rate is equal to

$$\frac{\Delta m}{\Delta t} = \frac{\Delta(CV)}{\Delta t} = \frac{V \Delta C}{\Delta t} = V \frac{dC}{dt}. \quad (15)$$

Here, we have made the assumption that the volume of the CSTR is constant. This is usually a reasonable assumption for liquids, although it may not always be valid for gases. However,  $\frac{dm}{dt}$  will always be equal to  $\frac{d(VC)}{dt}$ .

Mass balance problems can be divided into those that are in steady state and those that are non-steady state. A steady-state situation is one in which things do not change with time---the incoming concentration and flow rate are constant, the outgoing flow rate is constant, and therefore the concentration in the control volume is constant. For steady-state systems, then,  $\frac{dm}{dt} = 0$ . Non-steady-state conditions result whenever flows start or stop, or when the concentration in an incoming stream changes. For non-steady-state situations,  $\frac{dm}{dt}$  is nonzero.

### Mass Flux in, .

The example in Figure 1 includes one pipe entering the CSTR. We will again use concentration measured in mass/volume units to calculate the flux entering the CSTR through the pipe.

Often, we know the volumetric flow rate,  $Q$ , of each input stream. For the example of Figure 1 the pipe has a flow rate of  $Q_{in}$ , with corresponding pollutant concentration of  $C_{in}$ . The mass flux is then given by

$$\dot{m}_{in} = Q_{in} \cdot C_{in} \quad (16)$$

If it is not immediately clear how one knows that  $Q \times C$  gives a mass flux, consider the units of each term:

$$\dot{m} = Q \cdot C$$

$$\left[ \frac{\text{mass}}{\text{time}} \right] = \left[ \frac{\text{volume}}{\text{time}} \right] \cdot \left[ \frac{\text{mass}}{\text{volume}} \right]$$

If the volumetric flow rate is not known, it may be calculated from other parameters. For example, if the fluid velocity  $v$  and the cross-sectional area  $A$  of the pipe are known, then  $Q = v \cdot A$ .

Another way to describe the flux is in terms of a **flux density  $J$**  times the area through which the flux occurs.  $J$  has units of  $\text{mass}/(\text{area} \cdot \text{time})$ , and we will study it in more detail when we cover diffusion in section 3. This type of flux notation is most useful at interfaces where there is no fluid flow, such as the interface between the air and water and the surface of a lake.

### Mass Flux out, .

The flux out of the CSTR is similarly equal to the product of volumetric flow rate in the exit pipe times the concentration in the exit pipe. Since the CSTR is well-mixed, the concentration in the liquid leaving the CSTR is equal to the concentration inside the CSTR. It is conventional to refer to the concentration within the CSTR simply as  $C$ . Thus,

$$\dot{m}_{out} = C_{CSTR} \cdot Q_{out} = C \cdot Q_{out}.$$

### Net Rate of Chemical Reaction, .

The term  $\dot{m}_{reaction}$  refers to the *net* rate of production of our pollutant from chemical reactions, in units of mass/time. Thus, if other compounds react to form our pollutant,  $\dot{m}_{reaction}$  will be greater than zero; if our pollutant reacts to form some other compounds, resulting in a loss of the pollutant,  $\dot{m}_{reaction}$  will be negative. Production or loss of a compound by a chemical reaction is usually described in terms of concentration, not mass. So it is necessary to multiply the chemical rate of change of *concentration* by the volume of the CSTR to obtain units of mass/time:

$$\dot{m}_{reaction} = \left. \frac{dM}{dt} \right|_{reaction} = V \cdot \left. \frac{dC}{dt} \right|_{reaction} \quad (17)$$

There are a number of possibilities for the form of  $\left. \frac{dC}{dt} \right|_{reaction}$ , and the resulting  $\dot{m}_{reaction}$ . The most common include:

1. **Conservative pollutant.** Pollutants with no chemical formation or loss are called *conservative* because their mass is conserved without any corrections for chemistry. For such compounds,  $\left. \frac{dC}{dt} \right|_{reaction} = 0$ , implying that  $\dot{m}_{reaction} = 0$  also.
2.  **$0^{th}$ -order decay.** The rate of loss of the pollutant is constant. For a pollutant with  $0^{th}$ -order decay,  $\left. \frac{dC}{dt} \right|_{reaction} = -k$  and  $\dot{m}_{reaction} = -V k$ .

3. **1<sup>st</sup>-order decay.** The rate of loss of the pollutant is directly proportional to its concentration:  $dC/dt|_{\text{reaction}} = -kC$ .  
For such a pollutant,  $\dot{m}_{\text{reaction}} = -VkC$ .
4. Production at a rate dependent on the concentrations of other compounds in the CSTR. In this situation, our pollutant is produced by chemical reactions involving other compounds in the CSTR, and  $dC/dt|_{\text{reaction}}$  is greater than zero.  
Examples of this type of situation will be given in Part III of the course.

## Reactor Analysis---the CSTR

*Reactor Analysis* refers to the use of mass balances to analyze pollutant concentrations in a control volume which is a chemical reactor. Do not let the term "reactor" fool you, however. The reactor can be any control volume we want it to be. So the term *reactor analysis* is used to describe the application of the mass balance process to environmental situations also. Reactor analyses can be divided into two types: CSTRs (Continuously Stirred Tank Reactors) and PFRs, or *Plug Flow Reactors*. We have defined CSTRs already---they are simply well-mixed tanks which are used to model well-mixed environmental reservoirs. Plug Flow Reactors are essentially pipes, and they are used to model things like rivers, in which fluid is not mixed in the upstream-downstream direction.

In this section, we will present examples of the types of situations CSTRs are used to model. Plug Flow Reactors are described and used in examples in the following section. Example [2.1](#) demonstrates the use of CSTR analysis to determine the concentration of a substance resulting from the mixing of two or more influent flows. This type of calculation will be used again in the third part of this course to determine the initial BOD loading in a river downstream of a sewage outflow. Examples [2.2](#) through [2.4](#) refer to the tank in Figure [1](#) and demonstrate steady-state and non-steady-state situations with and without first-order chemical decay. Calculations completely analogous to those in examples [2.2](#), [2.3](#), and [2.4](#) can be used to determine the concentration of sewage pollutants exiting a treatment reactor, the rate of increase of pollutant concentrations within a lake resulting from a new pollutant source, and the period required for pollutant levels to decay from a lake or reactor once the source is removed.

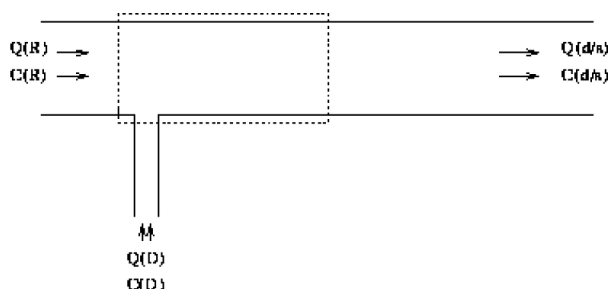


Figure 2: Phosphorus mixing problem.

