MASS BALANCES

This document reviews ***mass balances***. Mass balance equations are formal statements of the law of conservation of mass, and it is no exaggeration to think of them as the “$F = ma$” of environmental engineering. They represent the starting point, either explicitly or implicitly, for almost any environmental analysis, allowing us to keep track of any material as it moves through and/or is transformed in the environment. Mass balances help us answer questions about the rate at which pollutants accumulate in a system, the maximum concentration that a pollutant might reach at a point in a river following an upstream spill, or the size of a reactor that we have to build to achieve a desired percentage reduction in a pollutant’s concentration.

These types of balances are useful in areas other than water treatment. For example, when we keep track of total funds in a bank, we consider deposits, withdrawals, interest, and fees. Similarly, keeping track of population of 18-24 year-olds in Washington requires that we consider immigration, emigration, 18th birthdays, 25th birthdays, and deaths. Chemical accounting works the same way. A balance on the CO_2 in the room accounts for CO_2 entering or leaving through the door and windows, CO_2 being generated by breathing, and (if there are plants in the room) CO_2 being consumed by photosynthesis. Note, in all of these examples, that (1) it is critical that we define the object of interest and the boundaries of the system precisely; (2) moving something around inside the boundaries has no effect on the amount inside, and (3) we can know if something is inside or outside the system at a given instant, but we can’t tell how it got there or how long it has been there; all we know is that it is there. In mass balance equations, the region in which the accounting is being done is referred to as the ***control volume*** (***CV***).

In this course, we are most interested in keeping track of pollutants as they pass through aquatic systems (particularly water treatment processes), considering the possibility that they might undergo reaction while they are in the system. In general, these mass balances will have terms that account for ***advection*** of the pollutants (i.e., entry into or departure from the system with the flowing water), and ***reaction*** of the pollutant while it is in the system.

The flow of water into the system might be either steady or unsteady. Similarly, even if the flow rate is steady, the concentration of the pollutant in the influent stream might be steady or changing over time. The rate of the reaction is likely to depend on the concentration of the constituent, and possibly on the concentrations of other components of the solution. Often, the rate expression can be written as a simple function of the concentrations of the constituents, as we will see shortly. The local concentrations often depend on the extent of mixing in the system, which might range from negligible to very intense.

The various factors described above all affect the behavior of the system, and in particular, the concentrations of pollutants as they exit the system. Our goal is typically to predict those concentrations for specified operating conditions (which might either exist already or which we might specify as part of a reactor design). Essentially the same tools can be used to analyze experimental results, so that we can characterize certain unknown parameters in a system. Our approach is to write mass balances for idealized systems, predict the response of those systems under the ideal conditions, and then test real systems to see how closely they match our idealized expectations.

Mass balances take several forms. In some systems, no material enters or leaves the CV, and the rate of change is not considered important. In such systems, the mass balance simply states that everything that was present in the system at some initial time must be there at all later times, albeit perhaps in different forms. In systems with transport across the boundaries of the CV and/or where the rate of change is important, mass balances are written in terms of rates rather than absolute amounts: the rate at which material ***accumulates*** in the CV equals the net rate at which it is carried into the CV by flow (i.e., ***advection***), plus the net rate at which it is injected into or generated inside the CV by non-advective processes. Such processes might include ***addition*** of a dry chemical to the solution (we consider advection to include only liquid streams) or, more often, ***chemical reaction*** inside the system. Those who have taken the CEE 3xx curriculum have seen mass balances in CEE 350 and CEE 342 (where they might have been presented in the context of the ***Reynolds' Transport Theorem***, in conjunction with balances on energy and momentum).

In cases where we are dealing with *rates* of change, and where the chemical of interest (*i*) enters the CV only in water (not as an addition of dry materials), the mass balance can be expressed in a word equation as follows:

$$\begin{pmatrix}\text{Rate of increase}\\ \text{of storage of } i \text{ in}\\ \text{the control volume}\end{pmatrix} = \begin{pmatrix}\text{Net rate of}\\ \text{advection of } i \text{ into}\\ \text{the control volume}\end{pmatrix} + \begin{pmatrix}\text{Net rate of formation}\\ \text{of } i \text{ by reaction inside}\\ \text{the control volume}\end{pmatrix}$$

Because we will be dealing mostly with substances dissolved or dispersed in water, it is convenient to express the storage and transport terms in the above equation based on *concentrations*. Doing that, and translating the word equation into symbols yields:

$$\frac{d}{dt}\left(\int_{\text{CV}} c\,dV\right) = \sum_{\text{inflows}} Q_i c_i - \sum_{\text{outflows}} Q_i c_i + \int_{\text{CV}} r\,dV$$

where r is the *reaction rate* expression and corresponds to the rate of *generation* of i in the CV, with units of mass/volume-time. We often deal with substances that are destroyed by reactions, in which case r is negative. Note that, in the above equation, c is the concentration *inside* the CV and, in general, is different from the concentrations in the various inflow and outflow streams. The dimensions of each term in the above mass balance are mass/time.

