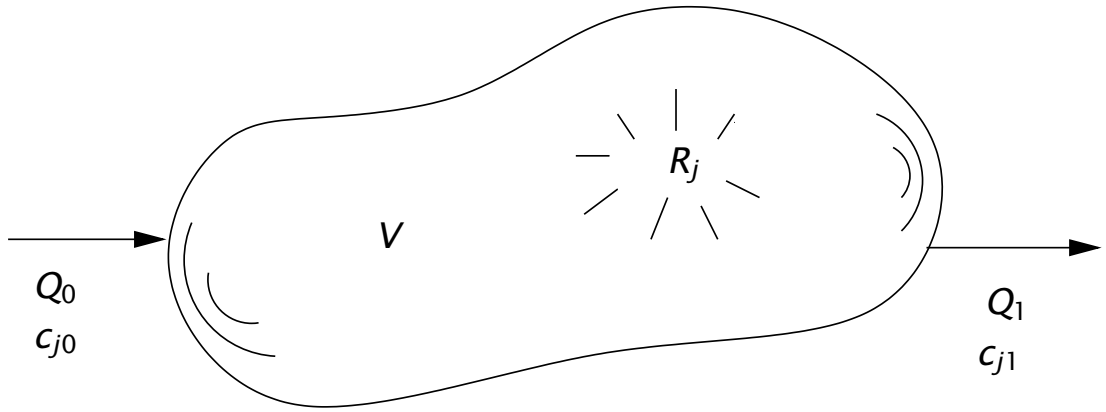
The Material Balance for Chemical Reactors

General Mole Balance

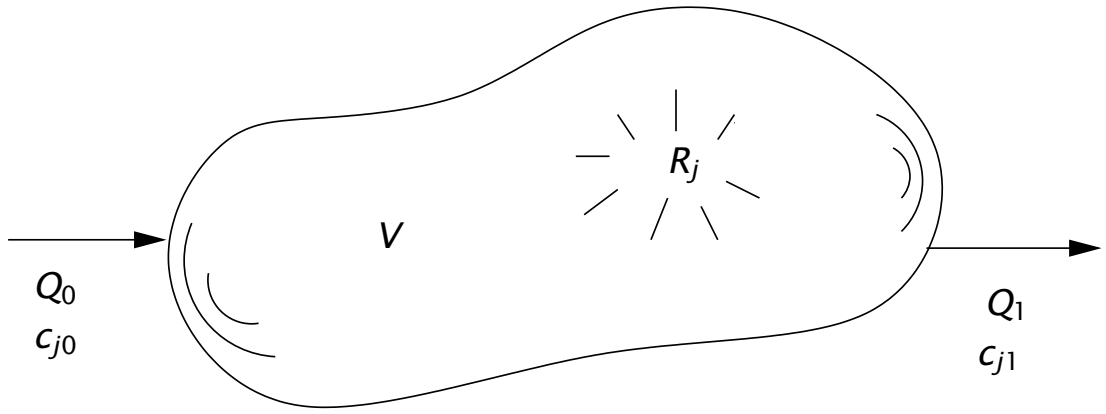


Conservation of mass

$$\left\{\begin{array}{c}\text{rate of}\\ \text{accumulation}\\ \text{of component } j\end{array}\right\} = \left\{\begin{array}{c}\text{rate of inflow}\\ \text{of component } j\end{array}\right\} - \left\{\begin{array}{c}\text{rate of outflow}\\ \text{of component } j\end{array}\right\}$$

$$+ \left\{\begin{array}{c}\text{rate of generation}\\ \text{of component } j \text{ by}\\ \text{chemical reactions}\end{array}\right\} \qquad (4.1)$$

General Mole Balance



Conservation of mass

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

General Mole Balance

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

- 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.
- Assuming component j enters and leaves the volume element only by convection with the inflow and outflow streams, i.e. 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.

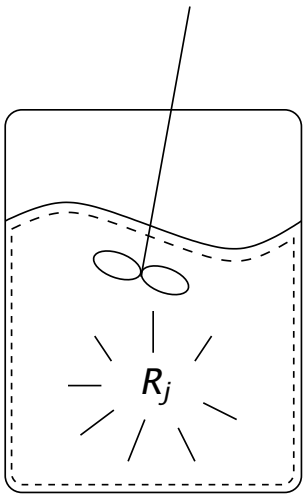
Rate expressions

- To solve the reactor material balance, we require an expression for the production rates, R_j

$$R_j = \sum_i \nu_{ij} r_i$$

- Therefore we require r_i as a function of c_j
- This is the subject of chemical kinetics, Chapter 5
- Here we use common reaction-rate expressions without derivation

The Batch Reactor



- The batch reactor is assumed well stirred
- Let the entire reactor contents be the reactor volume element

Batch Reactor

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

- Because the reactor is well stirred, the integrals in Equation 4.2 are simple to evaluate,

$$\int_{V_R} c_j dV = c_j V_R \qquad \int_{V_R} R_j dV = R_j V_R$$

- The inflow and outflow stream flowrates are zero, $Q_0 = Q_1 = 0$.

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

Reactor Volume

- Equation 4.5 applies whether the reactor volume is constant or changes during the reaction.
- If the reactor volume is constant (liquid-phase reactions)

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

- Use Equation 4.5 rather than Equation 4.6 if the reactor volume changes significantly during the course of the reaction.

Analytical Solutions for Simple Rate Laws

- In general the material balance must be solved numerically.
- If the reactor is isothermal, we have few components, the rate expressions are simple, then analytical solutions of the material balance are possible.
- We next examine derive analytical solutions for some classic cases.

First-order, irreversible

- Consider the first-order, irreversible reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{B}, \qquad r = kc_A$$

- The material balance for a constant-volume reactor gives

$$\frac{dc_A}{dt} = -kc_A \tag{4.8}$$

- Watch the sign!

First-order, irreversible

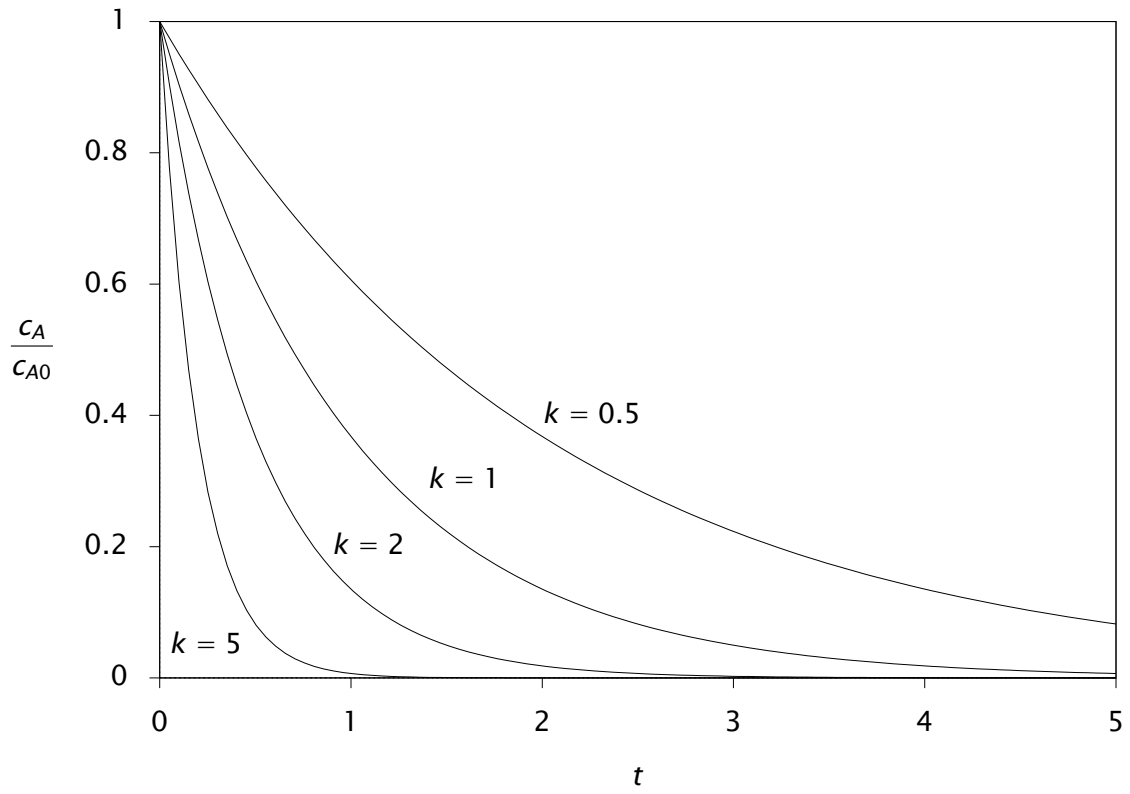
- We denote the initial concentration of A as c_{A0},

$$c_A(t) = c_{A0}, \qquad t = 0$$

- The solution to the differential equation with this boundary condition is

$$c_A = c_{A0} e^{-kt} \tag{4.9}$$

First-order, irreversible

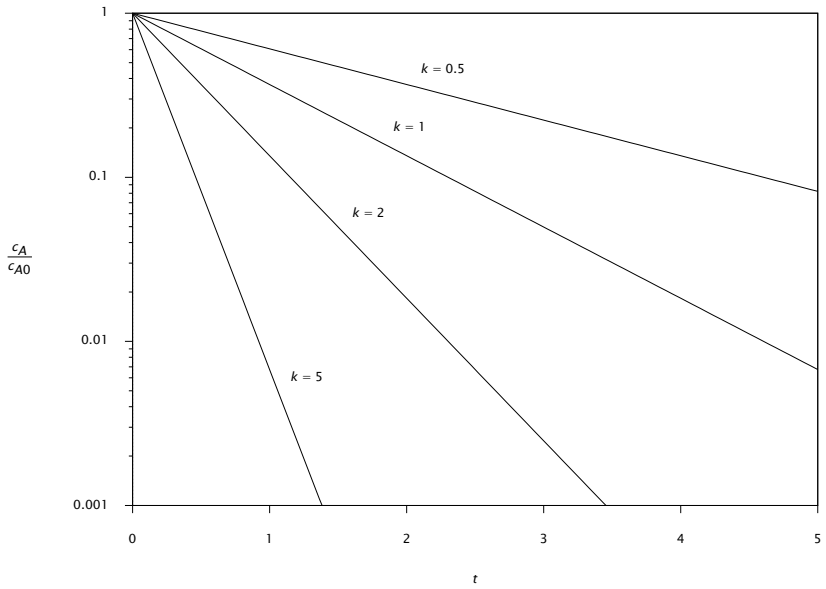


First-order, irreversible

- The A concentration decreases exponentially from its initial value to zero with increasing time.
- The rate constant determines the shape of this exponential decrease. Rearranging Equation 4.9 gives

$$\ln(c_A/c_{A0}) = -kt$$

First-order, irreversible



- One can get an approximate value of the rate constant from the slope of the straight line.
- This procedure is a poor way to determine a rate constant and should be viewed only as a rough approximation (Chapter 9).

