# 4

# The Material Balance for Chemical Reactors

## 4.1 General Mole Balance

Consider an arbitrary reactor volume element depicted in Figure 4.1, which has inlet and outlet streams with volumetric flowrates $Q_0$ and $Q_1$, respectively. The molar concentrations of component $j$ in the two streams are given by $c_{j0}$ and $c_{j1}$ and the production rate of component $j$ due to chemical reactions is $R_j$. The statement of conservation of mass for this system takes the form,

$$\left\{\begin{array}{c}\text{rate of}\\ \text{accumulation}\\ \text{of component } j\end{array}\right\} = \left\{\begin{array}{c}\text{rate of inflow}\\ \text{of component } j\end{array}\right\} - \left\{\begin{array}{c}\text{rate of outflow}\\ \text{of component } j\end{array}\right\} + \left\{\begin{array}{c}\text{rate of generation}\\ \text{of component } j \text{ by}\\ \text{chemical reactions}\end{array}\right\} \tag{4.1}$$

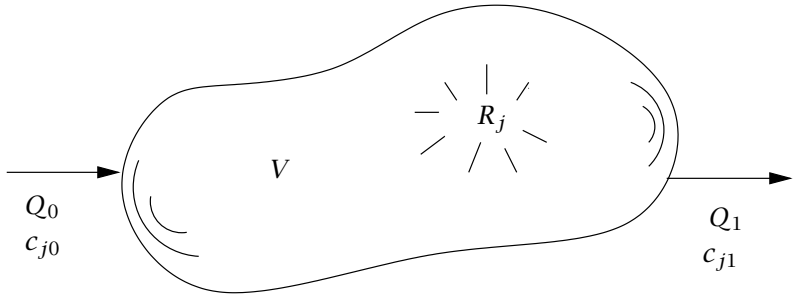


**Figure 4.1:** Reactor volume element.

In terms of the defined variables, we can write Equation 4.1 as,

$$\frac{d}{dt}\int_V c_j dV = Q_0 c_{j0} - Q_1 c_{j1} + \int_V R_j dV \tag{4.2}$$

Equation 4.2 applies to every chemical component in the system, $j = 1, 2, \ldots, n_s$, including inerts, which do not take place in any reactions. One can, of course, include volume elements with more than two flow streams by summing with the appropriate sign over all streams entering and leaving the reactor. For the balances in this chapter, there will be two or fewer flow streams. Notice also that we are assuming that component $j$ enters and leaves the reactor volume element only by convection with the inflow and outflow streams. In particular, we are neglecting diffusional flux through the boundary of the volume element due to a concentration gradient. The diffusional flux will be considered during the development of the material balance for the packed-bed reactor.

**Rate expressions.** To solve the reactor material balance, we require an expression for the production rate, $R_j$, for each component. As shown in Chapter 2, the production rate can be computed directly from the stoichiometry and the reaction rates for all reactions, $r_i$. Therefore we require an expression for the reaction rates in terms of the concentrations of the species. This topic occupies the majority of Chapter 5. For the purposes of illustrating the material balances in this chapter, we simply use some common reaction-rate expressions without derivation. These rate expressions may be regarded as empirical facts until the next chapter when the theoretical development of the rate expressions is provided.

## 4.2 The Batch Reactor

The batch reactor is assumed to be well stirred, so there are no concentration gradients anywhere in the reactor volume. In this case it is natural to consider the entire reactor contents to be the reactor volume element as in Figure 4.2, and $V = V_R$. Because the reactor is well stirred, the integrals in Equation 4.2 are simple to evaluate,

$$\int_{V_R} c_j dV = c_j V_R \tag{4.3}$$

$$\int_{V_R} R_j dV = R_j V_R \tag{4.4}$$

Because the reactor is charged with reactants at $t = 0$, and nothing is added or removed from the reactor until the stopping time, the inflow and outflow stream flowrates are zero, $Q_0 = Q_1 = 0$.

Substituting these results into Equation 4.2 gives the general batch reactor design equation,

$$\frac{d\left(c_j V_R\right)}{dt} = R_j V_R \tag{4.5}$$

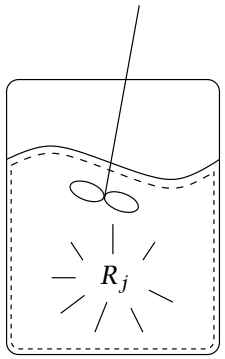


**Figure 4.2:** Batch reactor volume element.

Equation 4.5 applies whether the reactor volume is constant or changes during the course of the reaction. If the reactor volume is constant, which is sometimes a good approximation for liquid-phase reactions, $V_R$ can be divided out of both sides of Equation 4.5 to give

$$\frac{dc_j}{dt} = R_j \tag{4.6}$$

Be sure to use Equation 4.5 rather than Equation 4.6 if the reactor volume changes significantly during the course of the reaction.