Expressions for r must be determined from experiment. Typically, r depends on the concentration of the substance of interest, as well as the concentrations of other substances with which it reacts; *e.g.*, for a reaction between A and B to form product P, the rate of "generation" of A might be given by: $r_A = -kc_Ac_B$. Nevertheless, it is often acceptable to represent r_i as a simple function of just the concentration of i (c_i). Some commonly encountered expressions for r_i (dropping the subscript, since both r and c refer to the same species) include:

$r = -kc$ first order

$r = -kc^2$ second order

$r = -kc^n$ n^{th} order

$r = \dfrac{k_1 c}{k_2 + c}$ Michaelis-Menten

The dimensions of k are different for the different expressions, and must be such that r has dimensions of mass/volume-time. Note that, when this is done, all the terms in the mass balance have overall dimensions of mass/time.

The *average* concentration of i in a CV is the mass of i in the CV divided by the volume of the CV. However, the above expressions for r suggest that the rate of reaction of i is often dependent on its local concentration, so characterizing the average concentration in a CV might not be useful. In particular, if the CV contains fluid with varying concentrations, then the rate of reaction will also vary from point to point, and the average rate might not be the same as the rate based on the average concentration. Therefore, to solve the mass balance equation, we need to define a CV in which the concentration is uniform; in some cases, that requires that we choose a CV that is differentially small. Correspondingly, it is important to be able to characterize the ***mixing*** (or, more generally, the ***hydraulic characteristics***) of a reactor.

The mixing characteristics of a reactor are often represented in an idealized way. Usually, for systems with steady flow in and out, two limiting cases of mixing are considered. One limit is a ***complete-mix reactor*** (CMR). In such a reactor, the mixing is envisioned to be so intense that there are no gradients anywhere in the system. As a consequence, since the effluent must be taken from someplace within the system, the concentration of a pollutant in the effluent (c_{out}) has the same as that everywhere in the system (c). In addition, the fact that c is independent of location in a CMR means that the two integrals in the mass balance can be eliminated and converted into simpler expressions, as follows:

$$\frac{d}{dt}\left(\int_{\text{CV}} c\,dV \right) = \frac{d\left(cV\right)}{dt} \qquad\qquad \int_{\text{CV}} r\,dV = rV$$

At the other extreme, some reactors have minimal mixing and can be idealized as having no mixing whatsoever. These reactors are referred to as ***plug flow reactors*** (PFRs). In such reactors, water flows from one end to the other without interacting at all with the water upstream or downstream. As a result, the flow pattern can be visualized as beakers on a conveyor belt.

Reactors intended to behave like CMRs and like PFRs are very common in water treatment processes. CMRs are particularly useful for mixing chemicals into the bulk flow and also for concentration equalization (although this is not usually a major concern for drinking water systems), and PFRs are useful for treatment steps in which it is important to assure that all of the water remains in the reactor for approximately the same amount of time (e.g., disinfection processes). In addition, these models are applied to understand and predict the behavior of many natural aquatic systems, with lakes and ponds typically modeled as CMRs and rivers as PFRs.

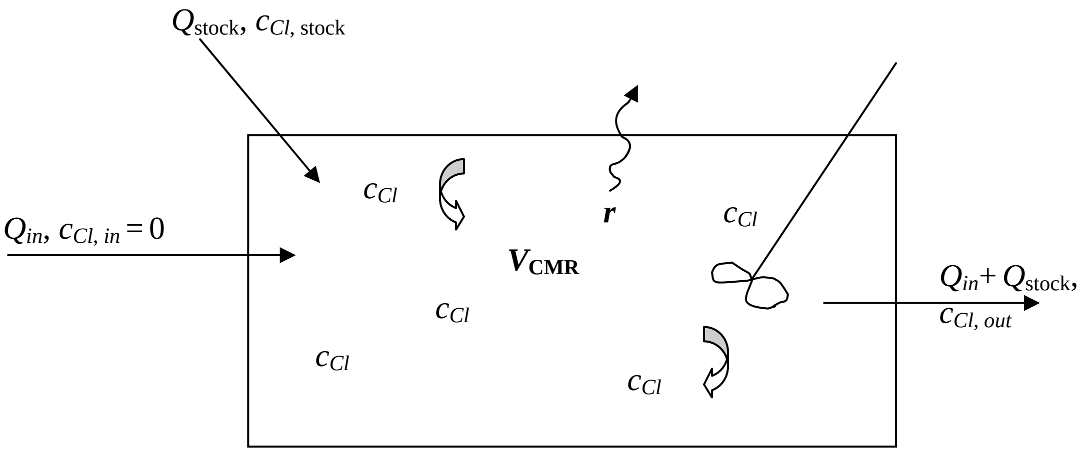
For both CMRs and PFRs, it is useful to define the ***mean hydraulic residence (retention, detention) time*** as $t_d = V/Q$. (This value is represented in the literature by a variety of symbols, including t_d, θ_h, and τ.) Note that the mean residence time is not necessarily the actual residence time of the majority of the fluid "parcels". In the case of PFRs, all parcels of fluid spend exactly t_d in the reactor; by contrast, in a CMR, parcels might spend anywhere from a very short to a very long time in the reactor, because at any instant after they enter the CV, they have a random likelihood of being near the outlet port; nevertheless, despite this continuum of actual residence times, the mean residence time is computed just as it is for a PFR (*i.e.*, as V/Q).