First-order, irreversible

The B concentration is determined from the A concentration.

1. Solve the material balance for component B,

$$\frac{dc_B}{dt} = R_B = kc_A \tag{4.10}$$

   with the initial condition for B, $c_B(0) = c_{B0}$
2. Note that the sum of c_A and c_B is constant.

$$\frac{d(c_A + c_B)}{dt} = R_A + R_B = 0$$

   Therefore, $c_A + c_B$ is a constant.

First-order, reversible

- The value is known at $t = 0$,

$$c_A + c_B = c_{A0} + c_{B0}$$

- So we have an expression for c_B

$$c_B = c_{A0} + c_{B0} - c_A$$
$$c_B = c_{B0} + c_{A0}(1 - e^{-kt}) \tag{4.11}$$

First-order, reversible

- Consider now the same first-order reaction, but assume it is reversible

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

- The reaction rate is $r = k_1 c_A - k_{-1} c_B$.
- The material balances for A and B are now

$$\frac{dc_A}{dt} = -r = -k_1 c_A + k_{-1} c_B \qquad c_A(0) = cA0$$
$$\frac{dc_B}{dt} = r \quad = k_1 c_A - k_{-1} c_B \qquad c_B(0) = c_{B0}$$

- Notice that $c_A + c_B = c_{A0} + c_{B0}$ remains constante

First-order, reversible

- Eliminate c_B in the material balance for A gives

$$\frac{dc_A}{dt} = -k_1 c_A + k_{-1}(c_{A0} + c_{B0} - c_A) \tag{4.13}$$

- How do we want to solve this one?
- Particular solution and homogeneous solution (see text)
- Laplace transforms (control course)
- Separation!

First-order, reversible

$$\frac{dc_A}{dt} = ac_A + b$$

$$\int_{c_{A0}}^{c_A} \frac{dc_A}{ac_A + b} = \int_0^t dt$$

$$\frac{1}{a} \ln(ac_A + b) \Big|_{c_{A0}}^{c_A} = t$$

$$c_A = c_{A0} e^{at} - \frac{b}{a}(1 - e^{at})$$

Substitute $a = -(k_1 + k_{-1})$, $b = k_{-1}(c_{A0} + c_{B0})$

First-order, reversible

$$c_A = c_{A0} e^{-(k_1 + k_{-1})t} + \frac{k_{-1}}{k_1 + k_{-1}}(c_{A0} + c_{B0}) \left[1 - e^{-(k_1 + k_{-1})t}\right] \tag{4.15}$$

- The B concentration can be determined by switching the roles of A and B and k_1 and k_{-1} in Reaction 4.12, yielding

$$c_B = c_{B0} e^{-(k_1 + k_{-1})t} + \frac{k_1}{k_1 + k_{-1}}(c_{A0} + c_{B0}) \left[1 - e^{-(k_1 + k_{-1})t}\right] \tag{4.16}$$

First-order, reversible

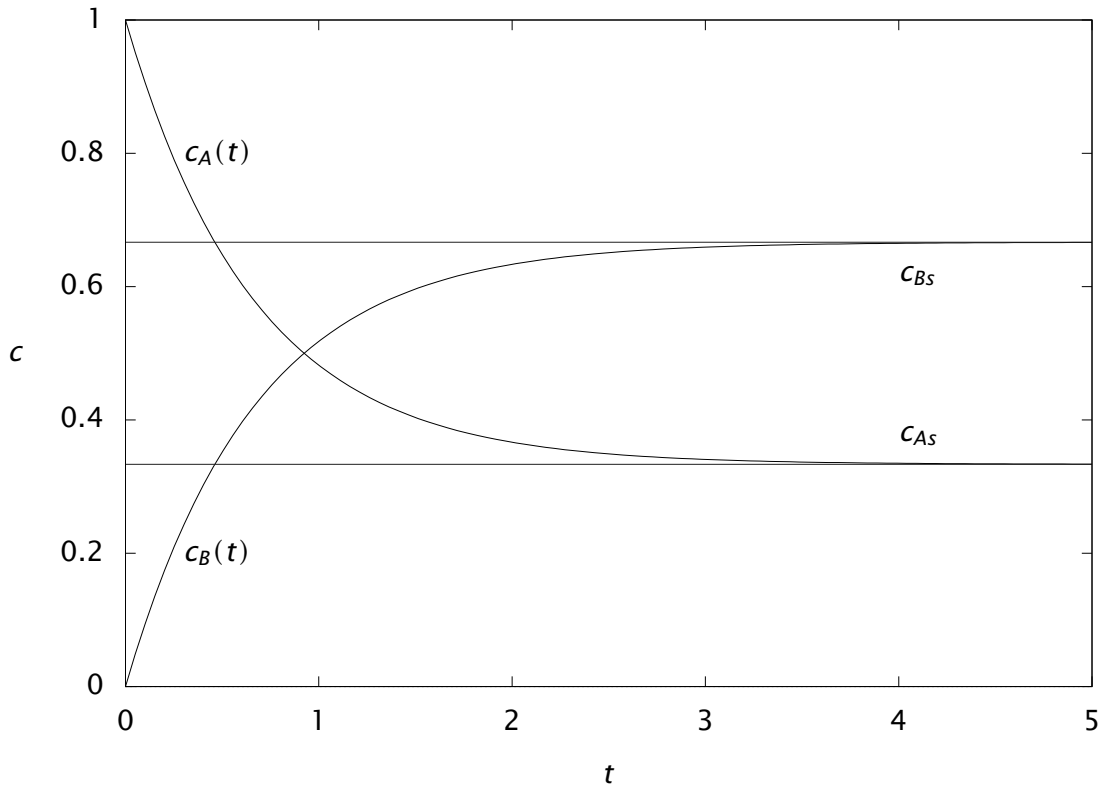


Figure 4.5: First-order, reversible kinetics in a batch reactor, $k_1 = 1$, $k_{-1} = 0.5$, $c_{A0} = 1$, $c_{B0} = 0$.

Nonzero steady state

- For the reversible reaction, the concentration of A does not go to zero.
- Taking the limit $t \longrightarrow \infty$ in Equation 4.15 gives

$$c_{As} = \frac{k_{-1}}{k_1 + k_{-1}}(c_{A0} + c_{B0})$$

in which c_{As} is the steady-state concentration of A.

Nonzero steady state

- Defining $K_1 = k_1/k_{-1}$ allows us to rewrite this as

$$c_{As} = \frac{1}{1 + K_1}(c_{A0} + c_{B0})$$

- Performing the same calculation for c_B gives

$$c_{Bs} = \frac{K_1}{1 + K_1}(c_{A0} + c_{B0})$$

Second-order, irreversible

- Consider the irreversible reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{B}$$

  in which the rate expression is second order, $r = kc_A^2$.
- The material balance and initial condition are

$$\frac{dc_A}{dt} = -kc_A^2, \qquad c_A(0) = c_{A0} \tag{4.18}$$

- Our first nonlinear differential equation.

Second-order, irreversible

- Separation works here

$$\frac{dc_A}{c_A^2} = -k dt$$

$$\int_{c_{A0}}^{c_A} \frac{dc_A}{c_A^2} = -k \int_0^t dt$$

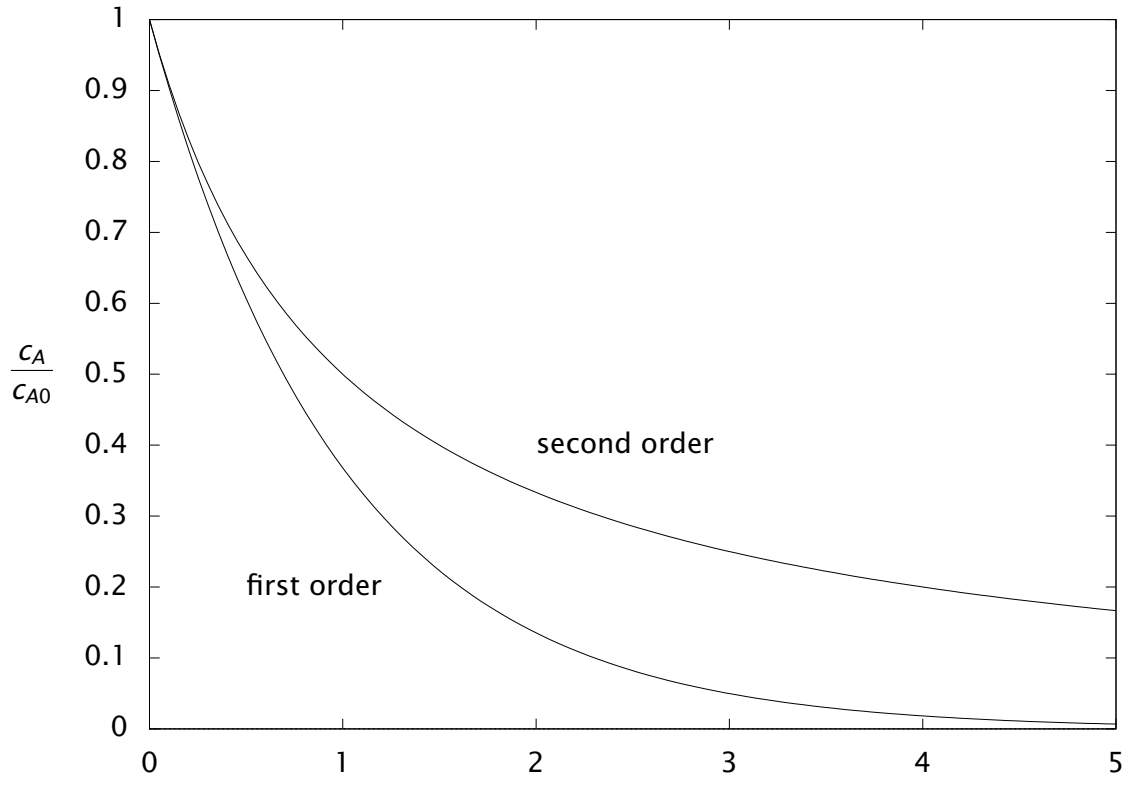
$$\frac{1}{c_{A0}} - \frac{1}{c_A} = -kt$$

- Solving for c_A gives

$$c_A = \left(\frac{1}{c_{A0}} + kt \right)^{-1} \tag{4.19}$$

- Check that this solution satisfies the differential equation and initial condition

Second-order, irreversible



- The second-order reaction decays *more slowly* to zero than the first-order reaction.