**Example 2.1. Mixing Problem** A sewage pipe from a wastewater treatment plant discharges  $1.0 \text{ m}^3/\text{s}$  of effluent containing  $5.0 \text{ mg/l}$  of phosphorus compounds (reported as  $\text{mg P/l}$ ) into a river with an upstream flow rate of  $25 \text{ m}^3/\text{s}$  and a phosphorus concentration of  $0.010 \text{ mg P/l}$  (see Figure [2](#)). What is the resulting concentration of phosphorus in the river downstream of the sewage outflow, in units of  $\text{mg/l}$ ?

**Solution:** To solve this problem, we will apply two mass balances to determine first the downstream volumetric flow rate ( $Q_{d/s}$ ) and, second, the downstream phosphorus concentration ( $C_{d/s}$ ). But first, we must select a control volume. To ensure that the input and output fluxes cross the control volume boundaries, the control volume must cross the river upstream and downstream of the sewage outlet and must cross the sewage pipe. The selected control volume is shown in Figure [2](#) as a dotted line. We must assume that the control volume extends down the river far enough that the sewage and the river water become well-mixed before leaving the control volume. As long as that assumption is met, it makes absolutely no difference to our analysis how far downstream the control volume extends.

Before beginning our analysis, we should determine whether this is a steady-state or non-steady-state problem, and whether the chemical reaction term will be nonzero. Since the problem statement does not refer to time at all, and it seems reasonable to assume that both the river and sewage have been flowing for some time and will continue to flow, this is a steady-state problem. Sewage does participate in chemical and biological reactions. However, we are interested here in *mixing*---that is, in what concentration results right after the two flows mix. So we will assume that the mixing occurs instantly, without sufficient time for any reactions to occur.

(a)

What is  $Q_{d/s}$ ? We will conduct a mass balance on the total river-water mass. In this case, the "concentration" of river water in mass/volume units is simply the density of the water,  $\rho$ .

$$\begin{aligned}\frac{dm}{dt} &= \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{rxn} \\ &= \rho Q_{in} - \rho Q_{out} + 0,\end{aligned}$$

where the term  $\dot{m}_{rxn}$  has been set to zero because we are ignoring chemical reaction. Since this is a steady-state problem,  $dm/dt = 0$ . Therefore, as long as the density  $\rho$  is constant,  $Q_{in} = Q_{out}$ , or  $(Q_R + Q_D) = 26 \text{ m}^3/\text{s} = Q_{d/s}$ .

(b)

What is  $C_{d/s}$ ? Again, we have steady-state with no chemical formation or decay:

$$\begin{aligned}\frac{dm}{dt} &= \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{rxn} \\ 0 &= (C_R Q_R + C_{sewage} Q_{sewage}) - C_{d/s} Q_{d/s} + 0, \text{ or} \\ C_{d/s} &= \frac{C_R Q_R + C_{sewage} Q_{sewage}}{Q_{d/s}}\end{aligned}$$

Plugging in, we find that

$$\begin{aligned}C_{d/s} &= \frac{(0.010 \text{ mg/l})(25 \text{ m}^3/\text{s}) + (5.0 \text{ mg/l})(1.0 \text{ m}^3/\text{s})}{26 \text{ m}^3/\text{s}} \\ &= 0.20 \text{ mg/l}\end{aligned}$$

**Example 2.2. Steady-state CSTR with 1<sup>st</sup>-order Decay** The CSTR shown in Figure 1 is used to treat an industrial waste, using a reaction which destroys the waste according to first-order kinetics:  $dC/dt|_{rxn} = -kC$ , where  $k = 0.216 \text{ day}^{-1}$ . The reactor volume is  $500 \text{ m}^3$ , the volumetric flow rate of the single inlet and exit is  $50 \text{ m}^3/\text{day}$ , and the inlet waste concentration is  $100 \text{ mg/l}$ . What is the outlet concentration?

**Solution:** An obvious control volume is the tank itself.  A single, constant outlet concentration is asked for and all problem conditions are constant. Therefore, this is a steady-state problem. The mass balance equation is

$$\begin{aligned}\frac{dm}{dt} &= \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{rxn} \\ 0 &= QC_{in} - QC - kCV.\end{aligned}$$

Solving for  $C$ , we find that

$$\begin{aligned}C &= C_{in} \cdot \frac{Q}{Q + kV}, \text{ or} \\ C &= C_{in} \cdot \frac{1}{1 + kV/Q}.\end{aligned}$$

The numerical solution is

$$\begin{aligned}C &= 100 \text{ mg/l} \cdot \frac{50 \text{ m}^3/\text{day}}{50 \text{ m}^3/\text{day} + (0.216 \text{ day}^{-1})(500 \text{ m}^3)} \\ &= 32 \text{ mg/l}\end{aligned}$$

**Example 2.3. Non-steady-state CSTR, Conservative Substance** The CSTR shown in Figure 1 is used with a conservative substance. The reactor is filled with clean water before it is started. After starting, waste containing a 100 mg/l of a pollutant is added at a flow rate of 50 m<sup>3</sup>/day. The volume of the reactor is 500 m<sup>3</sup>. What is the concentration exiting the reactor as a function of time after it is started?

*Solution:* The substance is conservative---therefore, there the chemical reaction term in the mass balance equation is equal to zero. The mass balance equation is

$$\begin{aligned}\frac{dm}{dt} &= \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{rxn} \\ V \frac{dC}{dt} &= QC_{in} - QC + 0, \text{ or} \\ \frac{dC}{dt} &= -(Q/V)(C - C_{in})\end{aligned}$$

Because of the extra term on the right ( $C_{in}$ ), this equation cannot be immediately solved in the way that example 2.4 was solved. However, if we make a change of variables, we can make the form of this equation similar to that of example 2.4. Let  $y = (C - C_{in})$ . Since  $C_{in}$  is constant,  $dy/dt = dC/dt - d(C_{in}/dt) = dC/dt$ . Therefore, the last equation above is equivalent to

$$\frac{dy}{dt} = -(Q/V)y$$

Rearranging and integrating,

$$\int_{y(0)}^{y(t)} \frac{dy}{y} = \int_0^t -(Q/V) dt$$

which yields

$$\begin{aligned}\ln \left( \frac{y(t)}{y(0)} \right) &= -(Q/V)t, \text{ or} \\ \frac{y(t)}{y(0)} &= e^{-(Q/V)t}\end{aligned}$$

If we now substitute  $C - C_{in}$  for  $y$ , we obtain

$$\begin{aligned}\frac{C - C_{in}}{C_0 - C_{in}} &= e^{-(Q/V)t}, \text{ or} \\ \frac{C - C_{in}}{-C_{in}} &= e^{-(Q/V)t}\end{aligned}$$

The second equation is obtained using the observation that  $C(0) = 0$ , since the tank is started clean. Rearranging, we can obtain

$$\begin{aligned}C - C_{in} &= -C_{in}e^{-(Q/V)t}, \text{ or} \\ C &= C_{in} \cdot (1 - e^{-(Q/V)t})\end{aligned}$$

This is the solution to the question posed in the problem statement. Note what happens as  $t \rightarrow \infty$ :  $e^{-(Q/V)t} \rightarrow 0$  and  $C \rightarrow C_{in}$ . This is not surprising, since this is a conservative substance. If we run the reactor for a long enough period, the concentration in the reactor will eventually reach the inlet concentration. Using the equation we have derived for  $C$  as a function of time, we could determine *how long* it would take for the concentration to reach, say, 90% of the inlet value.