In some cases, we need to consider time-varying flow rates and concentrations in reactors, but often we deal with systems that have stable conditions, so that the concentration of i at any location in the system is constant over time (even though it might vary from one location to the next). Such systems are referred to as being at ***steady state***, and are characterized by values of zero for the storage term in the mass balance.

One other type of reactor is worth mentioning at this time. A ***batch*** reactor is one that has no flow in or out; i.e., $Q = 0$. Batch reactors are virtually always assumed to be well-mixed.

Example 1. We wish to disinfect a solution flowing at 0.8 m^3/s as it passes through an intensely mixed 3600-m^3 tank. The influent contains 10^4 bacterial cells per liter and no chlorine, and we plan to dose it with a stock solution containing 1000 mg/L at a rate that will cause the chlorine concentration in the tank to be 2 mg/L. The chlorine reacts with the water in such a way that it is depleted at a rate (in mg/L-h) given by $r_{Cl} = \left(-0.20/\text{h}\right)c_{Cl}$. When exposed to chlorine, the bacterial die off at a rate (in cells/L-s) given by: $r_{bact} = -\dfrac{\left(0.05/\text{s}\right)c_{Cl}}{1\text{ mg/L} + c_{Cl}}c_{bact}$. When the system is operating at steady state, what flow rate of stock solution is required, and what bacterial concentration should be expected in the effluent from the tank?

Solution. A schematic of the process is as follows.



The reactor is a CMR with steady flows. As a result, the Cl concentration is the same everywhere inside the tank (c_{Cl}), and that concentration is also the concentration in the effluent (since the effluent must come from somewhere inside). However, this effluent concentration is different from $c_{Cl,\,in}$. Applying the mass balance equation to Cl, we find:

$$\frac{d}{dt}\left(\int_{\mathrm{CV}} c_{Cl}\,dV\right) = \sum_{\text{inflows}} Q_j c_{Cl,\,j} - \sum_{\text{outflows}} Q_j c_{Cl,\,j} + \int_{\mathrm{CV}} r_{Cl}\,dV \qquad (1)$$

where each j represents a different inflow or outflow stream. The system is operating at steady state, so the term on the left of the equation is zero. And, because the tank is a CMR, the reaction rate will be the same throughout the tank, which allows us to take r_{Cl} be taken outside the integral on the far right. Therefore, noting that there are two inflows (the main inflow stream and the stock solution containing Cl) and one outflow, and that the main inflow stream contains no chlorine, we can write:

$$0 = Q_{in}\cancel{c_{Cl,in}} + Q_{stock}c_{Cl,stock} - \left(Q_{in} + Q_{stock}\right)c_{Cl} + r_{Cl}V$$

$$0 = Q_{stock}\left(c_{Cl,stock} - c_{Cl}\right) - Q_{in}c_{Cl} + r_{Cl}V$$

$$Q_{stock} = \frac{Q_{in}c_{Cl} - r_{Cl}V}{c_{Cl,stock} - c_{Cl}}$$

Substituting $\left(-0.20\,/\,\mathrm{h}\right)c_{Cl}$ for r_{Cl} and carrying out the necessary algebra, we find:

$$Q_{stock} = \frac{Q_{in}c_{Cl} - \left[\left(-0.2\,/\,\mathrm{h}\right)c_{Cl}\right]V}{c_{Cl,stock} - c_{Cl}} = \frac{\left(Q_{in} + \left(0.2\,/\,\mathrm{h}\right)V\right)c_{Cl}}{c_{Cl,stock} - c_{Cl}}$$

$$= \frac{\left[\left(0.8\ \mathrm{m^3/s}\right)\left(3600\ \mathrm{s/h}\right) + \left(0.2\,/\,\mathrm{h}\right)\left(3600\ \mathrm{m^3}\right)\right]\left(2\ \mathrm{mg/L}\right)}{1000\ \mathrm{mg/L} - 2\ \mathrm{mg/L}} = 7.21\frac{\mathrm{m^3}}{\mathrm{h}} = 2.00\frac{\mathrm{L}}{\mathrm{s}}$$