Another second-order, irreversible

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{C} \qquad r = kc_A c_B$$

- The material balance for components A and B are

$$\frac{dc_A}{dt} = -r = -kc_A c_B$$
$$\frac{dc_B}{dt} = -r = -kc_A c_B$$

- Subtract B's material balance from A's to obtain

$$\frac{d(c_A - c_B)}{dt} = 0$$

Another second-order, irreversible

- Therefore, $c_A - c_B$ is constant, and

$$c_B = c_A - c_{A0} + c_{B0} \tag{4.23}$$

- Substituting this expression into the material balance for A yields

$$\frac{dc_A}{dt} = -kc_A(c_A - c_{A0} + c_{B0})$$

- This equation also is separable and can be integrated to give (you should work through these steps),

$$c_A = (c_{A0} - c_{B0}) \left[1 - \frac{c_{B0}}{c_{A0}} e^{(c_{B0} - c_{A0})kt} \right]^{-1}, \qquad c_{A0} \neq c_{B0} \tag{4.24}$$

Another second-order, irreversible

- Component B can be computed from Equation 4.23, or by switching the roles of A and B in Reaction 4.20, giving

$$c_B = (c_{B0} - c_{A0}) \left[1 - \frac{c_{A0}}{c_{B0}} e^{(c_{A0} - c_{B0})kt} \right]^{-1}$$

- What about component C? C's material balance is

$$\frac{dc_C}{dt} = k c_A c_B$$

and therefore, $d(c_A + c_C)/dt = 0$. The concentration of C is given by

$$c_C = c_{A0} - c_A + c_{C0}$$

Another second-order, irreversible

- Notice that if $c_{A0} > c_{B0}$ (Excess A), the steady state

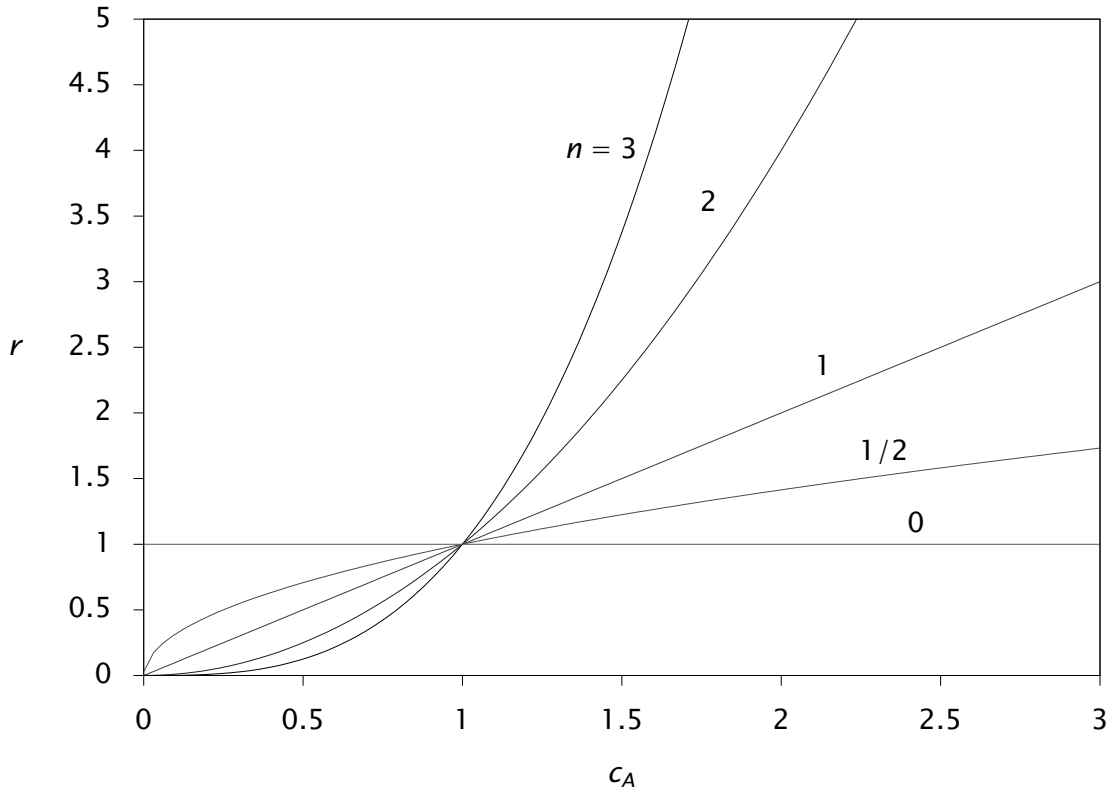
$$c_{As} = c_{A0} - c_{B0}$$
$$c_{Bs} = 0$$
$$c_{Cs} = c_{B0} + c_{C0}$$

- For $c_{B0} > c_{A0}$ (Excess B), the steady state is

$$c_{As} = 0$$
$$c_{Bs} = c_{B0} - c_{A0}$$
$$c_{Cs} = c_{A0} + c_{C0}$$

nth-order, irreversible

The nth-order rate expression $r = kc_A^n$



nth-order, irreversible

$$\mathrm{A} \xrightarrow{k} \mathrm{B} \qquad r = kc_A^n$$

$$\frac{dc_A}{dt} = -r = -kc_A^n$$

- This equation also is separable and can be rearranged to

$$\frac{dc_A}{c_A^n} = -kdt$$

- Performing the integration and solving for c_A gives

$$c_A = \left[c_{A0}^{-n+1} + (n-1)kt\right]^{\frac{1}{-n+1}}, \qquad n \neq 1$$

nth-order, irreversible

- We can divide both sides by c_{A0} to obtain

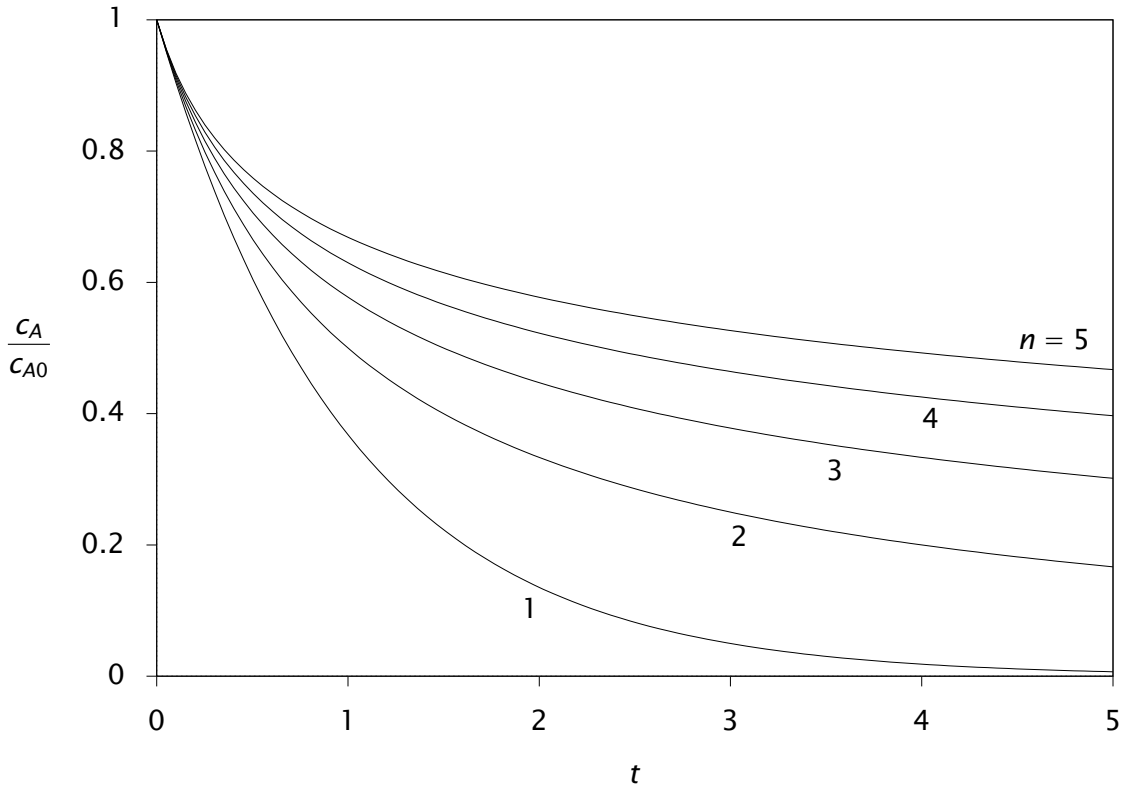
$$\frac{c_A}{c_{A0}} = [1 + (n-1)k_0 t]^{\frac{1}{-n+1}}, \qquad n \neq 1 \tag{4.25}$$

in which

$$k_0 = k c_{A0}^{n-1}$$

has units of inverse time.

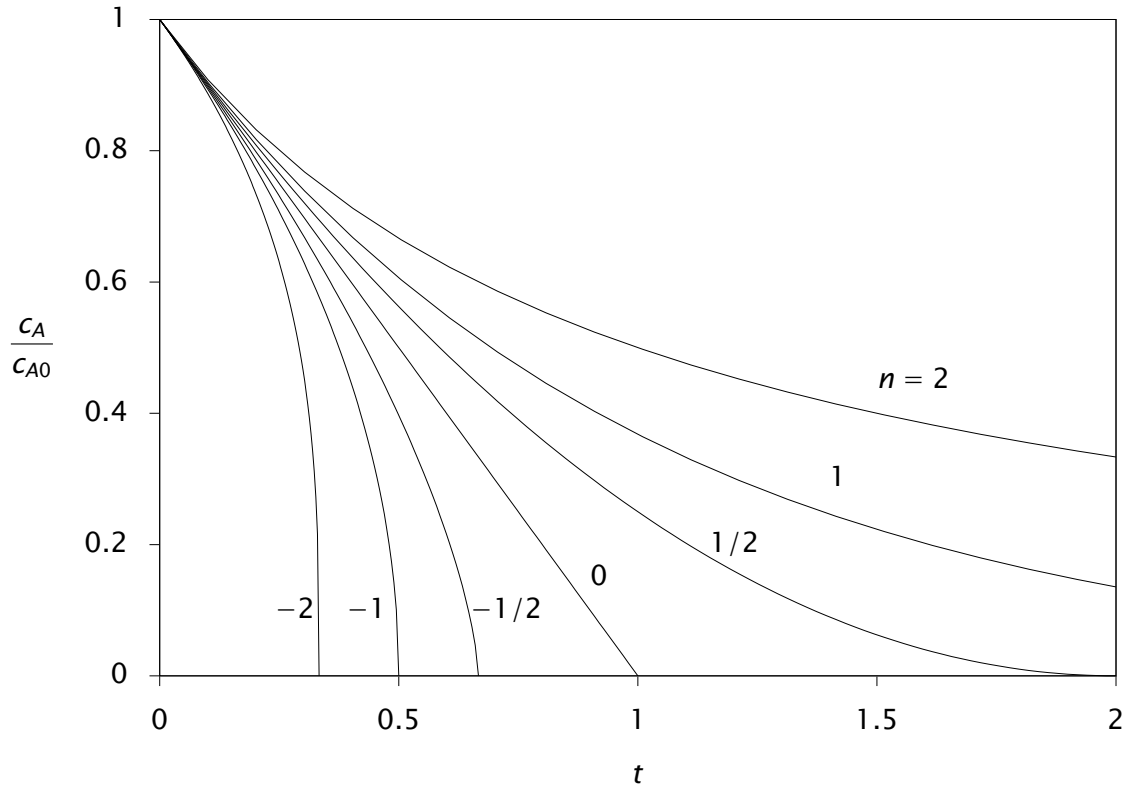
nth-order, irreversible



- The larger the value of n, the more slowly the A concentration approaches zero at large time.