**Example 2.4. Non-steady-state CSTR with 1<sup>st</sup>-order Decay** The manufacturing process that generates the waste in example 2.2 has to be shut down, and, starting at  $t=0$ , the concentration  $C_{in}$  entering the CSTR is set to 0. What is the outlet concentration as a function of time after the concentration is set to 0? How long does it take the tank concentration to reach 10% of its initial, steady-state value?

*Solution:* This is clearly a non-steady-state problem, because conditions change as a function of time. To solve it, we will again use the tank as our control volume. The mass balance equation is

$$\begin{aligned}\frac{dm}{dt} &= \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{rxn} \\ V \frac{dC}{dt} &= 0 - QC - kCV, \text{ or} \\ \frac{dC}{dt} &= -(Q/V + k)C.\end{aligned}$$

(a)

To determine  $C$  as a function of time, we must solve the differential equation. Rearranging and integrating:

$$\int_{C(0)}^{C(t)} \frac{dC}{C} = \int_0^t -(Q/V + k) dt$$

which yields

$$\ln(C) - \ln(C(0)) = -(Q/V + k)t.$$

Since  $(\ln(x) - \ln(y))$  is equal to  $\ln(x/y)$ ,

$$\ln\left(\frac{C}{C(0)}\right) = -(Q/V + k)t$$

and, exponentiating both sides,

$$\frac{C(t)}{C(0)} = e^{-(Q/V + k)t}.$$

Plugging in the values from the problem, with  $C(0)$  equal to the steady-state solution of 32 mg/l yields

$$\begin{aligned}C(t) &= 32 \text{ mg/l} \cdot \exp\left(\left(\frac{50 \text{ m}^3/\text{day}}{500 \text{ m}^3} + \frac{0.216}{\text{day}}\right)t\right) \\ &= 32 \text{ mg/l} \cdot e^{-\frac{0.316}{\text{day}}t}\end{aligned}$$

(b)

How long will it take the concentration to reach 10% of its initial, steady-state value? That is, at what value of  $t$  is  $C(t)/C(0) = 0.10$ ? At the time when  $C(t)/C(0) = 0.10$ , we have

$$\frac{C}{C(0)} = 0.10 = \exp\left(-\frac{0.316}{\text{day}}t\right)$$

Taking the natural logarithm of both sides,

$$\begin{aligned}\ln(0.10) &= -2.303 = -\frac{0.316}{\text{day}}t, \text{ or} \\ t &= 7.3 \text{ days}.\end{aligned}$$

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## The Plug Flow Reactor

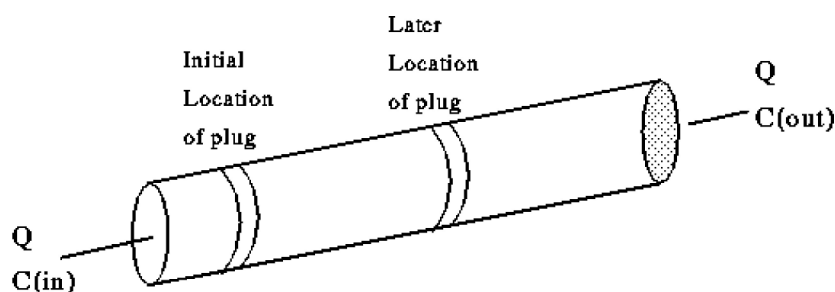


Figure 3: The Plug Flow Reactor

The *Plug Flow Reactor (PFR)* is used to model the chemical transformation of compounds as they are transported in "pipes." The "pipe" may represent a river, a region between two mountain ranges through which air flows, or a variety of other conduits through which liquids or gases flow. Of course, it can even represent a pipe. A schematic diagram of a PFR is shown in Figure 3.

As fluid flows down the PFR, the fluid is mixed in the radial direction, but mixing does not occur in the axial direction---each *plug* of fluid is considered a separate entity as it flows down the pipe. However, as the plug of fluid flows downstream, time passes. Therefore, there is an implicit time dependence even in steady-state PFR problems. *However, because the velocity of the fluid in the PFR is constant, time and downstream distance are interchangeable:  $t = x/v$ .* We will use this observation together with the mass balance formulations we have worked with already to determine how pollutant concentrations vary during flow down a PFR.

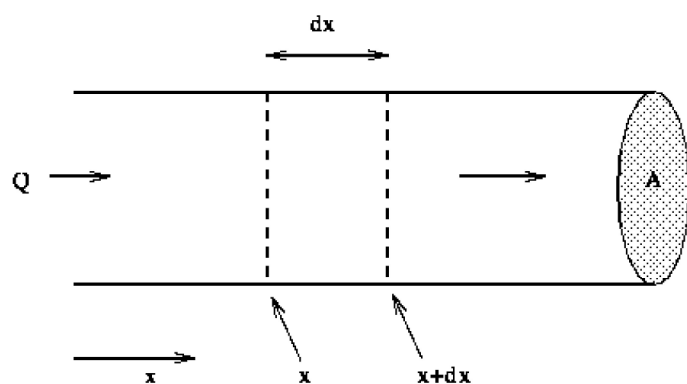


Figure 4: Closeup of a single plug of fluid in a plug flow reactor

To develop the equations which describe pollutant concentration in the plug of fluid as it flows down the PFR, we will conduct a mass balance on a control volume which encloses a section of the PFR of infinitesimally small thickness  $dx$ , as shown in Figure 4. Since the thickness is small, we can assume that the fluid in that region of the PFR is well-mixed. The mass balance equation for this control volume is

$$\begin{aligned} \frac{dm}{dt} &= \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{rxn} \\ 0 &= QC(x) - QC(x+dx) - V \left. \frac{dC}{dt} \right|_{rxn} \end{aligned} \quad (18)$$

We have set  $dm/dt$  equal to zero, indicating that this is a steady-state problem. We are assuming here that conditions at a given location in the PFR are constant. Concentrations can still vary along the PFR, however.

Noting that the volume of our control volume is given by  $V = A \cdot dx$ , dividing by  $dx$ , and rearranging, we obtain

$$\frac{C(x+dx) - C(x)}{dx} = \frac{A}{Q} \left. \frac{dC}{dt} \right|_{rxn} \quad (19)$$

In the limit as  $dx \rightarrow 0$ , the left hand side becomes the derivative  $dC/dx$ , so we obtain



$$\frac{dC}{dx} = \frac{A}{Q} \left. \frac{dC}{dt} \right|_{rxn} \quad (20)$$

As discussed earlier,  $dC/dt|_{rxn}$  can take a variety of forms, depending on the type(s) of chemical reaction that are occurring.