Note that, if the Cl were just diluted and did not react, the stock solution (1000 mg/L) would have to be diluted 500x to yield a concentration in the reactor of 2 mg/L. A 500x-dilution corresponds to a stock solution flow rate of (800 L/s)/500, or 1.6 L/s. Thus, the reaction increases the required dosing rate by 25%; more generally, the key point is that, by using a mass balance, we were able to carry out a mathematically simple analysis to answer an important question that we previously did not know how to address.

We can determine the expected bacterial population in the effluent by writing a mass balance on the organisms:

$$\frac{d}{dt}\left(\int_{\mathrm{CV}} c_{bact}\,dV\right)=\sum_{\mathrm{inflows}} Q_i c_{bact,i}-\sum_{\mathrm{outflows}} Q_i c_{bact,i}+\int_{\mathrm{CV}} r_{bact}\,dV$$

$$0=Q_{in}c_{bact,in}+Q_{stock}\,\cancel{c_{bact,stock}}-\left(Q_{in}+Q_{stock}\right)c_{bact}+r_{bact}V$$

$$=Q_{in}c_{bact,in}-\left(Q_{in}+Q_{stock}\right)c_{bact}-\left\{\frac{\left(3.0\ \mathrm{min}^{-1}\right)c_{Cl}}{1\ \mathrm{mg/L}+c_{Cl}}c_{bact}\right\}V$$

$$c_{bact}=\frac{Q_{in}c_{bact,in}}{\left(Q_{in}+Q_{stock}\right)+\dfrac{\left(3.0\ \mathrm{min}^{-1}\right)c_{Cl}}{1\ \mathrm{mg/L}+c_{Cl}}V}$$

$$=\frac{\left(0.8\dfrac{\mathrm{m}^3}{\mathrm{s}}\right)\left(10^4\ \dfrac{\mathrm{cells}}{\mathrm{L}}\right)}{\left(0.8\dfrac{\mathrm{m}^3}{\mathrm{s}}+4.3\dfrac{\mathrm{m}^3}{\mathrm{h}}\left(\dfrac{1\ \mathrm{h}}{3600\ \mathrm{s}}\right)\right)+\dfrac{\left(3.0\ \mathrm{min}^{-1}\right)\left(2\ \mathrm{mg/L}\right)}{1\ \mathrm{mg/L}+2\ \mathrm{mg/L}}\left(\dfrac{1\ \mathrm{min}}{60\ \mathrm{s}}\right)\left(3600\ \mathrm{m}^3\right)}=66\frac{\mathrm{cells}}{\mathrm{L}}$$

Thus, the bacterial concentration is reduced from 10,000 to 66 cells/L as the water passes through the tank. More generally, we see that by knowing the inputs, the reactor volume, and the reaction rate expression, we were able to use the mass balance to find the concentration inside the reactor, and also in the effluent. In other situations, we might know the influents, the rate expression, and the required effluent quality, and want to determine the reactor volume required to achieve the target; a similar approach can be used.

The preceding example presented a mass balance analysis for a CMR with flow, operating at steady-state and with two specific reaction rate expressions. Many systems have only a single significant inflow and outflow, or no flow at all. In the following pages, four general categories of reactors are identified, and expressions are developed for the change in pollutant concentration that can be expected in those systems. One or two example calculations are then shown for each category.

Case 1: Steady-state CMR, receiving a reactive substance with any reaction rate *r*.

$$\cancel{\frac{d\left(Vc\right)}{dt}}=Qc_{in}-Qc_{out}+rV$$

$$Q\left(c_{in}-c_{out}\right)=-rV$$

$$c_{in} - c_{out} = -r\frac{V}{Q} = -rt_d \qquad (2)$$

The results for first-order and second-order decay reactions are:

First order: $$c_{in} - c = k_1 c t_d \qquad (3a)$$

$$c = \frac{c_{in}}{1 + k_1 t_d}; \qquad t_d = \frac{1}{k_1}\left(\frac{c_{in}}{c_{out}} - 1\right) \qquad (3b, c)$$

Second order: $$c_{in} - c = k_1 c^2 t_d \qquad (4a)$$

$$c = \frac{-1 + \sqrt{1 + 4k_2 t_d c_{in}}}{2k_2 t_d}; \qquad t_d = \frac{1}{k_2 c_{out}}\left(\frac{c_{in}}{c_{out}} - 1\right) \qquad (4b, c)$$

***Example* 2.** Under certain circumstances, the rate of oxidation of iron to a form that precipitates out of solution is second order: $r_{Fe^{2+}} = -k_2 c^2_{Fe^{2+}}$, with $k_2 = 6000\,M^{-1}\text{s}^{-1}$. If these conditions apply, what mean residence time is required in a CMR at steady-state to lower the Fe^{2+} concentration from 4 μM to 0.2 μM? If the flow rate is 0.5 m^3/s, what size tank is required?