### 4.2.1 Analytical Solutions for Simple Rate Laws

In complex and realistic situations, the material balance for the batch reactor must be solved numerically. However, if the reactor is isothermal, and the rate laws are assumed to be quite simple, then analytical solutions of the material balance are possible. Analytical solutions are valuable for at least two reasons. First, due to the closed form of the solution, analytical solutions provide insight that is difficult to achieve with numerical solutions. The effect of parameter values on the solution is usually more transparent, and the careful study of analytical solutions can often provide insight that is hard to extract from numerical computations. Secondly, even if one must compute a numerical solution for a problem of interest, the solution procedure should be checked for errors by comparison to known solutions. Comparing a numerical solution procedure to an analytical solution for a simplified problem provides some assurance that the numerical procedure has been constructed correctly. Then the verified numerical procedure can

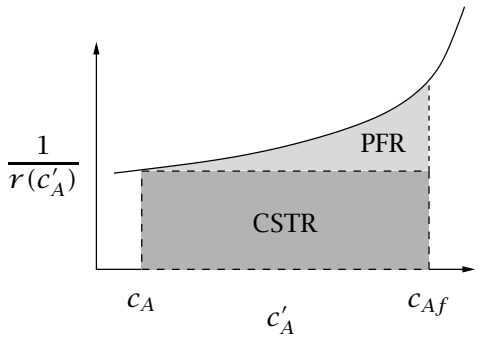


**Figure 4.25:** To achieve the same conversion, the CSTR is smaller than the PFR for irreversible, $n$th-order kinetics, negative order, $n < 0$.

**Example 4.8: The PFR versus CSTR with separation**

We have noticed that a PFR achieves higher conversion than an equivalent volume CSTR for the irreversible reaction with first-order kinetics

$$\mathrm{A} \longrightarrow \mathrm{B} \qquad r = k\mathrm{c_A}$$

Consider the case in which we add separation. Find a single CSTR and separator combination that achieves the same conversion as the PFR. You may assume a perfect separation of A and B, the feed is a pure A stream, and $k\theta = 1$ for the PFR.

**Solution**

The PFR achieves a fractional conversion of A

$$x_{\mathrm{PFR}} = 1 - N_A/N_{A0} = 1 - \exp(-k\theta) = 0.632$$

For an equivalent volume CSTR without separation, the conversion of A is

$$x_{\mathrm{CSTR}} = 1 - N_A/N_{A0} = k\theta/(1 + k\theta) = 0.5$$

The goal is to increase the achievable conversion in the CSTR using separation. Education in chemical engineering principles leads one immediately to consider recycle of the unreacted A as a means to increase this conversion. Consider the flowsheet depicted in Figure 4.26. A fraction of the outflow from the CSTR is recycled, the product B is removed and the unreacted A is combined with the feed as the inflow of the CSTR.

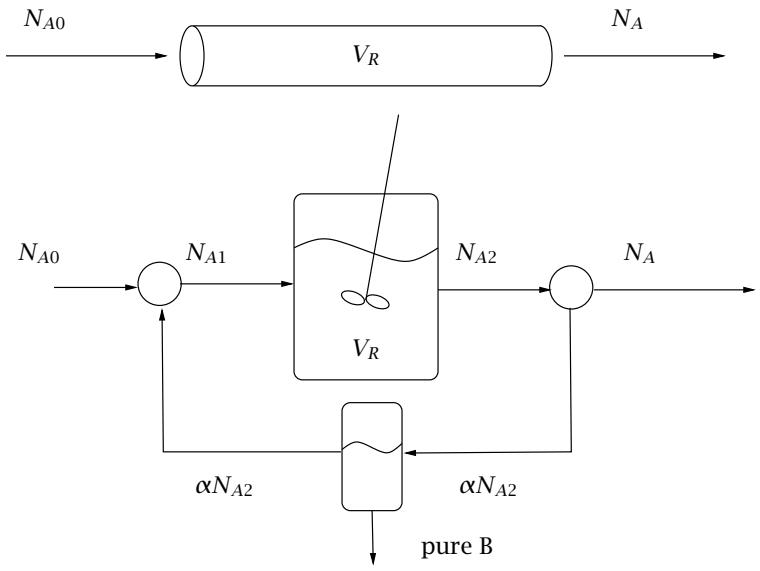


**Figure 4.26:** PFR versus CSTR with recycle and separation.

Given the assumption of perfect separation, we can achieve essentially complete conversion of A for $k\theta = 1$ with complete recycle, so our goal here is to calculate the fractional recycle, $\alpha$, that achieves exactly the PFR conversion. For $k\theta < 1$ the achievable conversion is less than one as discussed in Exercise 4.14.