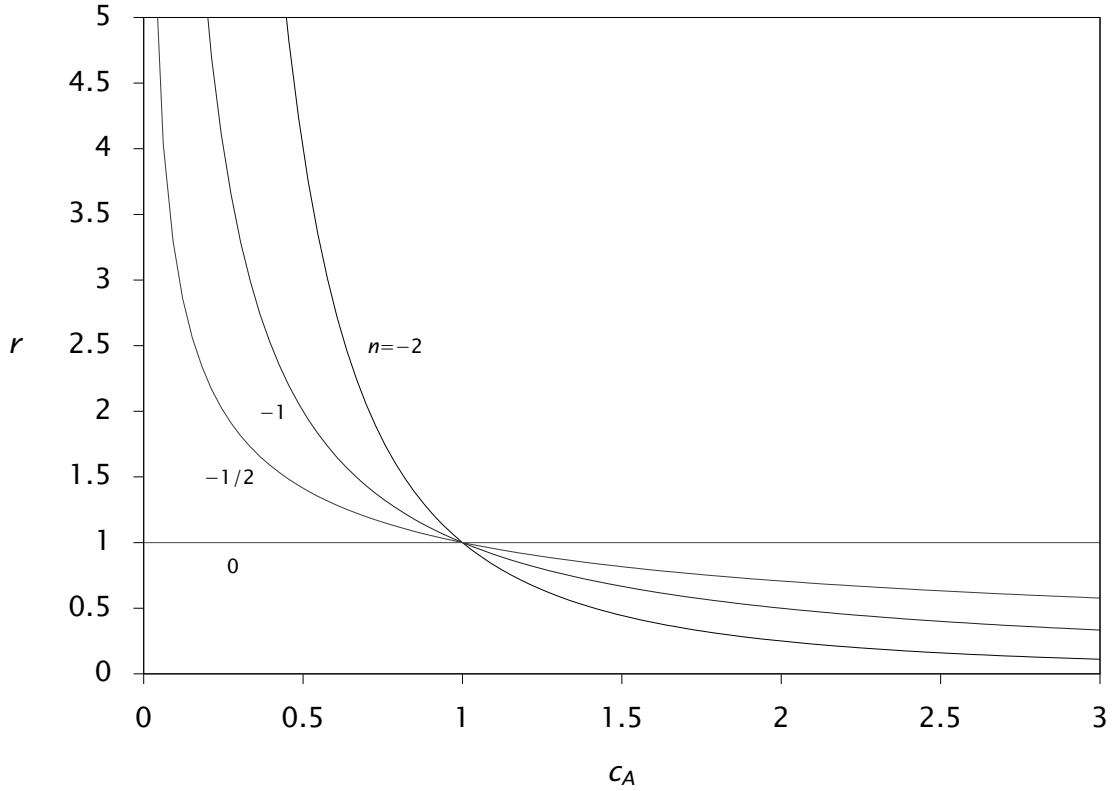
nth-order, irreversible

- Exercise care for $n < 1$, c_A reaches zero in *finite time*.



Negative order, inhibition

- For $n < 0$, the rate decreases with increasing reactant concentration; the reactant *inhibits the reaction*.



Negative order, inhibition

- Inhibition reactions are not uncommon, but watch out for small concentrations. Notice the rate becomes unbounded as c_A approaches zero, which is not physically realistic.
- When using an ODE solver we may modify the right-hand sides of the material balance

$$\frac{dc_A}{dt} = \begin{cases} -kc_A^n, & c_A > 0 \\ 0, & c_A = 0 \end{cases}$$

- Examine the solution carefully if the concentration reaches zero.

Two reactions in series

- Consider the following two irreversible reactions,

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}$$
$$\mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

- Reactant A decomposes to form an intermediate B that can further react to form a final product C.
- Let the reaction rates be given by simple first-order rate expressions in the corresponding reactants,

$$r_1 = k_1 c_A$$
$$r_2 = k_2 c_B$$

Two reactions in series

- The material balances for the three components are

$$\begin{aligned}\frac{dc_A}{dt} &= R_A = -r_1 &&= -k_1 c_A \\ \frac{dc_B}{dt} &= R_B = r_1 - r_2 &&= k_1 c_A - k_2 c_B \\ \frac{dc_C}{dt} &= R_C = r_2 &&= k_2 c_B\end{aligned}$$

- The material balance for component A can be solved immediately to give $c_A = c_{A0} e^{-k_1 t}$ as before.

Two reactions in series – B

- The material balance for B becomes

$$\frac{dc_B}{dt} + k_2 c_B = k_1 c_{A0} e^{-k_1 t}$$

  Oops, not separable, now what?

- Either Laplace transform or particular solution, homogeneous equation approach produces

$$c_B = c_{B0} e^{-k_2 t} + c_{A0} \frac{k_1}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right], \qquad k_1 \neq k_2 \tag{4.30}$$

Two reactions in series – C

- To determine the C concentration, notice from the material balances that $d(c_A + c_B + c_C)/dt = 0$. Therefore, c_C is

$$c_C = c_{A0} + c_{B0} + c_{C0} - c_A - c_B$$

Two reactions in series

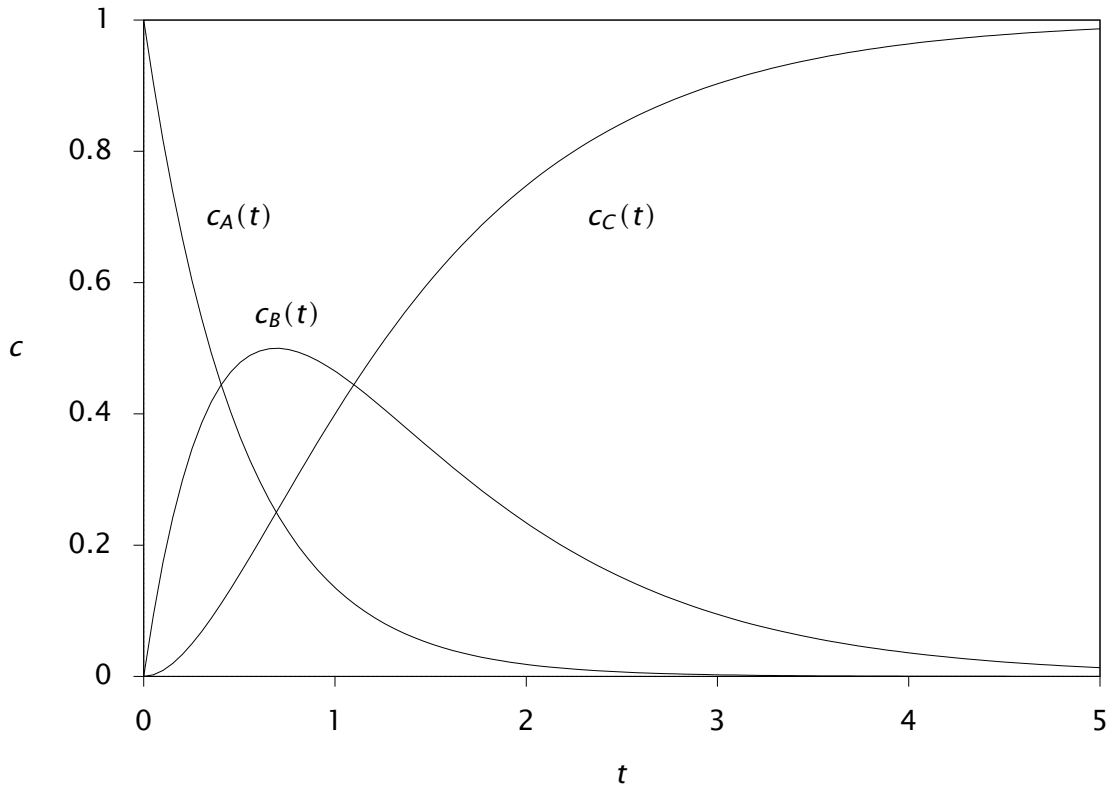


Figure 4.11: Two first-order reactions in series in a batch reactor, $c_{A0} = 1$, $c_{B0} = c_{C0} = 0$, $k_1 = 2$, $k_2 = 1$.

Two reactions in parallel

- Consider next two parallel reactions of A to two different products, B and C,

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}$$
$$\mathrm{A} \xrightarrow{k_2} \mathrm{C}$$

- Assume the rates of the two irreversible reactions are given by $r_1 = k_1 c_A$ and $r_2 = k_2 c_A$.

Two reactions in parallel

- The material balances for the components are

$$\frac{dc_A}{dt} = R_A = -r_1 - r_2 = -k_1 c_A - k_2 c_A$$
$$\frac{dc_B}{dt} = R_B = r_1 = k_1 c_A$$
$$\frac{dc_C}{dt} = R_C = r_2 = k_2 c_A$$

Two reactions in parallel

- The material balance for A can be solved directly to give

$$c_A = c_{A0} e^{-(k_1+k_2)t} \tag{4.33}$$

- Substituting $c_A(t)$ into B's material balance gives

$$\frac{dc_B}{dt} = k_1 c_{A0} e^{-(k_1+k_2)t}$$

- This equation is now separable and can be integrated directly to give

$$c_B = c_{B0} + c_{A0} \frac{k_1}{k_1 + k_2} \left(1 - e^{-(k_1+k_2)t}\right) \tag{4.34}$$

Two reactions in parallel

- Finally, component C can be determined from the condition that $c_A + c_B + c_C$ is constant or by switching the roles of B and C, and k_1 and k_2 in Equation 4.34,

$$c_C = c_{C0} + c_{A0} \frac{k_2}{k_1 + k_2} \left(1 - e^{-(k_1+k_2)t}\right) \tag{4.35}$$