Solution. For the given conditions (second order reaction in a steady-state CMR), we can substitute known values into Equation 4c to determine the required t_d to accomplish the desired degree of reaction. The result is:

$$t_d = \frac{1}{\left(6000M^{-1}s^{-1}\right)\left(0.2\text{x}10^{-6}M\right)\left(60 \text{ s/min}\right)}\left(\frac{4\text{x}10^{-6}M}{0.2\text{x}10^{-6}M} - 1\right) = 26.4 \text{ min}$$

Then, according to Equation 3:

$$V = Qt_d = \left(0.5\frac{\text{m}^3}{\text{s}}\right)\left(26.4 \text{ min}\right)\left(\frac{60 \text{ s}}{\text{min}}\right) = 792 \text{ m}^3$$

***Example* 3.** Air is to be bubbled through the solution in the reactor described above, in order to strip out of the solution trace amounts of a solvent that have contaminated the water. The rate of loss of the solvent from the solution can be characterized by the equation $r = -\left(0.03/\text{min}\right)c$, where c is the solvent concentration. What fraction of the solvent will be removed from the water as it passes through the reactor?

Solution. The removal of solvent from the solution is characterized by a first-order rate equation. Since the reactor is a steady-state CMR, the change in c is therefore given by Equation 3b. Substituting known values into that equation, we find:

$$\frac{c}{c_{in}} = \frac{1}{1+k_1 t_d} = \frac{1}{1+\left(0.03/\min\right)\left(26.4\ \min\right)} = 0.558$$

Thus, 55.8% of the solvent will remain in the solution, and 44.2% will be removed.

Case 2: Non-steady-state CMR, receiving a non-reactive substance (tracer)

Another situation of interest is the non-steady state response of a CMR to a step change in the input concentration of a non-reactive substance ($r = 0$), commonly referred to as a ***tracer***. Tracers are used as diagnostic tools to determine mixing patterns in reactors and to assess whether reactors have dead space. Consider a CMR with a single inflow and single outflow, both of the same magnitude (so that V is constant), which contains some concentration of tracer at time zero [$c(0)$]. Then, right at $t = 0$, the input concentration of tracer changes to c_{in}, which is different from $c(0)$. We wish to predict the tracer concentration exiting the CMR at all subsequent times ($t > 0$). To do so, we begin by writing the mass balance equation for the tracer. Because $r = 0$, the generic mass balance for a CMR can be simplified as follows:

$$\frac{d\left(Vc\right)}{dt} = Qc_{in} - Qc_{out} + \cancel{rV}$$

$$\frac{dc}{c_{in} - c_{out}} = \frac{Q}{V}dt = \frac{1}{t_d}dt$$

Equating c with c_{out} (because the reactor is a CMR), carrying out the integration for the constant value of c_{in} (at $t > 0$), and rearranging, we find:

$$-\ln\frac{c_{in} - c\left(t\right)}{c_{in} - c\left(0\right)} = \frac{t-0}{t_d} = \frac{t}{t_d}$$

$$\ln\frac{c_{in} - c\left(t\right)}{c_{in} - c\left(0\right)} = -\frac{t}{t_d}$$

$$c\left(t\right) = c_{in} - \left(c_{in} - c\left(0\right)\right)\exp\left(-\frac{t}{t_d}\right) \qquad (5)$$

In many cases, rather than a step change in tracer input concentration, a tracer that is not present in the "normal" influent is added as a spike at the time designated $t = 0$, and no more is added thereafter. In that case, the added tracer immediately disperses throughout the reactor (this is the nature of a CMR), so $c(0)$ equals the mass of tracer added divided by the volume of water in the CMR. Then, at all $t > 0$, c_{in} is zero. Thus, rather than a gradual increase in tracer concentration to c_{in} (as occurs when $c(0) = 0$ and $c_{in} > 0$), the tracer concentration following a spike input gradually decreases from $c(0)$ to 0. Despite these differences, both scenarios are characterized by the same mass balance equation, so both obey Equation 5; the result for the spike input can be obtained by substituting $c_{in} = 0$ into that equation, yielding:

$$c(t) = c(0)\exp\left(-\frac{t}{t_d}\right) \tag{6}$$

The mass of tracer (or, for that matter, any constituent) that exits over any short period dt is given by $c\,Q\,dt$, so the mass that has exited from time zero until some later time t is $\int_0^t Qcdt$.