Notice first that the mean residence time of the CSTR, $\theta'$, is less than that for the PFR, $\theta$, because the flowrate has increased due to the recycle. Notice that with perfect separation, pure A streams are combined at the mixer, and $Q_0/Q_1 = N_{A0}/N_{A1}$ so

$$\theta' = V_R/Q_1 = (V_R/Q_0)(Q_0/Q_1) = \theta N_{A0}/N_{A1}$$

We may consider four variables to specify the state of the system: $\alpha, N_{A1}, N_{A2}, N_A$; and we can write three component A material balances for the reactor, splitter at reactor exit and mixer at reactor inlet

$$\begin{aligned} \text{reactor:} \quad & N_{A2} = N_{A1}/(1 + k\theta N_{A0}/N_{A1}) \\ \text{splitter:} \quad & N_A = (1 - \alpha)N_{A2} \\ \text{mixer:} \quad & N_{A1} = N_{A0} + \alpha N_{A2} \end{aligned}$$

The separator balance is trivial because the separation of A is perfect, and, therefore, the molar flow of A is conserved across the recycle

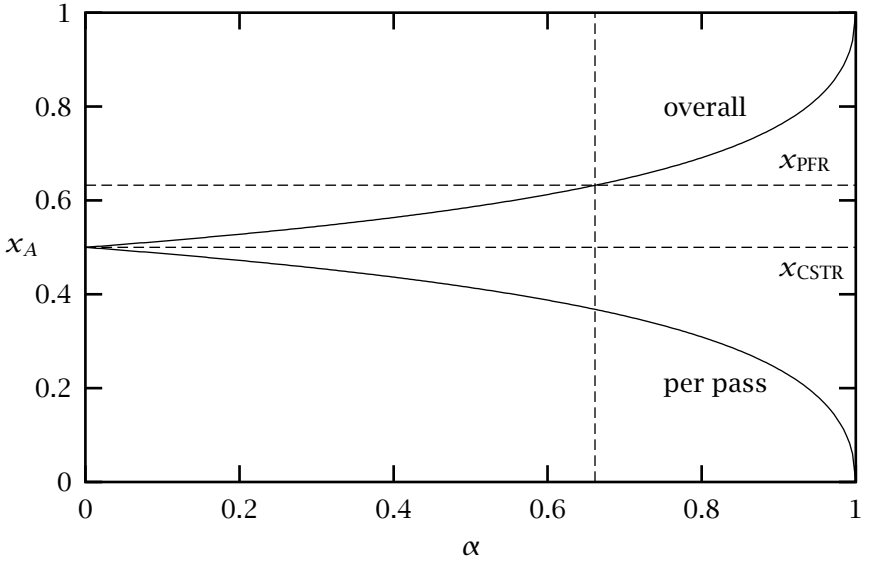


**Figure 4.27:** Overall and per-pass conversion of A as a function of fractional recycle, $\alpha$.

stream. Because the inlet flow of A is not specified, it is convenient to divide the preceding equations by $N_{A0}$, define dimensionless molar flows, and rearrange to obtain

$$\begin{aligned} \text{reactor:} \quad & \overline{N}_{A2}(1 + k\theta/\overline{N}_{A1}) - \overline{N}_{A1} = 0 \\ \text{splitter:} \quad & \overline{N}_A - (1-\alpha)\overline{N}_{A2} = 0 \\ \text{mixer:} \quad & 1 + \alpha\overline{N}_{A2} - \overline{N}_{A1} = 0 \end{aligned} \tag{4.91}$$

We can specify a single variable as known and solve for the remaining three with the three equations. For example, if we specify the recycle fraction, $\alpha$, we can solve Equations 4.91 for $\overline{N}_A, \overline{N}_{A1}, \overline{N}_{A2}$, and compute the conversion from $x_A = 1 - \overline{N}_A$. Figure 4.27 shows the resulting conversion of A plotted as a function of $\alpha$. We can see from Figure 4.27 that the PFR conversion is achieved at about $\alpha = 0.65$. If we want a more accurate answer, we can set $\overline{N}_A = \exp(-k\theta) = 0.3678$ and solve

numerically for $\alpha, \overline{N}_{A1}, \overline{N}_{A2}$, with Equations 4.91[1] , and the result is

$$\alpha = 0.6613$$

□

**CSTR equivalence principle.** Example 4.8 is motivated by a recent result of Feinberg and Ellison called the CSTR equivalence principle of reactor-separator systems [4]. This surprising principle states:

> For a given reaction network with $n_i$ linearly independent reactions, any steady state that is achievable by any reactor-separator design with total reactor volume $V$ is achievable by a design with *not more than* $n_i + 1$ *CSTRs*, also of total reactor volume $V$. Moreover the concentrations, temperatures and pressures in the CSTRs are arbitrarily close to those occurring in the reactors of the original design.

Applying this principle to the last example, we know that any achievable concentration of the PFR for a single reaction is achievable with a CSTR and separation. Note the number of CSTRs can be reduced from $n_i + 1$ to $n_i$ in certain situations, such as the one considered in Example 4.8. And we know the concentration in the CSTR will be achieved somewhere in the PFR.