Two reactions in parallel

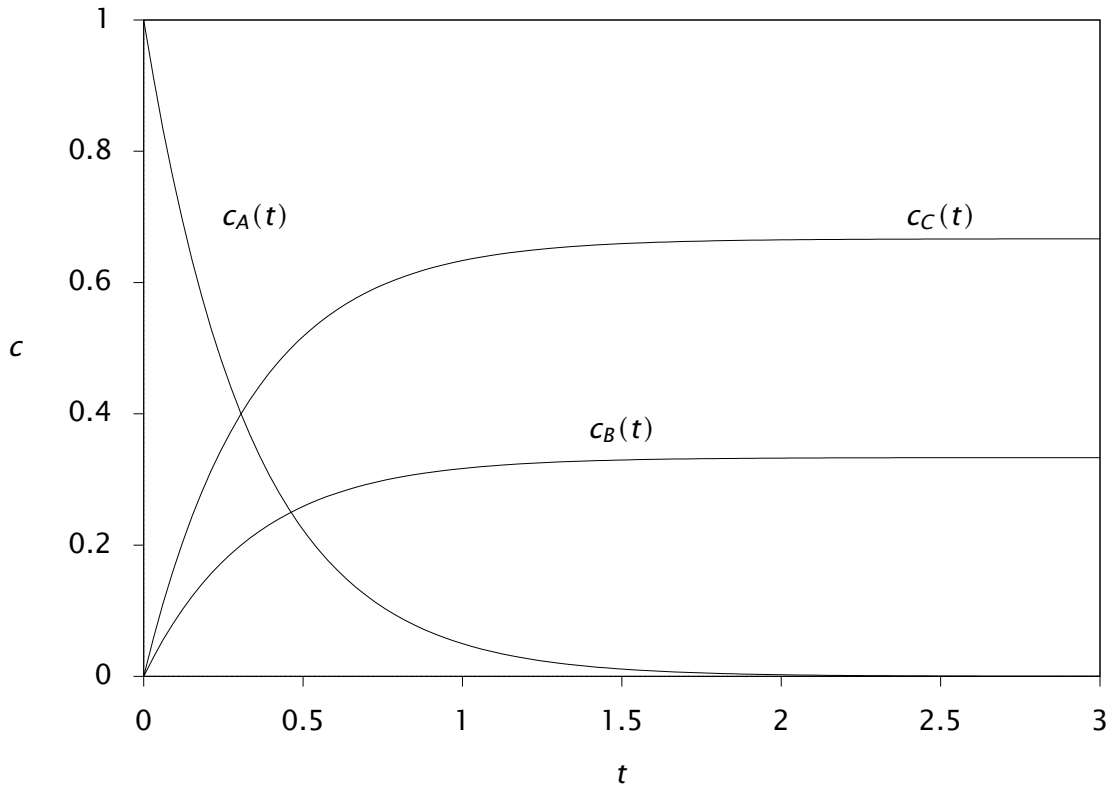


Figure 4.12: Two first-order reactions in parallel in a batch reactor, $c_{A0} = 1$, $c_{B0} = c_{C0} = 0$, $k_1 = 1$, $k_2 = 2$.

Two reactions in parallel

- Notice that the two parallel reactions *compete* for the same reactant, A
- The rate constants determine which product is favored
- Large values of k_1 / k_2 favor the formation of component B compared to C and vice versa

Conversion, Yield, Selectivity

There are several ways to define selectivity, yield and conversion, so be clear about the definition you choose.

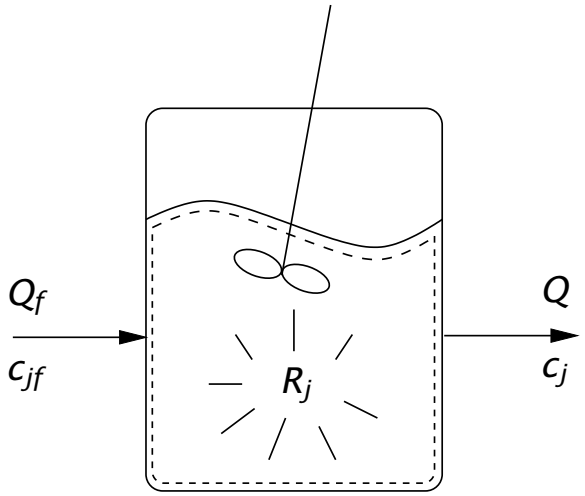
Point selectivity: The point (or instantaneous) selectivity is the ratio of the production rate of one component to the production rate of another component.

Overall selectivity: The overall selectivity is the ratio of the amount of one component produced to the amount of another component produced.

Yield: The yield of component j is the fraction of a reactant that is converted into component j.

Conversion: Conversion is normally defined to be the fraction of a component that has been converted to products by the reaction network. Conversion has several definitions and conventions. It is best to state the definition in the context of the problem being solved.

The Continuous-Stirred-Tank Reactor (CSTR)



Writing the material balance for this reactor gives

$$\frac{d\left(c_j V_R\right)}{dt} = Q_f c_{jf} - Q c_j + R_j V_R, \quad j = 1, \ldots, n_s \tag{4.36}$$

CSTR – Constant Density

- If the reactor volume is constant and the volumetric flowrates of the inflow and outflow streams are the same, Equation 4.36 reduces to

$$\frac{dc_j}{dt} = \frac{1}{\tau}(c_{jf} - c_j) + R_j \tag{4.37}$$

- The parameter

$$\tau = V_R / Q_f$$

  is called the **mean residence time** of the CSTR.
- We refer to this balance as the constant-density case. It is often a good approximation for liquid-phase reactions.

CSTR – Steady State

- The steady state of the CSTR is described by setting the time derivative in Equation 4.36 to zero,

$$0 = Q_f c_{jf} - Q c_j + R_j V_R \tag{4.38}$$

- Conversion of reactant j is defined for a steady-state CSTR as follows

$$x_j = \frac{Q_f c_{jf} - Q c_j}{Q_f c_{jf}} \qquad \text{(steady state)} \tag{4.39}$$

- One can divide Equation 4.38 through by V_R to obtain for the constant-density case

$$c_j = c_{jf} + R_j \tau \qquad \text{(steady state, constant density)} \tag{4.40}$$

Transient behavior of the CSTR

- Consider a first-order, liquid-phase reaction in an isothermal CSTR

$$\mathrm{A} \xrightarrow{k} 2\mathrm{B} \qquad r = kc_A$$

the feed concentration of A is $c_{Af} = 2$ mol/L, the residence time of the reactor is $\tau = 100$ min, and the rate constant is $k = 0.1$ min^{-1}.

1. Find the steady-state concentration of A in the effluent for the given feed.
2. Plot the concentration of A versus time for constant feed concentration $c_{Af} = 2$ mol/L if the reactor is initially filled with an inert so $c_{A0} = 0$ mol/L.
3. Plot the concentration of A versus time for constant feed concentration $c_{Af} = 2$ mol/L if the reactor is initially filled with feed so $c_{A0} = 2$ mol/L.

Transient CSTR Solution. Part 1

- Liquid phase: assume the fluid density is constant.

$$c_A = c_{Af} + R_A\tau$$

- Substituting the production rate $R_A = -kc_A$ and solving for c_A gives the steady-state concentration

$$c_{As} = \frac{c_{Af}}{1 + k\tau}$$

- Substituting in the numerical values gives

$$c_{As} = \frac{2 \text{ mol/L}}{1 + (0.1 \text{ min}^{-1})(100 \text{ min})} = 0.182 \text{ mol/L}$$

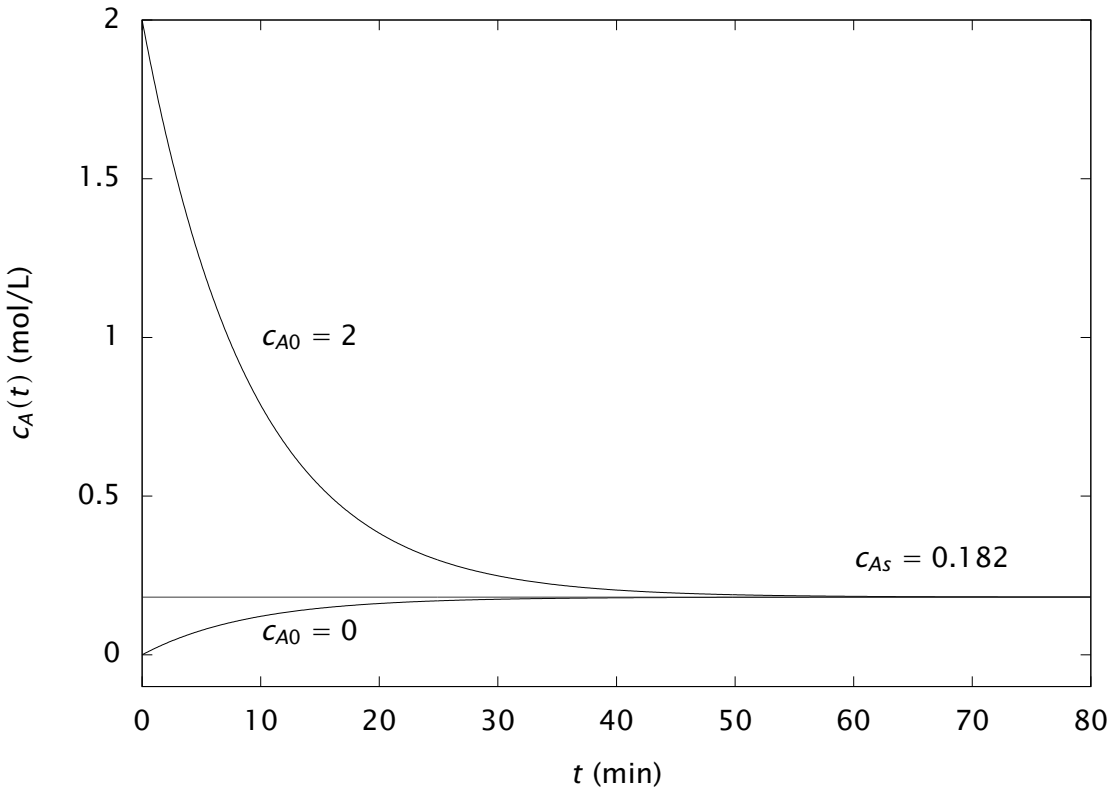
Parts 2 and 3

$$\frac{dc_A}{dt} = \frac{1}{\tau}(c_{Af} - c_A) - kc_A \tag{4.41}$$
$$c_A(0) = c_{A0}$$

- This equation is also separable. The analytical solution is

$$c_A(t) = c_{A0}e^{-(1/\tau+k)t} + \frac{c_{Af}}{1+k\tau}\left[1 - e^{-(1/\tau+k)t}\right] \tag{4.42}$$

Parts 2 and 3



- Both solutions converge to the same steady-state even though the starting conditions are quite different.

Phenol production in a CSTR

- Consider the reaction of cumene hydroperoxide (CHP) to phenol and acetone

$$(C_6H_5)C(CH_3)_2OOH \longrightarrow (C_6H_5)OH + (CH_3)_2CO$$
$$\text{CHP} \longrightarrow \text{phenol} + \text{acetone}$$

- The reaction is pseudo-first-order

$$r = kc_{\text{CHP}}$$

- Find the reactor volume to achieve 85% conversion of CHP at steady state. The flowrate into the reactor is $Q_f = 26.9\ \text{m}^3/\text{hr}$ and $k = 4.12\ \text{hr}^{-1}$.