- No reaction.  $dC/dt|_{rxn} = 0$ . From equation 20, this means that  $dC/dx = 0$ ---there is no variation of concentration along the pipe. (Of course, this result is obvious, since if there is no reaction the fluid is just moving along the pipe without changing in any way.)
- First-order reaction.  $dC/dt|_{rxn} = -kC$ . Plugging into equation 20 for this case, we obtain

$$\frac{dC}{dx} = -\frac{kA}{Q}C. \quad (21)$$

which can be integrated as follows:

$$\int_{C(0)}^{C(x)} \frac{dC}{C} = -\frac{kA}{Q} \int_0^x dx, \text{ giving} \quad (22)$$

$$\ln \left( \frac{C(x)}{C(0)} \right) = -\frac{kA}{Q}x, \text{ or} \quad (23)$$

$$C(x)/C(0) = e^{-(kA/Q)x}. \quad (24)$$

Therefore, for a PFR of length  $l$ ,

$$C_{out}/C_{in} = e^{-(kA/Q)l} \quad (25)$$

$$= e^{-(kV/Q)}, \quad (26)$$

where the volume of the PFR,  $V$ , is equal to the length times time area.

Equation 26 describes the way in which concentration decreases during passage down a PFR with loss via a first-order reaction. Note that, since the time which passes during transport down the PFR is equal to  $t = V/Q$ , equation 26 is equivalent to

$$C(t)/C(0) = e^{-kt}, \quad (27)$$

which is the solution to the differential equation which describes the loss of a pollutant by first-order kinetics:  $dC/dt = -kC$ .

That is, in a plug flow reactor time and distance are interchangeable, and the concentration at any location in the PFR may be calculated simply by determining the chemical decay during the time it took to reach that location.

### Comparison of the PFR to the CSTR.

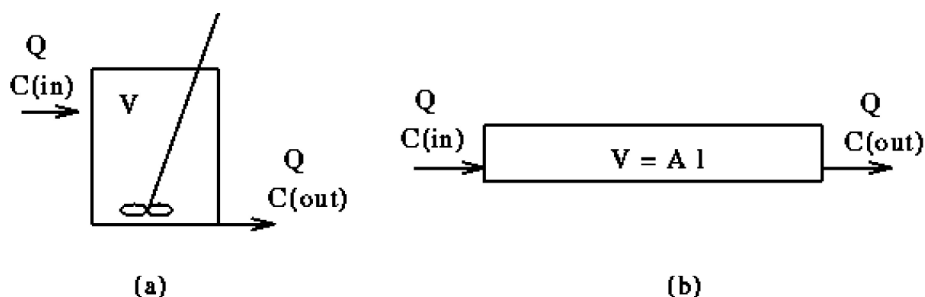


Figure 5: Continuously Stirred Tank Reactor (a) and Plug Flow Reactor (b) used to compare the efficiency of the two reactor types

The CSTR and the PFR are fundamentally different. When a parcel of fluid enters the CSTR, it is immediately mixed throughout the entire volume of the CSTR. In contrast, each parcel of fluid entering the PFR remains separate during its passage through the reactor. This difference results in differing behavior. We will look at these differences for one special case: the continuous addition of a pollutant to each reactor, with destruction of the pollutant within the reactor according to first-order kinetics. The two reactors are shown in Figure 5.

We will assume that the incoming concentration ( $C_{in}$ ), the flow rate ( $Q$ ), and the first-order reaction rate constant ( $k$ ) are given and are the same for both reactors. Then, we will consider two common problems: (1) if we know the volume  $V$  (same for both reactors), what is the resulting outlet concentration ( $C_{out}$ )? and (2) if we need a specified outlet concentration, what volume of reactor is required? Table 2 summarizes the results of this comparison.

Table 2: Comparison of CSTR and PFR

1. $C_{out}$ , given $C_{in}$ , $V$ , $Q$ , and $k$ . <sup>a</sup>	
<b>CSTR</b>	<b>PFR</b>
$C_{out} = \frac{C_{in}}{1 + kV/Q}$	$C_{out} = C_{in} \exp(-kV/Q)$
$C_{out}/C_{in} = 0.333$	$C_{out}/C_{in} = 0.135$
2. $V$ , given $C_{in}$ , $C_{out}$ , $Q$ , and $k$ . <sup>b</sup>	
<b>CSTR</b>	<b>PFR</b>
$V = (C_{in}/C_{out} - 1) \cdot (Q/k)$	$V = -(Q/k) \ln(C_{out}/C_{in})$
$V = 950 \text{ l}$	$V = 150 \text{ l}$

<sup>a</sup> $V = 100 \text{ l}$ ,  $Q = 5.0 \text{ l/s}$ ,  $k = 0.10 \text{ s}^{-1}$ .

<sup>b</sup> $C_{out}/C_{in} = 0.05$ ,  $Q = 5.0 \text{ l/s}$ ,  $k = 0.10 \text{ s}^{-1}$ .

The results shown in Table 2 indicate that, for equal reactor volumes, the plug flow reactor is more efficient than the CSTR and, for equal outlet concentrations, a smaller PFR is required. Why is this? The answer has to do with the fundamental difference between the two reactors. In a PFR, each and every molecule spends the same amount of time in the reactor; that period is equal to  $V/Q$ . Since first-order decay occurs according to  $C(t)/C(0) = \exp(-kt)$ , the concentration in each parcel of fluid entering the reactor drops by this amount. In contrast, in a CSTR there is no single amount of time that each small parcel of fluid spends in the reactor. Some parcels may spend a long time mixing around inside the CSTR; other parcels may, by chance, reach the exit in a relatively short time. Since all these parcels are mixed together and result in a single outlet concentration, an average value of  $C(t)/C(0)$  results.

To see why that average value is higher than the corresponding value for a PFR, consider what happens when  $kt = kV/Q$  is equal to 2, approximately the value in the first example of Table 2. Then,  $\exp(-kt) = \exp(-2.0) = 0.14$ . This is the value of  $C_{out}/C_{in}$  that would result in the PFR. Let's assume that we can model the mixing in the CSTR by splitting the fluid entering the CSTR into two parcels. The first parcel remains in the CSTR only one quarter of the time a parcel would take to pass through the PFR, while the second parcel remains in the CSTR four times as long as it would in the PFR. (So the average time spent in the CSTR by the two parcels is the same as the time spent in the PFR---both are equal to  $V/Q$ .) The concentration in the first parcel when it reaches the CSTR exit is determined by its value of  $kt$ , which is 4 times larger than the value for the PFR:  $C_{out}/C_{in} = \exp(-kt) = \exp(-4 \cdot 2.0) = \exp(-8.0) = 0.0003$ . The concentration in the second parcel is reduced less, because it spends a shorter time in the reactor:  $C_{out}/C_{in} = \exp(-kt) = \exp(-0.25 \cdot 2.0) = \exp(-0.5) = 0.61$ . The actual concentration in the exit of the CSTR in this situation would be the *average* of the concentrations in the two parcels, so  $C_{out}/C_{in} = (0.0003 + 0.61)/2.0 = 0.30$ .