## 4.8 Stochastic Simulation of Chemical Reactions

We wish to introduce next a topic of increasing importance to chemical engineers, stochastic (random) simulation. In stochastic models we simulate quite directly the random nature of the molecules. We will see that the deterministic rate laws and material balances presented in the previous sections can be captured in the stochastic approach by allowing the numbers of molecules in the simulation to become large. From this viewpoint, deterministic and stochastic approaches are complementary. Deterministic models and solution methods are quite efficient when the numbers of molecules are large and the random behavior is not important. The numerical methods for solution of the nonlinear differential equations of the deterministic models are

[1] Note one can solve this simple problem analytically as well. Eliminate $\alpha\overline{N}_{A2}$ from the second and third equations in Equation 4.91. Substitute the result into the first equation and solve the resulting quadratic equation.

also highly developed. The stochastic modeling approach is appropriate if the random nature of the system is one of the important features to be captured in the model. These situations are becoming increasingly important to chemical engineers as we explore reactions at smaller and smaller length scales. For example, if we are modeling the chemical transformation by reaction of only a few hundreds or thousands of molecules at an interface, we may want to examine explicitly the random fluctuations taking place. In biological problems, we often consider the interactions of only several hundred or several thousand protein molecules and cells. In sterilization problems, we may wish to model the transient behavior until every last organism is eliminated.

It is perhaps best to illustrate features of the stochastic approach with a simple example. Instead of the common case in which we have on the order of Avogadro's number of reacting molecules, assume we have only a hundred molecules moving randomly in the gas phase and we wish to follow the reaction

$$\mathrm{A} \xrightarrow{\mathrm{k_1}} \mathrm{B} \tag{4.92}$$

$$\mathrm{B} \xrightarrow{\mathrm{k_2}} \mathrm{C} \tag{4.93}$$

in a constant-volume batch reactor. In this section we take reaction statements quite literally. We assume these reactions are not merely observed stoichiometries, but actual molecular events.

The *probability* of reaction is assumed proportional to the

$$r_1 = k_1 x_A, \qquad r_2 = k_2 x_B$$

in which $x_j$ is the *number* of component $j$ molecules in the reactor volume. Note $x_j$ is an integer, unlike $c_j$ of the deterministic model, which is real. The reaction probabilities play the role of the rate expressions in the deterministic models. Given the stoichiometry and the reaction probabilities, we would like to simulate the expected behavior of the reaction network. One way to accomplish this task is the Gillespie algorithm, which we describe next. The basic idea of the Gillespie algorithm is to: (i) choose randomly the time at which the next reaction occurs, and (ii) choose randomly which reactions occurs at that time. Of course we do not choose completely randomly. If the total reaction probabilities are large, it is intuitively clear that the time interval until the next reaction should be small, and, if reaction probability $r_1$ is much larger than $r_2$, the first reaction is more likely to occur at the next reaction

time. The beauty of the Gillespie algorithm is the simple and statistically correct manner in which these two random choices are made.

In a series of papers, Gillespie makes an elegant argument for the use of stochastic simulation in chemical kinetic modeling [7, 8] and provides the following simulation algorithm [7, p.2345].

1. Initialize. Set integer counter $n$ to zero. Set the initial species numbers, $x_j(0), j = 1, \ldots n_s$. Determine stoichiometric matrix $\boldsymbol{\nu}$ and reaction probability laws (rate expressions)

   $$r_i = k_i h(x_j)$$

   for all reactions.

2. Compute reaction probabilities, $r_i = k_i h(x_j)$. Compute total reaction probability $r_{\text{tot}} = \sum_i r_i$.

3. Select two random numbers, $p_1, p_2$, from a uniform distribution on the interval $(0, 1)$. Let the time interval until the next reaction be

   $$\tau = -\ln(p_1)/r_{\text{tot}} \tag{4.94}$$

   Determine reaction $m$ to take place in this time interval. The idea here is to partition the interval (0,1) by the relative sizes of each reaction probability and then "throw a dart" at the interval to pick the reaction that occurs. In this manner, all reactions are possible, but the reaction is selected in accord with its probability. See Figure 4.28.

4. Update the simulation time $t(n+1) = t(n) + \tau$. Update the species numbers for the single occurrence of the $m$th reaction via

   $$x_j(n+1) = x_j(n) + \nu_{mj}, \qquad j = 1, \ldots n_s$$

   Let $n = n + 1$. Return to Step 2.

If $r_{tot}$ is the total probability for reaction, $e^{-r_{tot}\tau}$ is the probability that a reaction has not occurred during time interval $\tau$, which leads directly to Equation 4.94 for choosing the time of the next reaction. We will derive this fact in Chapter 8 when we develop the residence-time distribution for a CSTR. Shah, Ramkrishna and Borwanker call this time the "interval of quiescence," and use it to develop a stochastic simulation algorithm for particulate system dynamics rather than chemical kinetics [14].

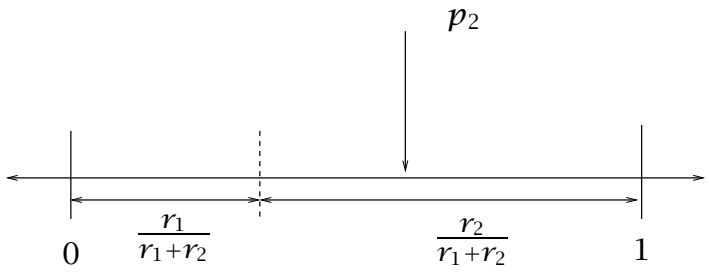


**Figure 4.28:** Randomly choosing a reaction with appropriate probability; the interval is partitioned according to the relative sizes of the reaction rates; a random number $p_2$ between zero and one is generated to determine the reaction; in this case, $m = 2$ and the second reaction is selected.