Phenol production

- Liquids at 85°C, so assume constant density and $Q = Q_f$.

$$c_A = c_{Af} + R_A\tau$$

$R_A = -kc_A$, and solving for the CHP concentration gives

$$c_A = \frac{c_{Af}}{1 + k\tau} \tag{4.43}$$

Phenol production

- The conversion of CHP (for $Q = Q_f$) is

$$x_A = \frac{c_{Af} - c_A}{c_{Af}} = 1 - \frac{c_A}{c_{Af}}$$

$$x_A = \frac{k\tau}{1 + k\tau}$$

- Solving this equation for τ gives

$$\tau = \frac{1}{k}\frac{x_A}{1 - x_A}$$

Phenol production

- Substituting the relation $\tau = V_R/Q_f$ and solving for V_R gives

$$V_R = \frac{Q_f x_A}{k(1 - x_A)}$$

- Substituting in the known values gives the required CSTR volume

$$V_R = \frac{(26.9\ \mathrm{m^3/hr})(0.85)}{(4.12\ \mathrm{hr^{-1}})(0.15)} = 37\ \mathrm{m^3}$$

The Semi-Batch Reactor

- The semi-batch reactor is a cross between the batch reactor and CSTR.
- The semi-batch reactor is initially charged with reactant, like the batch reactor, but allows a feed addition policy while the reaction takes place, like the CSTR.
- Normally there is no outflow stream.

The Semi-Batch Reactor

- We set $Q = 0$ in the CSTR material balance to obtain

$$\frac{d\left(c_j V_R\right)}{dt} = Q_f c_{jf} + R_j V_R, \quad j = 1, \ldots, n_s \tag{4.44}$$

- One may choose to operate a semi-batch reactor to control the reaction rate or heat release during reaction by slowly adding one of the reactants in the feed stream.
- Compared to the batch reactor, the semi-batch reactor provides more complete use of the reactor volume in reactions such as polymerizations that convert from lower density to higher density during the course of the reaction.

Volume Change Upon Reaction

$$\frac{d\left(c_j V_R\right)}{dt} = Q_f c_{jf} - Q c_j + R_j V_R \tag{4.45}$$

- Equation 4.45 covers both the batch, CSTR and semi-batch reactors, depending on how we specify Q_f and Q.
- If we multiply Equation 4.45 by the molecular weight of species j and sum over all species we obtain,

$$\frac{d(\sum_j c_j M_j V_R)}{dt} = Q_f \sum_j c_{jf} M_j - Q \sum_j c_j M_j + \sum_j R_j M_j V_R \tag{4.46}$$

- The term $\sum_j c_j M_j$ is simply the mass density of the reactor contents, which we denote ρ

$$\rho = \sum_{j=1}^{n_s} c_j M_j \tag{4.47}$$

Volume Change Upon Reaction

- The term $\sum_j c_{jf} M_j$ is the mass density of the feedstream, ρ_f.
- We know that conservation of mass in chemical reactions implies $\sum_j R_j M_j = 0$ (see Chapter 2). Substitution into Equation 4.46 leads to

$$\frac{d(\rho V_R)}{dt} = Q_f \rho_f - Q\rho \tag{4.48}$$

- Equation 4.48 is clearly a total mass balance, in which the total mass in the reactor changes in time due to the inflow and outflow of mass.
- Notice that chemical reactions play no role in the total mass balance.

Equation of state for the mixture

- If we have a single-phase system at equilibrium, the intensive variables c_j, T, P, completely specify all intensive variables of the system.
- In this chapter we consider T and P to be known, fixed quantities. Therefore, the density of the reaction mixture, which is an intensive variable, is known if the c_j are known.
- This relationship is one form of the equation of state for the mixture

$$\rho = \tilde{f}(T, P, c_1, c_2, \ldots, c_{n_s})$$

- Substituting the definition of density, we can express the equation of state as

$$f(c_1, c_2, \ldots, c_{n_s}) = 0$$

Equation of state for the mixture

- For example, we could express the equation of state in terms of the partial molar volumes as

$$\sum_j c_j \overline{V}_j = 1$$

  in which $\overline{V}_j$ is the partial molar volume of component j in the mixture.
- The partial molar volumes are functions of T, P and c_j.

Equation of state for the mixture — Ideal mixture

- If we assume an ideal mixture, this reduces to

$$\sum_j c_j V_j^\circ = 1, \qquad \text{ideal mixture}$$

  in which V_j° is the specific volume of pure component j, which is a function of only T and P.
- We assume that a thermodynamic equation of state is valid even when the reactor is not at equilibrium.

Constant density

- Because the reaction mixture density, ρ, is independent of composition, it does not vary with time either and we can set it to the feed value,

$$\rho = \rho_f$$

- The total mass balance then reduces to

$$\frac{dV_R}{dt} = Q_f - Q \tag{4.51}$$

  which is sometimes referred to as a "volume balance."
- This terminology should be avoided.

Constant density

$$\frac{dV_R}{dt} = Q_f - Q$$

- Batch reactor. For the batch reactor, $Q = Q_f = 0$. We can therefore conclude from Equation 4.51 that a batch reactor with constant density has constant volume.
- CSTR (dynamic and steady state). If the outflow of the CSTR is regulated so that the CSTR has constant volume, then we can conclude from Equation 4.51 that $Q = Q_f$.
- Semi-batch reactor. In the semi-batch reactor, the reactor is filled during operation so Q_f is specified and positive for some time and $Q = 0$. The solution to Equation 4.51 then determines the change in volume of the reactor during the filling operation.

Nonconstant density

Unknowns.

- In the general case, consider the following variables to fully determine the state of the reactor: T, P, n_j, V_R.
- We also require the value of Q to specify the right-hand sides of the material balances.
- The set of unknowns is n_j, V_R, Q.
- We therefore have $n_s + 2$ unknowns.

Equations.

- We have the n_s equations from the component mole balances.
- The equation of state provides one additional equation.
- The final equation is provided by a statement of reactor operation.

Nonconstant density – reactor operation

1. Constant-volume reactor. The constant-volume reactor can be achieved by allowing overflow of the reactor to determine flowrate out of the reactor. In this situation, V_R is specified as the additional equation.
2. Constant-mass reactor. The constant-mass reactor can be achieved if a differential pressure measurement is used to control the flowrate out of the reactor and the reactor has constant cross-sectional area. In this situation ρV_R is specified as the additional equation.
3. Flowrate out of the reactor is specified. This type of operation may be achieved if the flowrate out of the reactor is controlled by a flow controller. In this case $Q(t)$ is specified. A semi-batch reactor is operated in this way with $Q = 0$ until the reactor is filled with the reactants.

Nonconstant density – reactor operation

- See the text for the derivation.

$$\frac{dV_R}{dt} = Q_f \frac{\sum_j f_j c_{jf}}{\sum_j f_j c_j} - Q + \frac{\sum_i \Delta f_i r_i V_R}{\sum_j f_j c_j} \tag{4.53}$$

- in which f_j is

$$f_j = \frac{\partial f}{\partial c_j}$$

- and Δf_i is

$$\Delta f_i = \sum_j \nu_{ij} f_j = \sum_j \nu_{ij} \frac{\partial f}{\partial c_j}$$

which is a change in a derivative property upon reaction.

Nonconstant density – idea mixture

- For the ideal mixture we have $f(c_j) = \sum_j c_j V_j^\circ - 1 = 0$.

$$f_j = V_j^\circ$$

the pure component specific volumes

- The Δf_i are given by

$$\Delta f_i = \Delta V_i^\circ$$

the change in specific volume upon reaction i.

- So the reactor volume can be calculated from

$$\frac{dV_R}{dt} = Q_f - Q + \sum_i \Delta V_i^\circ r_i V_R$$

Nonconstant density

Unknowns ($n_S + 2$):	$V_R, Q, n_j, \quad j = 1, \ldots, n_S$			
Component balances:	$\frac{dn_j}{dt} = Q_f c_{jf} - Q c_j + R_j V_R, \quad j = 1, \ldots, n_S$			
Defined quantities:	$n_j = c_j V_R \qquad \rho = \sum_j c_j M_j \qquad \Delta V_i^\circ = \sum_j \nu_{ij} V_j^\circ$			
	(i) constant density: $\rho = \rho_0$		(ii) ideal mixture: $\sum_j c_j V_j^\circ = 1$	
1. vol	$V_R = V_{R0}$	$Q = Q_f$	$V_R = V_{R0}$	$Q = Q_f + \sum_i \Delta V_i^\circ r_i V_R$
2. mass	$V_R = V_{R0}$	$Q = Q_f$	$\frac{dV_R}{dt} = Q_f(1 - \rho_f/\rho) + \sum_i \Delta V_i^\circ r_i V_R$	$Q = Q_f \rho_f / \rho$
3. Q	$\frac{dV_R}{dt} = Q_f - Q$	Q specified	$\frac{dV_R}{dt} = Q_f - Q + \sum_i \Delta V_i^\circ r_i V_R$	Q specified

Table 4.1: Reactor balances for constant-density and ideal-mixture assumptions.

Nonconstant density

Unknowns ($n_S + 2$):	$V_R, Q, n_j, \quad j = 1, \ldots, n_S$			
Component balances:	$\frac{dn_j}{dt} = Q_f c_{jf} - Q c_j + R_j V_R, \quad j = 1, \ldots, n_S$			
Defined quantities:	$n_j = c_j V_R \qquad \rho = \sum_j c_j M_j \qquad \Delta f_i = \sum_j \nu_{ij} \frac{\partial f}{\partial c_j}$			
Equation of state:	$f(c_1, c_2, \ldots, c_{n_S}) = 0$			
	DAEs		ODEs	
1. vol	$V_R = V_{R0}$	$f(c_j) = 0$	$V_R = V_{R0}$	$Q = Q_f \frac{\sum_j f_j c_{jf}}{\sum_j f_j c_j} + \frac{\sum_i \Delta f_i r_i V_R}{\sum_j f_j c_j}$
2. mass	$\rho V_R = \rho_0 V_{R0}$	$f(c_j) = 0$	$\frac{dV_R}{dt} = Q_f \frac{\sum_j f_j c_{jf}}{\sum_j f_j c_j} - Q + \frac{\sum_i \Delta f_i r_i V_R}{\sum_j f_j c_j}$	$Q = Q_f \rho_f / \rho$
3. Q	Q specified	$f(c_j) = 0$	$\frac{dV_R}{dt} = Q_f \frac{\sum_j f_j c_{jf}}{\sum_j f_j c_j} - Q + \frac{\sum_i \Delta f_i r_i V_R}{\sum_j f_j c_j}$	Q specified

Table 4.2: Reactor balances for general equation of state.

Semi-batch polymerization

- Consider a solution polymerization reaction, which can be modeled as a first-order, irreversible reaction

$$\mathrm{M} \xrightarrow{k} \mathrm{P} \qquad r = k c_M$$

- A 20 m^3 semi-batch reactor is initially charged with solvent and initiator to half its total volume.
- A pure monomer feed is slowly added at flowrate $Q_{f0} = 1$ m^3/min to fill the reactor in semi-batch operation to control the heat release.