Example 4. Due to algal growth in a water supply reservoir in a neighborhood, the water has acquired an unpleasant taste. The compound is non-degradable, and the water utility has decided that the best way to deal with the situation is simply to flush the contaminant out of the system. The reservoir contains 11,000 m^3 of water, and the proposal is to pump 300 m^3/h of clean water through the system and discharge the effluent to the sewer system until 95% of the offending compound has been removed. If the reservoir is intensely mixed, how much flushing water will be required?

Solution. The compound is non-reactive and therefore behaves as a tracer. The contaminant concentration in the flushing water is zero, so Equation 6 applies. When 95% of the contaminant has been flushed out, the concentration will be 5% of the initial concentration, so:

$$\frac{c(t)}{c(0)} = 0.05 = \exp\left(-\frac{t}{t_d}\right)$$

$$t = -t_d \ln(0.05)$$

The hydraulic detention time in the reservoir during the flushing operation will be:

$$t_d = \frac{V}{Q} = \frac{11{,}000\ \mathrm{m}^3}{300\ \mathrm{m}^3/\mathrm{h}} = 36.7\ \mathrm{h}$$

so the required flushing time and the volume of flushing water will be:

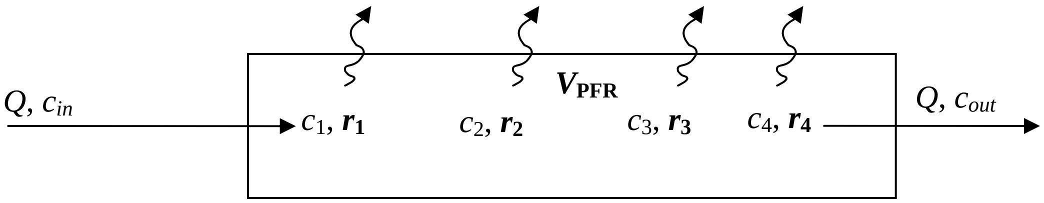
$$t = -t_d \ln(0.05) = -(36.7\ \mathrm{h})(-3.00) = 110\ \mathrm{h}$$

$$V_{req'd} = Qt_d = 300\ \mathrm{m}^3/\mathrm{h}(110\ \mathrm{h}) = 33{,}000\ \mathrm{m}^3$$

Case 3: Steady-state PFR, receiving a reactive substance

Although many reactors are intensely mixed, with the goal of achieving the ideal case of a CMR, other reactors are designed to have minimal mixing, with the ideal being no mixing at all.

As noted above, the ideal, limiting case for such a situation is the PFR. In a PFR, the water does not mix at all with water that came into the reactor earlier or water that comes in later. In effect, each droplet of water flows through the PFR completely "unaware" that other water is also present; each droplet might as well be in a separate container, moving through reactor as though the container were on a conveyor belt. If a substance is undergoing a reaction in such a container, its concentration will change as it moves. Correspondingly, the concentration in a PFR changes as a function of the amount of time that the solution is in the reactor, and hence as a function of the location of the water in the reactor (*i.e.*, for a substance that is being destroyed, the concentration decreases from the inlet to the outlet). This is the primary difference between a CMR and a PFR.



Like CMRs, PFRs can be operated at steady-state. However, in the case of a PFR, even though the concentration at any particular location is constant over time, the concentration varies from one location to the next. When we analyze the amount of reaction in a PFR at steady-state, we might try to start with Equation 2, which is the mass balance equation for a CMR at steady-state:

$$\cancel{\frac{d\left(Vc\right)}{dt}} = Qc_{in} - Qc_{out} + rV \tag{2}$$

However, if we try to substitute an expression for r into Equation 2 for a PFR, we encounter a problem: r is likely to have different values at different locations in the reactor, since r depends on c, and c varies from one location to another in the reactor. (Recall that, in a CMR, we could equate c at all points inside the reactor with c_{out}; therefore, r had the same value everywhere in the reactor.) To overcome this problem, rather than choosing the whole reactor as the control volume for our analysis, we choose a differential volume (in which the concentration can be considered to be uniform). In that case, the mass balance equation becomes:

$$0 = Qc - Q\left(c + \frac{dc}{dx}dx\right) + rAdx$$

$$Q\frac{dc}{dx} = rA$$

$$\frac{dc}{r} = \frac{A}{Q}dx$$

$$\int_{c_{in}}^{c_{out}} \frac{dc}{r} = \frac{A}{Q}\int_0^L dx = \frac{AL}{Q} = \frac{V}{Q} = t_d \qquad (7)$$