Thus, the resulting value of  $C_{out}/C_{in}$  for the CSTR is higher than that for the PFR (0.30 versus 0.14), even though the average residence time is the same for both reactors. The reason for this is illustrated in Figure 6, and results from the fact that concentration decays exponentially with time for a first-order reaction. Thus, the parcel that spends a shorter period of time in the CSTR exits with a concentration that is increased significantly relative to the PFR. However, the parcel that spends a longer period in the CSTR exits with a concentration that is decreased only a small amount (again, relative to the PFR).

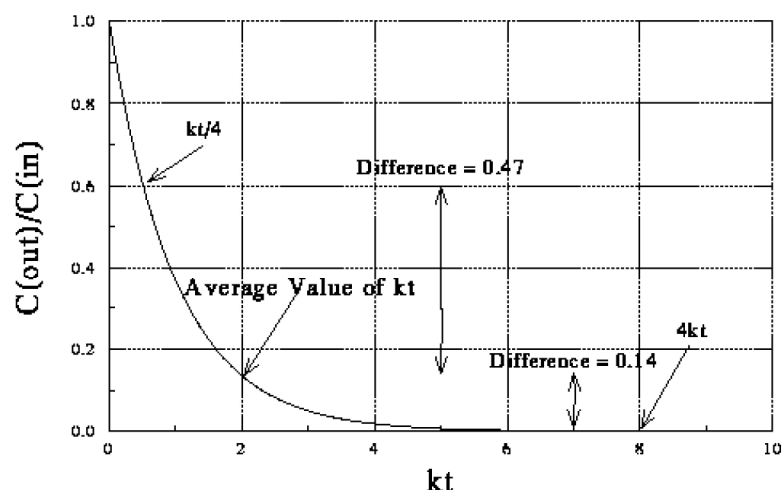


Figure 6: The exponential decrease in outlet concentration according to  $C_{out}/C_{in} = \exp(-kt)$ . The average value of  $kt$  shown corresponds to the PFR. The smaller and larger values of  $kt$  are the values for two hypothetical parcels passing through the CSTR. The faster parcel, with a lower value of  $kt$ , experiences an increase in  $C_{out}/C_{in}$  of 0.47, while the slower parcel experiences a much smaller decrease in  $C_{out}/C_{in}$  of only 0.14. The result is that the average value of  $C_{out}/C_{in}$  is higher for the CSTR than for the PFR.

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**Example 2.5. Required Volume in a PFR** Determine the volume required for a PFR to obtain the same degree of pollutant reduction as the CSTR in example 2.2. Assume that the flow rate and first-order decay rate constant are unchanged ( $Q = 50 \text{ m}^3/\text{day}$ ,  $k = 0.216 \text{ day}^{-1}$ ).

*Solution:* The CSTR in example 2.2 achieved a pollutant decrease of  $C_{out}/C_{in} = 32/100 = 0.32$ . From equation 26,

$$\begin{aligned} \frac{C_{out}}{C_{in}} &= e^{-(kV/Q)}, \text{ or} \\ 0.32 &= \exp(-0.216 \text{ day}^{-1}V/50 \text{ m}^3/\text{day}). \end{aligned}$$

Solving for  $V$ , we obtain

$$\begin{aligned} V &= \ln(0.32) \cdot \frac{50 \text{ m}^3/\text{day}}{-0.216 \text{ day}^{-1}} \\ &= 264 \text{ m}^3. \end{aligned}$$

As expected, this volume is smaller than the 500  $\text{m}^3$  required for the CSTR in example 2.2.

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## Retention Time and Other Expressions for .

A number of terms are used to describe the average period spent in a given reactor. The terms *retention time*, *detention time*, and *residence time* are all used to refer to  $V/Q$ , the average period spent in the reactor. This parameter has units of time. As

discussed above, for a plug flow reactor the retention time is actually the time spent in the reactor. However, for a CSTR the retention time is the *average* period spent in the reactor.

The reciprocal of the retention time,  $Q/V$ , has units of inverse time---the same units as a first-order rate constant. This value is sometimes referred to as the *exchange rate*.

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**Example 2.6. Retention Time in CSTR and PFR** Calculate the retention times in the CSTR of example 2.2 and the PFR of example 2.5.

*Solution:* For the CSTR in example 2.2,

$$\tau = V/Q = (500 \text{ m}^3)/(50 \text{ m}^3/\text{day}) = 10 \text{ days}.$$

For the PFR in example 2.5,

$$\tau = V/Q = (264 \text{ m}^3)/(50 \text{ m}^3/\text{day}) = 5.3 \text{ days}.$$

---

Table 3: Volume and Flows for the Great Lakes

Lake	Volume $10^9 \text{ m}^3$	Outflow $10^9 \text{ m}^3/\text{yr}$
Superior	12000	67
Michigan	4900	36
Huron	3500	161
Erie	468	182
Ontario	1634	211

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Source: Chapra, S. C. and K. H. Reckhow, *Engineering Approaches for Lake Management. Volume 2. Mechanistic Modeling*, Butterworth Publishers, Boston, 1983.

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**Example 2.7. Retention Times for the Great Lakes** Calculate the retention times for Lake Michigan and Lake Ontario using the data given in Table 3.

*Solution:* Again, we can calculate the retention times as  $\tau = V/Q$ . Note that we are assuming that the lakes can be modeled as CSTRs (or PFRs, but a CSTR makes more sense for a lake). This assumption is not far off for retention times significantly longer than one year.

For Lake Michigan,  $\tau = (4900 \times 10^9 \text{ m}^3)/(36 \times 10^9 \text{ m}^3/\text{yr}) = 136 \text{ years}$ .

For Lake Ontario,  $\tau = (1634 \times 10^9 \text{ m}^3)/(212 \times 10^9 \text{ m}^3/\text{yr}) = 8 \text{ years}$ .

The higher flow and smaller volume of Lake Ontario results in a significantly shorter retention time. This means that pollutant concentrations can increase in Lake Ontario much more quickly than they can in Lake Michigan, but it also means that concentrations will drop much more quickly in Lake Ontario if a pollutant source is eliminated.

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## Energy Balance

Modern society is dependent on the use of energy. Such use requires transformations in the form of energy and control of energy flows. For example, when coal is burned at a power plant, the chemical energy present in the coal is converted to heat, which is then converted in the plant's generators to electrical energy. Eventually, the electrical energy is converted back into

heat for warmth or used to turn motors. However, energy flows and transformation are also the cause of environmental problems. Thermal heat energy from electrical power plants can result in increased temperature in rivers used for cooling water; "greenhouse" pollutants in the atmosphere alter the energy balance of the earth and may cause significant increases in global temperatures in the future; and many of our uses of energy are themselves associated with emissions of pollutants.