Figure 4.29 shows the results of this algorithm when starting with $x_A = 100$ molecules. Notice the random aspect of the simulation gives a rough appearance to the number of molecules versus time, which is quite unlike any of the deterministic simulations presented in Section 4.2. In fact, because the *number* of molecules is an integer, the simulation is actually discontinuous with jumps between simulation times. But in spite of the roughness, we already can make out the classic behavior of the series reaction: loss of starting material A, appearance and then disappearance of the intermediate species B, and slow increase in final product C. Note also that Figure 4.29 is only *one* simulation of the stochastic model. Unlike the deterministic models, if we repeat this simulation, we obtain a different sequence of random numbers and a different simulation. To talk about expected or average behavior of the system, we must perform many of these random simulations and then compute the averages of quantities we wish to report.

Next we explore the effect of increasing the initial number of A molecules on a single simulation. The results for 1000 and 4000 initial A molecules are shown in Figures 4.30 and 4.31, respectively. We see the random fluctuations become less pronounced. Notice that even with only 4000 starting molecules, Figure 4.31 compares very favorably with the deterministic simulation shown in Figure 4.11 of Section 4.2.

Another striking feature of the stochastic approach is the trivial

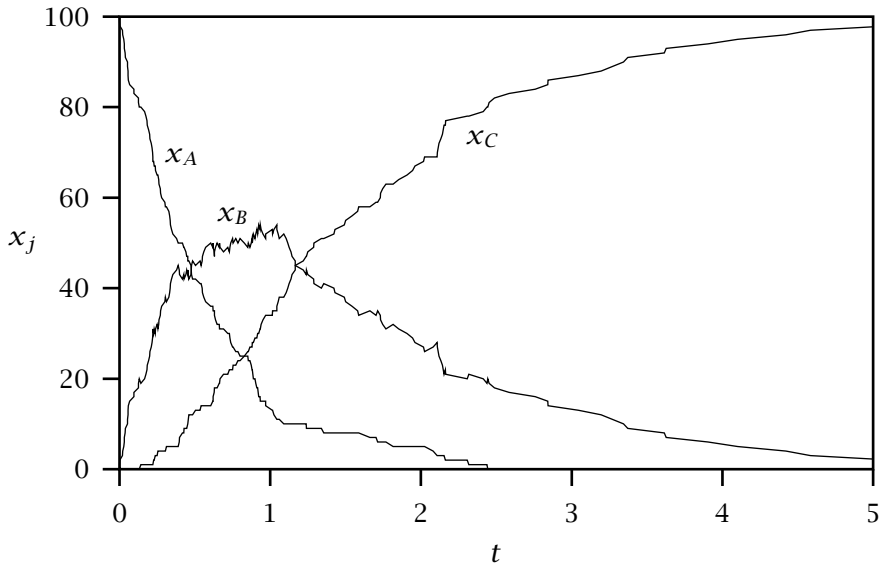


**Figure 4.29:** Stochastic simulation of the first-order reactions A⟶B⟶C starting with 100 A molecules.

level of programming effort required to make the simulations. In fact, the biggest numerical challenge is producing the random numbers,[2] and many well-developed algorithms are available for that task. The computational time required for performing the stochastic simulation may, however, be large. The solution time depends on the number of simulation steps, and also on whether or not we must repeat the simulations to calculate averages. Usually large numbers of simulation steps are chosen when one has large numbers of initial molecules. If reliable deterministic rate laws are available, at some point it becomes more efficient to use the deterministic models as the number of molecules increases.

But the stochastic approach is invaluable in several ways. It builds a clear intuitive connection between the microscopic and the macroscopic. The microscopic level is characterized by discontinuous, random molecular motion and the probability of collision as the basis for chemical reaction rate. The macroscopic level is characterized by

[2]It is more accurate to use the term pseudo-random number here to distinguish something we compute from a truly random number.