First order: $$\int_{c_{in}}^{c_{out}} \frac{dc}{-k_1 c} = t_d \qquad (8a)$$

$$\ln\frac{c_{out}}{c_{in}} = -k_1 t_d$$

$$c_{out} = c_{in}\exp\left(-k_1 t_d\right); \qquad t_d = \frac{1}{k_1}\ln\frac{c_{out}}{c_{in}} \qquad (8b, c)$$

Second order: $$\int_{c_{in}}^{c_{out}} \frac{dc}{-k_2 c^2} = t_d \qquad (9)$$

$$c_{out} = \frac{c_{in}}{1 + k_2 t_d c_{in}}; \qquad t_d = \frac{1}{k_2}\left(\frac{1}{c_{out}} - \frac{1}{c_{in}}\right) \qquad (9b, c)$$

***Example* 5**. In Example 3, we computed that 44.2% of a solvent in a water supply would be stripped in a CMR with a hydraulic detention time of 26.4 min, if the removal of the solvent obeyed the rate equation $r = -\left(0.03/\text{min}\right)c$. What fraction of the solvent would be removed in a PFR with the same detention time, if the rate expression were also the same?

Solution. Plugging values into Equation 8b:

$$c_{out} = c_{in}\exp\left(-k_1 t_d\right)$$

$$\frac{c_{out}}{c_{in}} = \exp\left\{-\frac{0.03}{\text{min}}\left(26.4\ \text{min}\right)\right\} = 0.453$$

Since 45.3% of the solvent remains in the solution, 54.7% has been stripped. Apparently, the PFR is more effective than the CMR at stripping the pollutant out of the water, even though they have the same residence time (and therefore the same reactor volume, for a given flow rate).

Case 4: Batch reactor containing a reactive substance

The final type of system that we will consider is a batch reactor, *i.e.*, a reactor that has no flow in or out. Batch reactors are useful for investigating reaction rates and are occasionally used for treatment processes. Batch reactors operate under non-steady-state conditions. In this case, the volume is constant, and the mass balance simplifies to:

$$\frac{d\left(Vc\right)}{dt} = \cancel{Qc}_{in} - \cancel{Qc}_{out} + rV$$

$$\frac{dc}{dt} = r \tag{10}$$

$$\int_{c(0)}^{c(t)} \frac{dc}{r} = \int_{0}^{t} dt = t \tag{11}$$

Note that this result is identical to that for a PFR system (Equation 11), with the substitution of $c(0)$, $c(t)$, and t for c_{in}, c_{out}, and t_d, respectively. We conclude that *the extent of reaction in a PFR with influent concentration* c_{in} *and residence time* t_d *is identical to the extent of reaction that would occur in a batch reactor with the same initial solution [c(0)], after a reaction time equal to the detention time of the PFR. This conclusion applies regardless of the details of the reaction rate* r. The reason that this result is obtained is that a PFR is identical to "beakers on a conveyor belt." The beakers represent a batch of fluid that is moving through space, but is not mixing with the water upstream or downstream. Since the extent of reaction in a beaker doesn't depend on whether the beaker is sitting still or moving, it makes sense that the amount of reaction that has occurred in an imaginary beaker (on the conveyor belt) is the same as the amount that would occur if the beaker were stationary, if the time of reaction in the stationary beaker were the same as the detention time in the PFR.

***Example* 6**. What fraction of the solvent would be removed from the influent solution from Examples 3 and 5, if the solution were placed in a batch reactor for a time equal to t_d, and if the rate expression was the same in the batch reactor as in the reactors with flow?

Solution. The removal in the batch reactor would be identical to that in the PFR (and greater than that in the CMR), *i.e.*, 54.7% of the contaminant would be removed from the solution.

The results for all the systems described above are summarized in Table 1.

Table 1a. Summary of Performance of CMRs at Steady State for n^{th} Order Reactions

Reaction order, n ($r = -k_n c^n$)	c_{out}	$\dfrac{c_{out}}{c_{in}}$	t_d
0	$c_{in} - k_0 t_d$	$1 - \dfrac{k_0 t_d}{c_{in}}$	$\dfrac{c_{out}}{k_0}\left(\dfrac{c_{in}}{c_{out}} - 1\right)$
1	$\dfrac{c_{in}}{1 + k_1 t_d}$	$\dfrac{1}{1 + k_1 t_d}$	$\dfrac{1}{k_1}\left(\dfrac{c_{in}}{c_{out}} - 1\right)$
2	$\dfrac{-1 + \sqrt{1 + 4k_2 t_d c_{in}}}{2k_2 t_d}$	$\dfrac{1}{1 + k_2 t_d c_{out}}$	$\dfrac{1}{k_2 c_{out}}\left(\dfrac{c_{in}}{c_{out}} - 1\right)$
any n	Numerical solution	$\dfrac{1}{1 + k_n t_d c_{out}^{n-1}}$	$\dfrac{1}{k_n c_{out}^{n-1}}\left(\dfrac{c_{in}}{c_{out}} - 1\right)$