We can keep track of the movement of energy and changes in its form using *energy balances*, which are analogous to the mass balances we discussed in the previous section. We can do this because of the law of *conservation of energy* which states that energy can neither be produced nor destroyed. (Conservation of energy is sometimes referred to as the first law of thermodynamics.) As long as we consider all the possible forms of energy, there is no term in energy balances which is analogous to the chemical reaction term in mass balances. That is, we can treat energy as a conservative substance.

## Forms of Energy

Table 4: Forms of Energy

	Representation for Energy or Change in Energy
Heat Internal Energy	$\Delta E = (\text{mass})C\Delta T$
Chemical Internal Energy	$\Delta E = \Delta H_{rxn}$ at constant volume
Gravitational Potential	$\Delta E = (\text{mass})(\Delta \text{height})$
Kinetic	$E = (\text{mass})(\text{velocity})^2/2$
Electromagnetic	$E = (\text{Planck's constant})(\text{photon frequency})$

**This table lists only the more common forms of energy—those which you will routinely encounter in environmental engineering problems.**

The forms of energy can be divided two types: *internal energy* and *external energy*. Energy which is a part of the molecular structure or organization of a given substance is internal. Energy which results from the location or motion of the substance is external. Examples of external energy include gravitational potential energy and kinetic energy. Gravitational potential energy is the energy gained when a mass is moved to a higher location above the earth. Kinetic energy is the energy which results from the movement of objects. When a rock thrown off of a cliff accelerates toward the ground, the sum of kinetic and potential energy is conserved (neglecting friction)---as it falls it loses potential energy, but increases in speed, gaining kinetic energy. Examples of some common forms of energy are given in Table 4.

Heat is a form of internal energy. It results from the random motions of atoms. Heat is thus really a form of kinetic energy, although it is considered separately. When you heat a pot of water, you are adding energy to the water. That energy is stored in the form of internal energy, and the change in internal energy of the water is given by

$$\text{Change in internal energy} = (\text{mass of H}_2\text{O}) \cdot C \cdot \Delta T, \quad (28)$$

where **C** is the heat capacity or specific heat of the water, with units of [energy]/([mass][temperature]). Heat capacity is a property of a given material. For water, the heat capacity is 1 BTU/(lb · °F), or 4184 J/(kg · °C).

*Chemical internal energy* reflects the energy in the chemical bonds of a substance. This form of energy is composed of two parts:

1. The strengths of the atomic bonds in the substance. When chemical reactions occur, if the sum of the energies of the products is less than that for the reactants, a reduction in chemical internal energy has occurred. As a result of the conservation of energy, this leftover energy must show up in a different form. Usually, the energy is released as heat. This fact is used to our advantage when we burn fuel.
2. The energy in the bonds between molecules. This energy depends on the phase of the material---whether it is a solid, liquid, or gas. The energy required to change phases is known as the *latent heat*. Values of the latent heat of fusion (the energy released when a material changes from liquid to solid phase) and the latent heat of condensation or vaporization (the energy released when a substance changes from gas to liquid phase) are tabulated for many substances. When a substance changes from solid to liquid or from liquid to gas, it gains internal energy. This energy must come from somewhere. For example, when water evaporates it takes up energy from its surroundings, and this is why evaporation of sweat cools us.

## Conducting an Energy Balance

In analogy with the mass balance equation (equation 14), we will use the following equation to conduct energy balances:

$$\left( \begin{array}{c} \text{Change in} \\ \text{internal} \\ \text{plus} \\ \text{external} \\ \text{energy per} \\ \text{unit time} \end{array} \right) = \left( \begin{array}{c} \text{energy flux} \\ \text{in} \end{array} \right) - \left( \begin{array}{c} \text{energy flux} \\ \text{out} \end{array} \right), \text{ or} \quad (29)$$

$$\frac{dE}{dt} = \dot{E}_{in} - \dot{E}_{out} \quad (30)$$

We will illustrate the use of this relationship with some examples.

**Example 28. Heating water** A 40-gallon electric water heater is used to heat tap water (temperature  $50_{\circ}F$  ( $10_{\circ}C$ )). The heating level is set to the maximum level while several people take consecutive showers. If, at the maximum heating level, the heater uses 5 kW of electricity, and the water use rate is a continuous 2 gallons/min, what will be the temperature of the water exiting the heater? Assume that the system is at steady-state and that the heater is 100% efficient; that is, it is perfectly insulated and all of the energy used goes to heat the water.

*Solution:* Our control volume for this problem is the water heater. We note that (since the system is at steady-state), the internal energy of the water in the water heater is constant. The energy added is used to heat water entering the water heater to the temperature at the outlet. The energy flux into the water heater comes from two sources: the heat content of the water entering the heater and the electrical heating element. The energy flux out of the water heater is just the internal energy of the water leaving the system. There is no net conversion of other forms of energy. Therefore, equation 30 may be rewritten as

$$0 = (\dot{m}_{H_2O} C T_{in} + 5 \text{ kW}) - \dot{m}_{H_2O} C T_{out}$$

Each term of this equation is an *energy flux*, and has the units of (energy/time). To solve, we need to use the same units in each term. We will use the definition of watts: **watts are defined as Joules/s**. In addition, we need to convert the water flow rate (gallons/min) to mass of water per unit time, using the density of water. Combining the first and third terms we obtain

$$\begin{aligned} 0 &= \frac{2 \text{ gal } H_2O}{\text{min}} \cdot \frac{3.785 \text{ l}}{\text{gal}} \cdot \frac{1.0 \text{ kg}}{\text{l}} \cdot \frac{4184 \text{ J}}{\text{kg} \cdot ^{\circ}C} \cdot (T_{in} - T_{out}) + \frac{5000 \text{ J}}{\text{s}} \cdot \frac{60 \text{ s}}{\text{min}} \\ &= 3.16 \times 10^4 \frac{\text{J}}{\text{min} \cdot ^{\circ}C} \cdot (T_{in} - T_{out}) + 3.00 \times 10^5 \frac{\text{J}}{\text{min}}, \text{ or} \\ T_{out} &= T_{in} + 9.5^{\circ}C \\ &= (10 + 9.5) = 19.5^{\circ}C \end{aligned}$$

which is a cold shower! (You may have foreseen this answer if you have ever taken a shower after the hot water in the tank was used up by previous showerers.)

**Example 29. Heating water** From the previous example, we see that if one wants a hot shower, it is necessary to wait until the water in the tank can be reheated. How long would it take the temperature to reach  $130_{\circ}F$  ( $54_{\circ}C$ ) if no hot water were used during the heating period and the water temperature started at  $20_{\circ}C$ ?