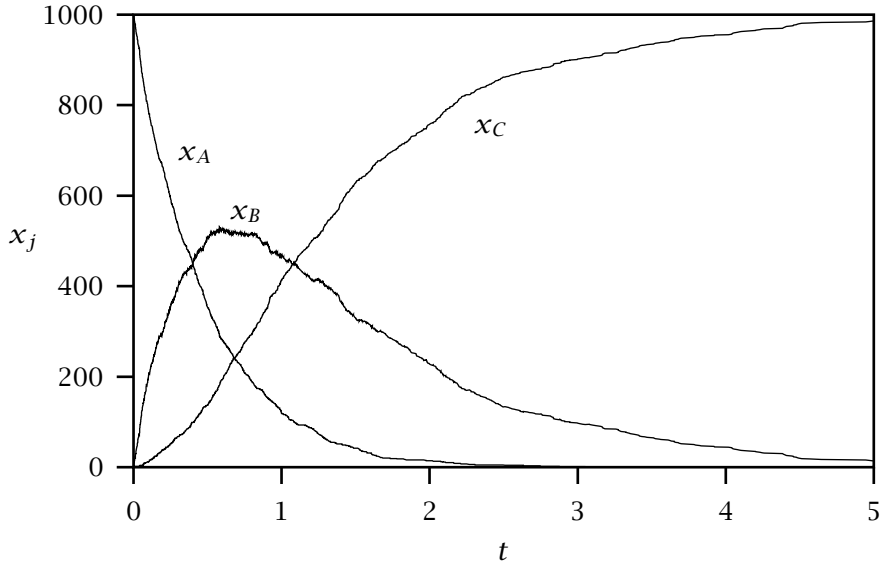


**Figure 4.30:** Stochastic simulation of the first-order reactions A⟶B⟶C starting with 1000 A molecules.

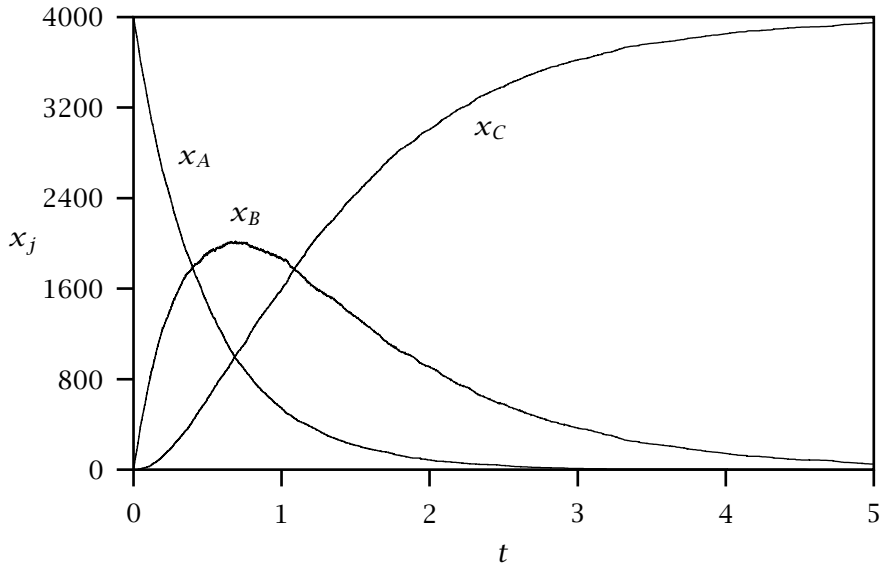


**Figure 4.31:** Stochastic simulation of the first-order reactions A⟶B⟶C starting with 4000 A molecules.

smoothly varying concentrations, and deterministic rate laws and material balances. Watching the transition in Figures 4.29–4.31 and then finally to the deterministic Figure 4.11 is a nice illustration of this connection and provides logical support for the construction of the deterministic rate laws. It is possible to prove that the average of stochastic simulations converges to the deterministic simulation as the number of molecules becomes large, which is known as the thermodynamic limit.

As stressed earlier, the random fluctuations may be an important physical behavior to include in the model. In this situation, the stochastic approach is essential and a deterministic approach cannot be substituted. We illustrate with the hepatitis B virus model introduced in Chapter 1.

**Example 4.9: Stochastic versus deterministic simulation of a virus model**

Consider the hepatitis B virus model given in Chapter 1.

$$\text{nucleotides} \xrightarrow{\text{cccDNA}} \text{rcDNA} \tag{4.95}$$

$$\text{nucleotides} + \text{rcDNA} \longrightarrow \text{cccDNA} \tag{4.96}$$

$$\text{amino acids} \xrightarrow{\text{cccDNA}} \text{envelope} \tag{4.97}$$

$$\text{cccDNA} \longrightarrow \text{degraded} \tag{4.98}$$

$$\text{envelope} \longrightarrow \text{secreted or degraded} \tag{4.99}$$

$$\text{rcDNA} + \text{envelope} \longrightarrow \text{secreted virus} \tag{4.100}$$

Assume the system starts with a single cccDNA molecule, and no rcDNA and no envelope protein, and use the following rate constants

$$\begin{bmatrix} x_A & x_B & x_C \end{bmatrix}^T = \begin{bmatrix} 1 & 0 & 0 \end{bmatrix}^T \tag{4.101}$$

$$\boldsymbol{k}^T = \begin{bmatrix} 1 & 0.025 & 1000 & 0.25 & 2 & 7.5 \times 10^{-6} \end{bmatrix} \tag{4.102}$$

Compare the results of a deterministic simulation to the average of 500 stochastic simulations. If these results are not the same, explain why not.