Semi-batch polymerization

- Consider two cases for the subsequent reactor operation.
  1. The monomer feed is shut off and the reaction goes to completion.
  2. The monomer feed is adjusted to keep the reactor filled while the reaction goes to completion.
- Calculate the total polymer mass production, and the percentage increase in polymer production achieved in the second operation.

The physical properties

- You may assume an ideal mixture
- The densities of monomer and polymer are

$$\rho_M = 800 \text{ kg/m}^3 \qquad \rho_P = 1100 \text{ kg/m}^3$$

- The monomer molecular weight is $M_M = 100$ kg/kmol
- The rate constant is $k = 0.1$ min^{-1}.

Semi-batch polymerization

- While the reactor is filling, the monomer mole balance is

$$\frac{d(c_M V_R)}{dt} = Q_{f0} c_{Mf} - k c_M V_R$$

  in which $c_{Mf} = \rho_M / M_M$ is given, and $Q_f = Q_{f0}$ is constant during the filling operation.
- We denote the total number of moles of monomer by $M = c_M V_R$, and can write the monomer balance as

$$\frac{dM}{dt} = Q_{f0} c_{Mf} - kM \tag{4.54}$$
$$M(0) = 0$$

Semi-batch polymerization

- For an ideal mixture, the volume is given by

$$\frac{dV_R}{dt} = Q_{f0} + \Delta V k M \tag{4.55}$$
$$V_R(0) = 10 \text{ m}^3$$

  in which $\Delta V = (1/\rho_P - 1/\rho_M) M_M$

The polymer mass production

- To compute the polymer mass, we note from the stoichiometry that the mass production rate of polymer $\widetilde{R}_P$ is

$$\widetilde{R}_P = -R_M M_M$$

- The mass balance for total polymer $\widetilde{P}$ is given by

$$\frac{d\widetilde{P}}{dt} = \widetilde{R}_p V_R = k c_M M_M V_R = (k M_M) M \tag{4.56}$$

Semi-batch polymerization

- The text solves this problem analytically. Instead, let's solve it numerically.
- Let t_1 be the time that the reactor fills.
- We need an ODE solver that is smart enough to stop when the reactor fills, because we do not know this time t_1. The ODE solver needs to find it for us.
- `dasrt` is an ODE solver with the added capability to find the time at which some event of interest occurs.

Finding the time for filling the reactor

- The ODE solver finds the time at which $V_R = 20$ m^3

$$t_1 = 11.2 \text{ min}$$

- Note the reactor would have filled in 10 min if the density were constant.
- The extra time reflects the available volume created by converting some of the monomer to polymer during filling.
- After t_1 we consider the two operations.

Operation 1.

- In the first operation, $Q_f = 0$ after t_1.
- Notice the reactor volume decreases after t_1 because ΔV is negative.

Semi-batch polymerization

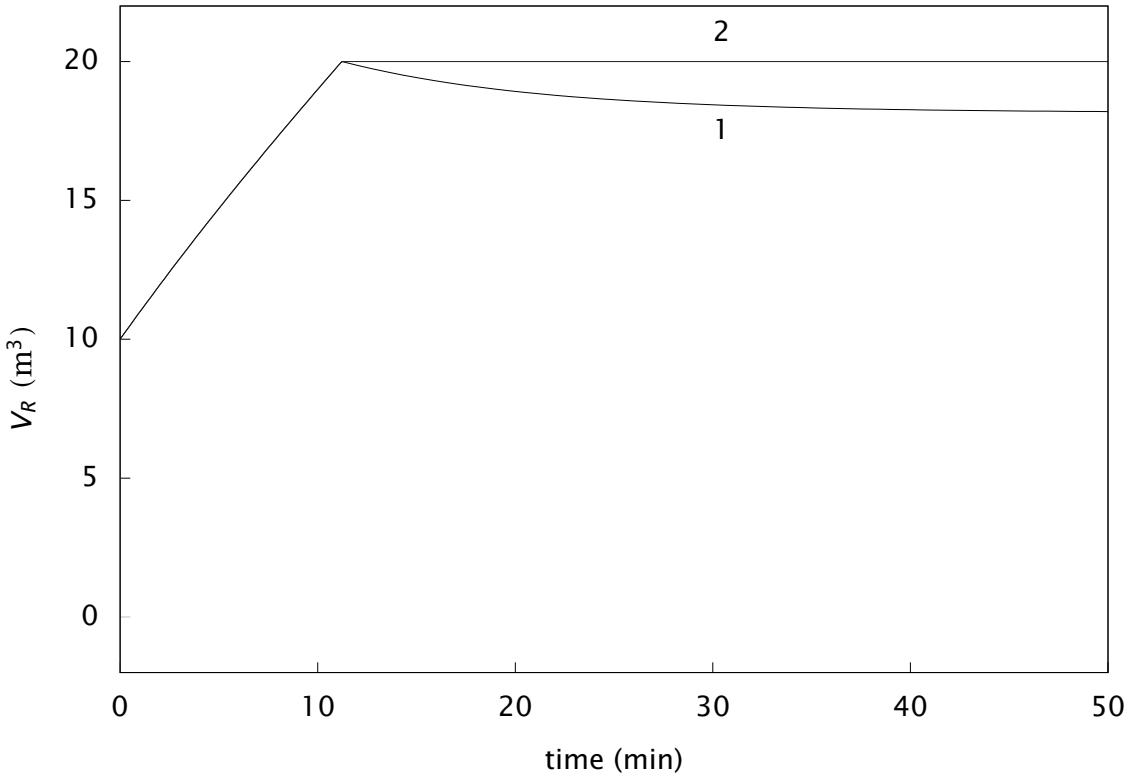


Figure 4.15: Semi-batch reactor volume for primary monomer addition (operation 1) and primary plus secondary monomer additions (operation 2).

Operation 2.

- Because the reactor volume is constant, we can solve Equation 4.55 for the feed flowrate during the secondary monomer addition

$$Q_f = -\Delta V k M$$

- Operation 2 is also shown in the figures.
- Notice the final polymer production is larger in operation 2 because of the extra monomer addition.

Polymer production rate

- We can perform an independent, simple calculation of the total polymer in operation 2. Useful for debugging the computation.
- In operation 2, 10 m^3 of polymer are produced because in an ideal mixture, the volumes are additive. Therefore

$$\widetilde{P}_2 = (V_R - V_{R0})\rho_P = 10\ m^3 \times 1100\ kg/m^3 = 11000\ kg$$

  in good agreement with the long-time solution for operation 2.
- The increase in production rate is

$$\frac{\widetilde{P}_2 - \widetilde{P}_1}{\widetilde{P}_1} \times 100\% = 22.5\%$$

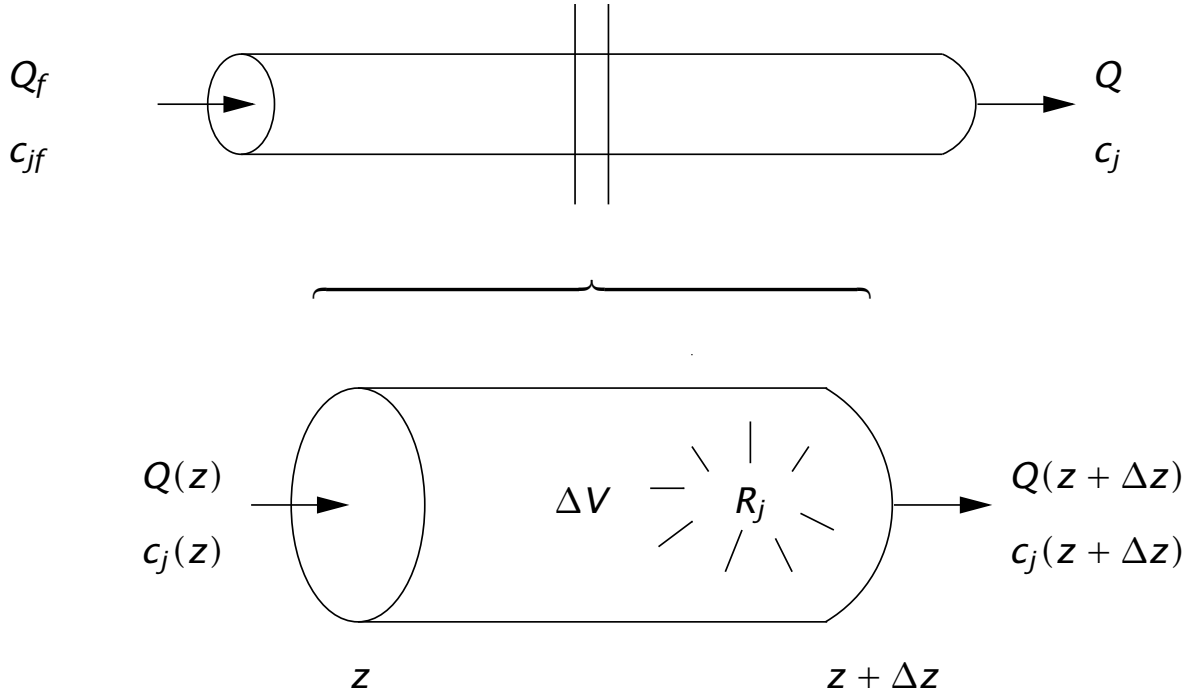
- By using the volume of the reactor more efficiently, the total polymer production increases 22.5%.

The Plug-Flow Reactor (PFR)

- Plug flow in a tube is an ideal-flow assumption in which the fluid is well mixed in the radial and angular directions.
- The fluid velocity is assumed to be a function of only the axial position in the tube.
- Plug flow is often used to approximate fluid flow in tubes at high Reynolds number. The turbulent flow mixes the fluid in the radial and angular directions.
- Also in turbulent flow, the velocity profile is expected to be reasonably flat in the radial direction except near the tube wall.