*Solution:* In this case, the only energy input is the electrical heat, and there is no energy leaving the tank. Therefore, the rate of increase in internal energy is equal to the rate that electrical energy is used:

$$(\text{mass of } H_2O) \cdot C \cdot \frac{\Delta \text{Temperature}}{\Delta \text{Time}} = 5000 \frac{\text{J}}{\text{s}}.$$

We will solve this for  $\Delta \text{Time}$ , given that  $\Delta \text{Temperature}$  is equal to  $(54 - 20 = 34)_{\circ}C$ .

$$\begin{aligned}
 \Delta Time &= \frac{(\text{mass of } H_2O) \cdot (C) \cdot (\Delta Temp)}{5000 \text{ J/s}} \\
 &= \frac{(40 \text{ gal } H_2O \cdot \frac{3.785 \text{ l}}{\text{gal}} \cdot \frac{1.0 \text{ kg}}{\text{l}}) (4184 \frac{\text{J}}{\text{kg} \cdot ^\circ\text{C}}) (130 - 20^\circ\text{C})}{5000 \text{ J/s}} \\
 &= 4.3 \times 10^3 \text{ s} = 1.2 \text{ hr}
 \end{aligned}$$

The two previous examples related to the controlled conversion and transfer of energy for a beneficial use. However, the use of energy for heat always results in some loss to the environment due to imperfect insulation, resulting in higher energy use or less heating than one would calculate. In addition, the *second law of thermodynamics* states that it is impossible to convert heat energy to work with 100% efficiency. Conversion of heat to work is essentially what is done in the generator of an electric power plant, and as a result a significant fraction of the energy released from fuel combustion is lost during the conversion. Modern large power plants convert fuel energy to electricity with an overall efficiency in the 30--35% range. The next example looks at what happens to the heat energy that is *not* converted to electricity. Finally, example 2.11 considers the implications of another aspect of the burning of fossil fuels in power plants, vehicles, and for heating. Whenever fossil fuels are burned, carbon atoms in the fuel are converted to carbon dioxide ( $\text{CO}_2$ ) and released into the atmosphere. As a result of this process, the  $\text{CO}_2$  concentration in the atmosphere is increasing at a rate of about 1 ppmv/year. Carbon dioxide contributes to the *greenhouse effect*, which is considered in example 2.11.

**Example 2.10. Thermal Pollution.** A 1000 MW ( $1000 \times 10^6 \text{ W}$ ) power plant is located next to a river and uses cooling water from the river to remove its waste heat. What is the resulting increase in river temperature? (The power plant has an overall efficiency of 33%. Assuming that all of the waste heat from the power plant is removed with cooling water and added to the adjacent river. The river flow rate is 100  $\text{m}^3/\text{s}$ .)

*Solution:* This problem is very similar to example 2.8, in that we are adding a specified amount of heat to a flow of water, and need to determine the resulting temperature rise. To solve, we first need to determine the amount of energy added. The power plant produces 1000 MW of electricity, but is only 33% efficient, meaning that it uses 3000 MW of fuel energy ( $3000 \text{ MW} = 1000 \text{ MW}/0.33$ ). The heat energy added to the river is the amount that is not converted to electricity, or ( $3000 - 1000 = 2000 \text{ MW}$ ). We can now write our energy balance over the region of the river to which the heat is added. We will use  $T_{in}$  to represent the temperature of the water upstream, and  $T_{out}$  to represent the temperature after heating:

$$\begin{aligned}
 \frac{dE}{dt} &= \dot{E}_{in} - \dot{E}_{out} \\
 0 &= \left( \begin{array}{c} 2000 \text{ MW} \\ \text{of heat} \\ \text{from power} \\ \text{plant} \end{array} \right) + (\dot{m}_{H_2O} \cdot C \cdot T_{H_2O,in}) - \dot{m}_{H_2O} \cdot C \cdot T_{H_2O,out}
 \end{aligned}$$

Rearranging, we obtain

$$\dot{m}_{H_2O} \cdot C \cdot T_{out} - T_{in} = 2000 \text{ MW}$$

The remainder of this problem is basically a problem of unit conversions. To obtain  $\dot{m}_{H_2O}$  requires multiplication of the given river volumetric flow rate by the density of water ( $1000 \text{ kg}/\text{m}^3$ ). We also use the heat capacity of water,  $C = 4184 \text{ J}/\text{kg} \cdot ^\circ\text{C}$ . Thus,

$$\begin{aligned}
 (100 \frac{\text{m}^3}{\text{s}} \cdot 1000 \frac{\text{kg}}{\text{m}^3}) \cdot (4184 \frac{\text{J}}{\text{kg} \cdot ^\circ\text{C}}) \cdot \Delta T &= 2000 \times 10^6 \text{ J/s, or} \\
 \Delta T &= 4.8^\circ\text{C}
 \end{aligned}$$

**Example 2.11. Earth's Energy Balance and the Greenhouse Effect.** *The global average surface temperature of the earth is determined by a balance between the energy added to the earth by the sun and the energy radiated away by the earth to space. Greenhouse gases, both natural and anthropogenic (or, human-affected), affect this energy balance. In this example, we will calculate the global average temperature without greenhouse gases and show the effect which greenhouse gases have on the earth's energy balance.*

*Solution:* We will write an energy balance, with our control volume as the entire earth. For this system, our goal is to calculate annual-average temperatures. Over time periods of  $\geq 1$  yr, it is reasonable to assume that the system is in steady state, so our energy balance is simply

$$\frac{dE}{dt} = \dot{E}_{in} - \dot{E}_{out}.$$

The energy flux in is equal to the solar energy intercepted by the earth. At the earth's distance from the sun, the sun radiates  $342 \text{ W/m}^2$ . We will refer to this value as  $S$ . The earth intercepts an amount of energy equal to  $S$  times the cross-sectional area of the earth:  $S \times \pi R_e^2$ . However, because the earth reflects part of this energy back to space,  $\dot{E}_{in}$  is equal to only 70% of this value:

$$\dot{E}_{in} = 0.7S\pi R_e^2.$$

The second term,  $\dot{E}_{out}$ , is equal to the energy radiated to space by the earth. The energy emitted per unit surface area of the earth is given by Boltzmann's Law:

$$\left( \begin{array}{c} \text{Energy} \\ \text{flux per} \\ \text{unit area} \end{array} \right) = \sigma T^4$$

where  $\sigma$  is Boltzmann's constant, equal to  $5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ . To obtain  $\dot{E}_{out}$ , we multiply this value by the total surface area of the earth,  $4\pi R_e^2$ . (We use the total surface area of the sphere here because energy is radiated away from the earth during both day and night.)

$$\dot{E}_{out} = 4\pi R_e^2 \sigma T^4$$

We can now solve our energy balance by setting  $\dot{E}_{in}$  equal to  $\dot{E}_{out}$ .

$$\begin{aligned} 4\pi R_e^2 \sigma T^4 &= 0.7S\pi R_e^2, \text{ or} \\ T^4 &= \frac{0.7S}{4\sigma} \end{aligned}$$

Plugging in the values for  $S$  and  $\sigma$  and taking the fourth root yields an average temperature of  $T=255_0 \text{ K}$ , or  $-18_0 \text{ C}$ .