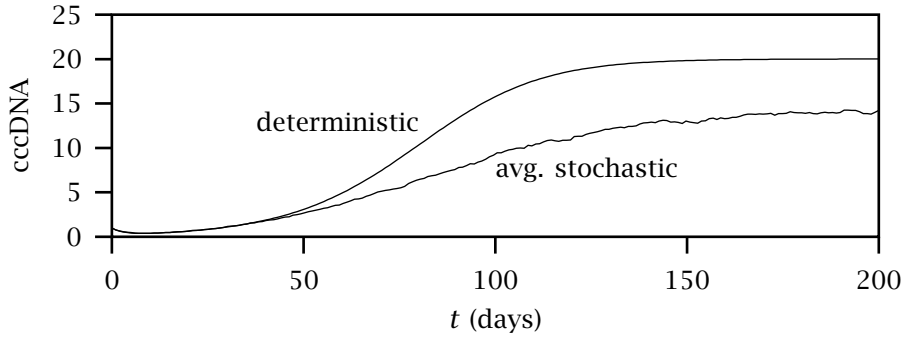


**Figure 4.32:** Species cccDNA versus time for hepatitis B virus model; deterministic and average stochastic models.

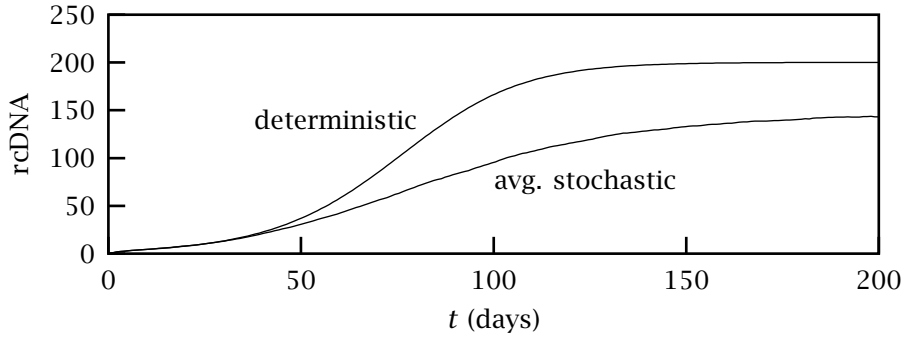


**Figure 4.33:** Species rcDNA versus time for hepatitis B virus model; deterministic and average stochastic models.

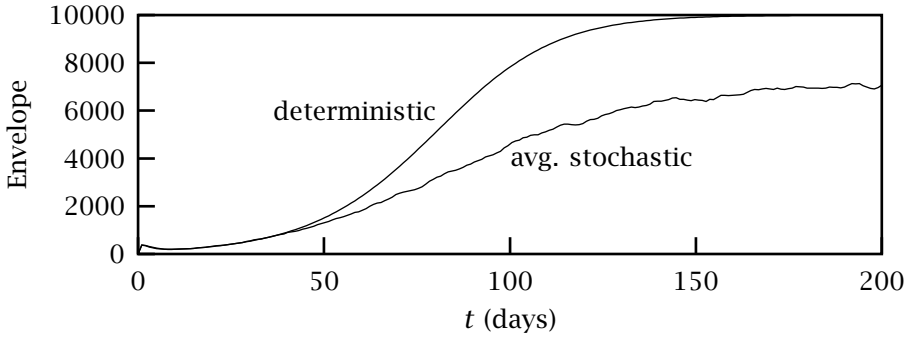


**Figure 4.34:** Envelope versus time for hepatitis B virus model; deterministic and average stochastic models.

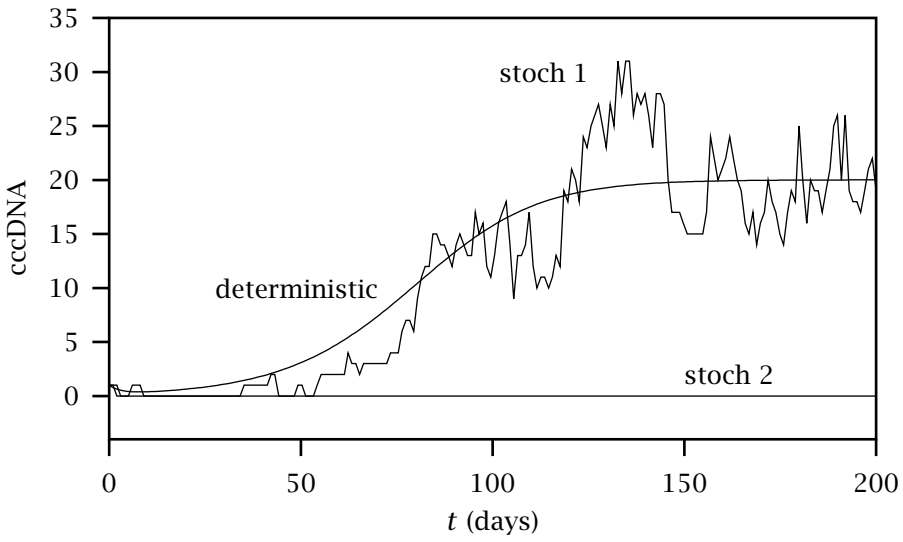


**Figure 4.35:** Species cccDNA versus time for hepatitis B virus model; two representative stochastic trajectories.

**Solution**

The reaction rates and production rates for Reactions 4.95–4.100 are given by

$$\begin{bmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \\ r_5 \\ r_6 \end{bmatrix} = \begin{bmatrix} k_1 x_A \\ k_2 x_B \\ k_3 x_A \\ k_4 x_A \\ k_5 x_C \\ k_6 x_B x_C \end{bmatrix} \qquad \begin{bmatrix} R_A \\ R_B \\ R_C \end{bmatrix} = \begin{bmatrix} r_2 - r_4 \\ r_1 - r_2 - r_6 \\ r_3 - r_5 - r_6 \end{bmatrix} \tag{4.103}$$

in which A is cccDNA, B is rcDNA, and C is envelope.

Figures 4.32–4.34 show the deterministic model simulation and an average of 500 stochastic simulations. Notice these results are *not* the same, and we should investigate why not. Figure 4.35 shows *two* representative stochastic simulations for only the cccDNA species. Notice the first stochastic simulation does fluctuate around the deterministic simulation as expected. The second stochastic simulation, however, shows complete extinction of the virus. That is another possible steady state for the stochastic model. In fact, it occurs for 125 of the 500

| | | |
|---|---|---|
| BATCH | $\frac{d(c_j V_R)}{dt} = R_j V_R$ | (4.104) |
| constant volume | $\frac{dc_j}{dt} = R_j$ | (4.105) |
| CSTR | $\frac{d(c_j V_R)}{dt} = Q_f c_{jf} - Q c_j + R_j V_R$ | (4.106) |
| constant density | $\frac{dc_j}{dt} = \frac{1}{\theta}(c_{jf} - c_j) + R_j$ | (4.107) |
| steady state | $c_j = c_{jf} + R_j \theta$ | (4.108) |
| SEMI-BATCH | $\frac{d(c_j V_R)}{dt} = Q_f c_{jf} + R_j V_R$ | (4.109) |
| PFR | $\frac{\partial c_j}{\partial t} = -\frac{\partial (c_j Q)}{\partial V} + R_j$ | (4.110) |
| steady state | $\frac{d(c_j Q)}{dV} = R_j$ | (4.111) |
| constant flowrate | $\frac{dc_j}{d\theta} = R_j, \qquad \theta = V/Q_f$ | (4.112) |

**Table 4.3:** Summary of mole balances for several ideal reactors.

simulations. So the *average* stochastic simulation in Figures 4.32–4.34 consist of 75% trajectories that fluctuate about the deterministic trajectory and 25% trajectories that go to zero. The two types of stochastic trajectories therefore explain why the average stochastic model is not equal to the deterministic model. We should bear this feature in mind when using deterministic models with small numbers of molecules. □