Table 1b. Summary of Performance of PFRs at Steady State or Batch Reactors for n^{th} Order Reactions(a)

Reaction order, n ($r = -k_n c^n$)	c_{out}	$\dfrac{c_{out}}{c_{in}}$	t_d
0	$c_{in} - k_0 t_d$	$1 - \dfrac{k_0 t_d}{c_{in}}$	$\dfrac{1}{k_0}\left(c_{in} - c_{out}\right)$
1	$c_{in} \exp(-k_1 t_d)$	$\exp(-k_1 t_d)$	$\dfrac{1}{k_1} \ln \dfrac{c_{in}}{c_{out}}$
2	$\dfrac{c_{in}}{1 + k_2 t_d c_{in}}$	$\dfrac{1}{1 + k_2 t_d c_{in}}$	$\dfrac{1}{k_2 c_{in}}\left(\dfrac{c_{in}}{c_{out}} - 1\right)$
any $n \neq 1$	$\left[(n-1)k_n t_d + c_{in}^{1-n}\right]^{\frac{1}{1-n}}$	$\left(1 + (n-1)k_n t_d c_{in}^{n-1}\right)^{\frac{1}{1-n}}$	$\dfrac{1}{(n-1)k_{\mathrm{n}} c_{in}^{n-1}}\left[\left(\dfrac{c_{in}}{c_{out}}\right)^{n-1} - 1\right]$

(a) For batch reactors, replace c_{in} with $c(0)$, c_{out} with $c(t)$, and t_d with t

Table 1c. Summary of Behavior of a Tracer In a CMR or PFR

Reactor Type	Equation	Notes
CMR	$c(t) = c_{in} - (c_{in} - c(0))\exp\left(-\frac{t}{t_d}\right)$	c_{out} at t for system with initial conc'n $c(0)$ and steady input of c_{in} thereafter
CMR	$c(t) = c(0)\exp\left(-\frac{t}{t_d}\right)$	c_{out} at t for system with initial conc'n $c(0)$ and $c_{in} = 0$ thereafter[a]
PFR	$c_{out} @ t = c_{in} @ (t - t_d)$	Regardless of input concentration, output is identical, but delayed by t_d

[a] For example, for a spike input at $t = 0$ and input of clean water thereafter

The preceding analyses can be extended to provide additional information or to explore the behavior of more complicated systems. For example, if we wanted to know the fraction of the water that was in a CMR at time zero that is still there at some future time, we could apply the following logic. Imagine that all the water in the tank contained a tracer at some known concentration at $t = 0$, and that the water entering the tank at all subsequent times contained no tracer. In that case, the fraction of the original mass of tracer remaining in the tank at any given time would correspond to the fraction of the water that remained. According to the CMR Case 2 analysis above, the concentration of tracer in the effluent from such a tank would be given by:

$$c(t) = \cancel{c_{in}}\left(1 - \exp\left(-\frac{t}{t_d}\right)\right) + c(0)\exp\left(-\frac{t}{t_d}\right)$$

$$= c(0)\exp\left(-\frac{t}{t_d}\right)$$

The mass of tracer in the reactor initially is $Vc(0)$, and the amount remaining at time t is $Vc(t)$, so the fraction of the original tracer mass that remains in the reactor at time t is:

$$\frac{c(t)}{c(0)} = \frac{c(0)\exp\left(-\frac{t}{t_d}\right)}{c(0)} = \exp\left(-\frac{t}{t_d}\right)$$

We find, therefore, for example, that after a time equal to twice the residence time (i.e., $t = 2t_d$), the fraction of the tracer remaining is $\exp(-2t_d/t_d)$, or $\exp(-2)$, which equals about 13.5%. Correspondingly, in a CMR, 13.5% of the water that is in the tank originally remains after two residence times.

Finally, note that CMRs and PFRs are idealized endpoints of a continuum of mixing. Intermediate degrees of mixing are modeled in various ways, but one of the most common is to imagine that a system consists of several CMRs in series. Both conceptual and mathematical analyses show that, as a single CMR is divided into more and more small CMRs in series, the reactor behaves more like a PFR, both for tracers and reactive substances.