This is too cold! In fact, the globally averaged temperature at the surface of the earth is much warmer:  $287_0 \text{ K}$ . The reason for the difference is the presence of gases in the atmosphere that absorb the infrared radiation emitted by the earth and prevent it from reaching space. We neglected these gases in our energy balance. However, if we denote the energy flux absorbed and retained by these gases by  $E_{greenhouse}$ , we can then correct our value for  $\dot{E}_{out}$ :

$$\dot{E}_{out} = 4\pi R_e^2 \sigma T^4 - E_{greenhouse}.$$

The reduction in  $\dot{E}_{out}$  which results from greenhouse gas absorption is sufficient to cause the higher observed surface temperature. Clearly, this is largely a natural phenomenon---surface temperatures were well above  $255_0 \text{ K}$  long before people began burning fossil fuels. The main natural greenhouse gas is water vapor. However, increasing atmospheric concentrations of carbon dioxide and other gases emitted by human activities are increasing the value of  $E_{greenhouse}$ . So far, this increase is approximately  $2 \text{ W/m}^2$  averaged over the entire earth, and projections indicate that the increase could be as high as  $5 \text{ W/m}^2$  over the next 50 years. According to our energy balance, this increase in  $E_{greenhouse}$  is expected to result in an increase in the globally averaged temperature. (There is considerable uncertainty in the precise value of the resulting increase, however, due to a number of complexities that we have not considered.)



## PROBLEMS

2.1. A pond is used to treat sewage wastewater before the liquid is discharged into a river. The inflow to the pond is sewage at a flow rate of  $Q = 4000 \text{ m}^3/\text{day}$  and with a BOD concentration of  $C_{in} = 25 \text{ mg/l}$ . The volume of the pond is  $20,000 \text{ m}^3$ . The purpose of the pond is to allow time for the decay of BOD to occur before discharge into the environment. BOD decays in the pond with a first-order rate constant equal to  $0.25/\text{day}$ . What is the BOD concentration at the outflow of the pond, in units of  $\text{mg/l}$ ?

answer:  $11 \text{ mg/l}$

2.2. For each of the following problems, would you use a steady-state or non-steady-state mass balance to obtain a solution? For each situation, also indicate whether the compound for which you would conduct a mass balance is conservative or non-conservative. **Give an explanation for each of your answers.** (You do not need to actually solve these problems.)

- (a) An accident has resulted in the release of a pollutant inside a chemical manufacturing plant. The spill released the pollutant into a lake near the chemical plant, which has a small stream flowing through it. How long would it take the pollutant, which is inert, to reach a safe level in the lake and in the stream leaving the lake?
- (b) Carbon dioxide ( $\text{CO}_2$ ) emissions from fossil fuel burning are mixed throughout the atmosphere. Assume that these emissions are mixed immediately throughout the entire atmosphere, and that  $\text{CO}_2$  does not degrade chemically. If you know the total emission rate of carbon dioxide and the volume of the atmosphere, what would be the rate of increase of atmospheric carbon dioxide levels in  $\text{ppm/yr}$ ?
- (c) An air freshener emits perfume into a room at a constant rate. The perfume is mixed throughout the room and diluted by the room ventilation flow, which is on continually. What is the resulting concentration of perfume in the room? (Note that the  $1^{\text{st}}$ -order decay rate constant of the perfume is very slow relative to the amount of time it takes to mix fresh air through the room.)

answer: (a) non-steady state

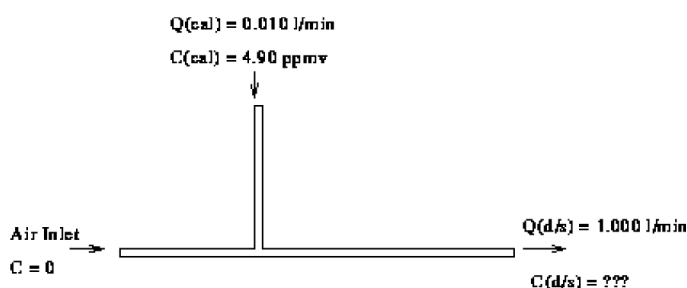


Figure 7: Gas calibration system.

2.3. A mixture of two gas flows is used to calibrate an air pollution measurement instrument. The calibration system is shown in Figure 7. If the calibration gas concentration  $C_{cal}$  is  $4.90 \text{ ppmv}$ , the calibration gas flow rate  $Q_{cal}$  is  $0.010 \text{ l/min}$ , and the total gas flow rate  $Q_{tot}$  is  $1.000 \text{ l/min}$ , what is the concentration of calibration gas after mixing ( $C_{d/s}$ )? (Assume that the concentration upstream of the mixing point is zero.)

answer:  $49.0 \text{ ppbv}$

2.4. You are in an old spy movie, and have been locked into a small room (volume  $1000 \text{ ft}^3$ ). You suddenly realize that a poison gas has just started entering the room through a ventilation duct. Recognizing the type of poison from its smell, you know that if the gas reaches a concentration of  $100 \text{ mg/m}^3$ , you will die instantly, but that you are safe as long as the concentration is less than  $100 \text{ mg/m}^3$ . If the ventilation air flow rate in the room is  $100 \text{ ft}^3/\text{min}$  and the incoming gas concentration is  $200 \text{ mg/m}^3$ , how long do you have to escape?

answer: 6.9 minutes

2.5. Sewage waste is added to a stream through a discharge pipe. The river flow rate upstream of the discharge point is  $Q_u/s = 8.7 \text{ m}^3/s$ . The discharge occurs at a flow of  $Q_d = 0.9 \text{ m}^3/s$  and has a BOD concentration of 50.0 mg/l. Assuming that the upstream BOD concentration is negligible

(a) What is the BOD concentration just downstream of the discharge point?

(b) If the stream has a cross sectional area of  $10 \text{ m}^2$ , what would the BOD concentration be 50 km downstream? (BOD is removed with a first-order decay rate constant equal to  $0.20 \text{ day}^{-1}$ )

answer: (a) 4.7 mg/l. (b) 4.2 mg/l

2.6. (a) Calculate the hydraulic residence times (the retention time) for Lake Superior and for Lake Erie using the data in Table 3.

(b) Assume that both lakes currently are polluted with the same compound at a concentration which is 10 times the maximum acceptable level. If all sources of the compound are removed, how long will it take the concentration to reach acceptable levels in each lake? Assume that the pollutant does not decay chemically.

(c) Comment on the significance of your answers.

answer: (a) Lake Superior: 179 years; Lake Erie: 3 years. (b) Lake Superior: 412 years; Lake Erie: 6 years.

2.7. How many watts of power would it take to heat 1 liter of water (weighing 1.0 kg) by  $10^\circ\text{C}$  in 1.0 hour? Assume that no heat losses occur, so that all of the energy expended goes into heating the water.

answer: 12 Watts

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