## 4.9 Summary

We have introduced four main reactor types in this chapter: the batch reactor, the continuous-stirred-tank reactor (CSTR), the semi-batch reactor, and the plug-flow reactor (PFR). Table 4.3 summarizes the mole balances for these four reactors. We also have introduced some of the basic reaction-rate expressions:

- first order, irreversible

- first order, reversible
- second order, irreversible
- $n$th order, irreversible
- two first-order reactions in series
- two first-order reactions in parallel
- two second-order, reversible reactions

We developed the equations required to compute the volume of the reactor if there is a significant volume change upon reaction. We require an equation of state for this purpose. Tables 4.1 and 4.2 describe the appropriate balances for a constant-density mixture, an ideal mixture, and a mixture with a general equation of state.

Several of these simple mass balances with basic rate expressions were solved analytically. In the case of multiple reactions with nonlinear rate expressions (i.e., not first-order reaction rates), the balances must be solved numerically. A high-quality ordinary differential equation (ODE) solver is indispensable for solving these problems. For a complex equation of state and nonconstant-volume case, a differential-algebraic equation (DAE) solver may be convenient.

We showed that the PFR achieves higher conversion than the CSTR of the same volume if the reaction rate is an increasing function of a component composition ($n > 0$ for an $n$th-order rate expression). Conversely, the CSTR achieves higher conversion than the same-volume PFR if the rate is a decreasing function of a component composition ($n < 0$).

Finally, we introduced stochastic simulation to model chemical reactions occurring with *small* numbers of molecules. Each of these random simulation trajectories has a rough appearance and the average of many of these simulations is required to show the expected system behavior. The stochastic model uses basic probability to compute reaction rate. The probability of occurrence of a given reaction is assumed proportional to the number of possible combinations of reactants for the given stoichiometry. Two pseudo-random numbers are chosen to determine: (i) the time of the next reaction and (ii) the reaction that occurs at that time. The smooth behavior of the macroscopic ODE models is recovered by the random simulations in the limit of large numbers of reacting molecules. With small numbers of molecules, however, the average of the stochastic simulation does not have to be equal to the deterministic simulation. We demonstrated this fact with the simple, nonlinear hepatitis B virus model.