Thin Disk Volume Element

Given the plug-flow assumption, it is natural to take a thin disk for the reactor volume element



Thin Disk Volume Element

- Expressing the material balance for the volume element

$$\frac{\partial\left(c_j \Delta V\right)}{\partial t} = c_j Q\big|_z - c_j Q\big|_{z+\Delta z} + R_j \Delta V$$

- Dividing the above equation by ΔV and taking the limit as ΔV goes to zero yields,

$$\underbrace{\frac{\partial c_j}{\partial t}}_{\text{accumulation}} = -\underbrace{\frac{\partial\left(c_j Q\right)}{\partial V}}_{\text{convection}} + \underbrace{R_j}_{\text{reaction}} \tag{4.64}$$

Length or volume as independent variable

- If the tube has constant cross section, A_c, then velocity, v, is related to volumetric flowrate by $v = Q/A_c$, and axial length is related to tube volume by $z = V/A_c$,
- Equation 4.64 can be rearranged to the familiar form [1, p.584]

$$\frac{\partial c_j}{\partial t} = -\frac{\partial \left(c_j v\right)}{\partial z} + R_j \tag{4.65}$$

Steady-State Operation

- Setting the time derivative in Equation 4.64 to zero gives,

$$\frac{d(c_j Q)}{dV} = R_j \tag{4.66}$$

- The product $c_j Q = N_j$ is the total molar flow of component j. One also can express the PFR mole balance in terms of the molar flow,

$$\frac{dN_j}{dV} = R_j \tag{4.67}$$

Volumetric Flowrate for Gas-Phase Reactions

- To use Equation 4.67 for designing a gas-phase reactor, one has to be able to relate the volumetric flowrate, Q, to the molar flows, $N_j, j = 1, 2, \ldots, n_s$.
- The important piece of information tying these quantities together is, again, the equation of state for the reaction mixture, $f(T, P, c_j) = 0$.
- Because the molar flow and concentration are simply related,

$$N_j = c_j Q \tag{4.68}$$

the equation of state is also a relation between temperature, pressure, molar flows, and volumetric flowrate.

Ideal Gas Equation of State

- The ideal-gas equation of state, $c = P/RT$, can be stated in terms of molar concentrations, c_j, as

$$\sum_j c_j = \frac{P}{RT}$$

- In terms of molar flows, the equation of state is

$$\frac{\sum_j N_j}{Q} = \frac{P}{RT}$$

- One can solve the previous equation for the volumetric flowrate,

$$Q = \frac{RT}{P} \sum_j N_j \tag{4.69}$$

Ideal Gas Equation of State

- To evaluate the concentrations for use with the reaction rate expressions, one simply rearranges Equation 4.68 to obtain

$$c_j = \frac{N_j}{Q} = \frac{P}{RT}\frac{N_j}{\sum_j N_j} \tag{4.70}$$

Volumetric Flowrate for Liquid-Phase Reactions

- Consider the equation of state for a liquid-phase system to be arranged in the form

$$\rho = f(T, P, c_j)$$

- The mass density is related to the volumetric flowrate and total mass flow, $M = \sum_j N_j M_j$, via

$$M = \rho Q \tag{4.71}$$

- Multiplying Equation 4.67 by M_j and summing on j produces

$$\frac{dM}{dV} = 0, \qquad M(0) = M_f$$

  in which M_f is the feed mass flowrate.

- **The total mass flow in a PFR is constant.**

Volumetric Flowrate for Liquid-Phase Reactions

- We can solve for the volumetric flowrate by rearranging Equation 4.71

$$Q = \frac{M_f}{\rho} \tag{4.72}$$

- If the liquid density is considered constant, $\rho = \rho_f$, then

$$Q = Q_f, \qquad \text{constant density} \tag{4.73}$$

  and the volumetric flowrate is constant and equal to the feed value.
- Equation 4.73 is used often for liquid-phase reactions.

Volumetric Flowrate for Liquid-Phase Reactions

- If we denote the time spent in the tube by $\tau = V/Q$, if Q is constant, we can rewrite Equation 4.66 as

$$\frac{dc_j}{d\tau} = R_j, \qquad \text{constant flowrate} \tag{4.74}$$

  which is identical to the constant-volume batch reactor.
- For the constant-flowrate case, the steady-state profile in a PFR starting from a given feed condition is also the transient profile in a batch reactor starting from the equivalent initial condition.

Single Reaction Systems – Changing flowrate in a PFR

- A pure vapor stream of A is decomposed in a PFR to form B and C

$$\mathrm{A} \xrightarrow{k} \mathrm{B} + \mathrm{C}$$

- Determine the length of 2.5 cm inner-diameter tube required to achieve 35% conversion of A. The reactor temperature is 518°C and the pressure is 2.0 atm. Assume the pressure drop is negligible.
- The reaction rate is first order in A, $k = 0.05$ sec^{-1} at the reactor temperature, and the feed flowrate is 35 L/min.

Changing flowrate in a PFR

- The mole balance for component A gives

$$\frac{dN_A}{dV} = R_A$$

- The production rate of A is $R_\mathrm{A} = -r = -kc_\mathrm{A}$.
- Substituting the production rate into the above equation gives,

$$\frac{dN_A}{dV} = -kN_A/Q \tag{4.75}$$

- The volumetric flowrate is not constant, so we use Equation 4.69, which assumes an ideal-gas equation of state,

$$Q = \frac{RT}{P}\left(N_\mathrm{A} + N_\mathrm{B} + N_\mathrm{C}\right) \tag{4.76}$$

Changing flowrate in a PFR

- The ideal-gas assumption is reasonable at this reactor temperature and pressure.
- One can relate the molar flows of B and C to A using the reaction stoichiometry. The mole balances for B and C are

$$\frac{dN_B}{dV} = R_B = r \qquad \frac{dN_C}{dV} = R_C = r$$

- Adding the mole balance for A to those of B and C gives

$$\frac{d\left(N_A + N_B\right)}{dV} = 0 \qquad \frac{d\left(N_A + N_C\right)}{dV} = 0$$

- The stoichiometry does not allow the molar flow $N_A + N_B$ or $N_A + N_C$ to change with position in the tube.

Changing flowrate in a PFR

- Because $N_A + N_B$ and $N_B + N_C$ are known at the tube entrance, one can relate N_B and N_C to N_A,

$$N_A + N_B = N_{Af} + N_{Bf}$$
$$N_A + N_C = N_{Af} + N_{Cf}$$

- Rearranging the previous equations gives,

$$N_B = N_{Af} + N_{Bf} - N_A$$
$$N_C = N_{Af} + N_{Cf} - N_A$$

- Substituting the relations for N_B and N_C into Equation 4.76 gives

$$Q = \frac{RT}{P}\left(2N_{Af} + N_{Bf} + N_{Cf} - N_A\right)$$

Changing flowrate in a PFR

- Because the feed stream is pure A, $N_{Bf} = N_{Cf} = 0$, yielding

$$Q = \frac{RT}{P}\left(2N_{Af} - N_A\right)$$

- Substituting this expression in Equation 4.75 gives the final mole balance,

$$\frac{dN_A}{dV} = -k\frac{P}{RT}\frac{N_A}{2N_{Af} - N_A}$$

- The above differential equation can be separated and integrated,

$$\int_{N_{Af}}^{N_A} \frac{2N_{Af} - N_A}{N_A} dN_A = \int_0^V -\frac{kP}{RT} dV$$

Changing flowrate in a PFR

- Performing the integration gives,

$$2N_{Af}\ln\left(N_A/N_{Af}\right) + \left(N_{Af} - N_A\right) = -\frac{kP}{RT}V$$

- The conversion of component j for a plug-flow reactor operating at steady state is defined as

$$x_j = \frac{N_{jf} - N_j}{N_{jf}}$$

- Because we are interested in the V corresponding to 35% conversion of A, we substitute $N_A = (1 - x_A)N_{Af}$ into the previous equation and solve for V,

$$V = -\frac{RT}{kP}N_{Af}\left[2\ln(1 - x_A) + x_A\right]$$

Changing flowrate in a PFR

- Because $Q_f = N_{Af}RT/P$ is given in the problem statement and the tube length is desired, it is convenient to rearrange the previous equation to obtain

$$z = -\frac{Q_f}{kA_c}\left[2\ln(1 - x_A) + x_A\right]$$

- Substituting in the known values gives

$$z = -\left(\frac{35 \times 10^3 \text{ cm}^3/\text{min}}{0.05 \text{ sec}^{-1}\ 60 \text{ sec/min}}\right)\left(\frac{4}{\pi(2.5 \text{ cm})^2}\right)\left[2\ln(1 - .35) + .35\right]$$

$$z = 1216 \text{ cm} = 12.2 \text{ m}$$

Multiple-Reaction Systems

- The modeler has some freedom in setting up the material balances for a plug-flow reactor with several reactions.
- The most straightforward method is to write the material balance relation for every component,

$$\frac{dN_j}{dV} = R_j, \qquad j = 1, 2, \ldots, n_s$$

$$R_j = \sum_{i=1}^{n_r} \nu_{ij} r_i, \qquad j = 1, 2, \ldots, n_s$$

- The reaction rates are expressed in terms of the species concentrations.
- The c_j are calculated from the molar flows with Equation 4.68
- Q is calculated from Equation 4.69, if an ideal-gas mixture is assumed.

Benzene pyrolysis in a PFR I

- Hougen and Watson [3] analyzed the rate data for the pyrolysis of benzene by the following two reactions.
- Diphenyl is produced by the dehydrogenation of benzene,

$$\begin{aligned} 2C_6H_6 &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_{12}H_{10} + H_2 \\ 2B &\rightleftharpoons D + H \end{aligned}$$

Benzene pyrolysis in a PFR

- Triphenyl is formed by the secondary reaction,

$$\begin{aligned} C_6H_6 + C_{12}H_{10} &\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_{18}H_{14} + H_2 \\ B + D &\rightleftharpoons T + H \end{aligned}$$

- The reactions are assumed to be elementary so that the rate expressions are

$$r_1 = k_1\left(c_B^2 - \frac{c_D c_H}{K_1}\right) \qquad r_2 = k_2\left(c_B c_D - \frac{c_T c_H}{K_2}\right) \qquad (4.79)$$

Benzene pyrolysis in a PFR

- Calculate the tube volume required to reach 50% total conversion of the benzene for a 60 kmol/hr feed stream of pure benzene.
- The reactor operates at 1033K and 1.0 atm.
- Plot the mole fractions of the four components versus reactor volume.

Benzene pyrolysis in a PFR

- The rate and equilibrium constants at $T = 1033\text{K}$ and $P = 1.0$ atm are given in Hougen and Watson,

$$k_1 = 7 \times 10^5 \text{ L/mol} \cdot \text{hr}$$
$$k_2 = 4 \times 10^5 \text{ L/mol} \cdot \text{hr}$$
$$K_1 = 0.31$$
$$K_2 = 0.48$$

Benzene pyrolysis in a PFR

- The mole balances for the four components follow from the stoichiometry,

$$\frac{dN_B}{dV} = -2r_1 - r_2$$
$$\frac{dN_D}{dV} = r_1 - r_2$$
$$\frac{dN_H}{dV} = r_1 + r_2$$
$$\frac{dN_T}{dV} = r_2$$

- The initial condition for the ODEs are $N_B(0) = N_{Bf}$ and $N_D(0) = N_H(0) = N_T(0) = 0$.

Benzene pyrolysis in a PFR

- The total molar flux does not change with reactor volume.

$$Q = \frac{RT}{P} N_{Bf} \tag{4.80}$$

- The rate expressions are substituted into the four ODEs and they are solved numerically.
- The total conversion of benzene, $x_B = (N_{Bf} - N_B)/N_{Bf}$, is plotted versus reactor volume in Figure 4.20.
- A reactor volume of 404 L is required to reach 50% conversion. The composition of the reactor versus reactor volume is plotted in Figure 4.21.

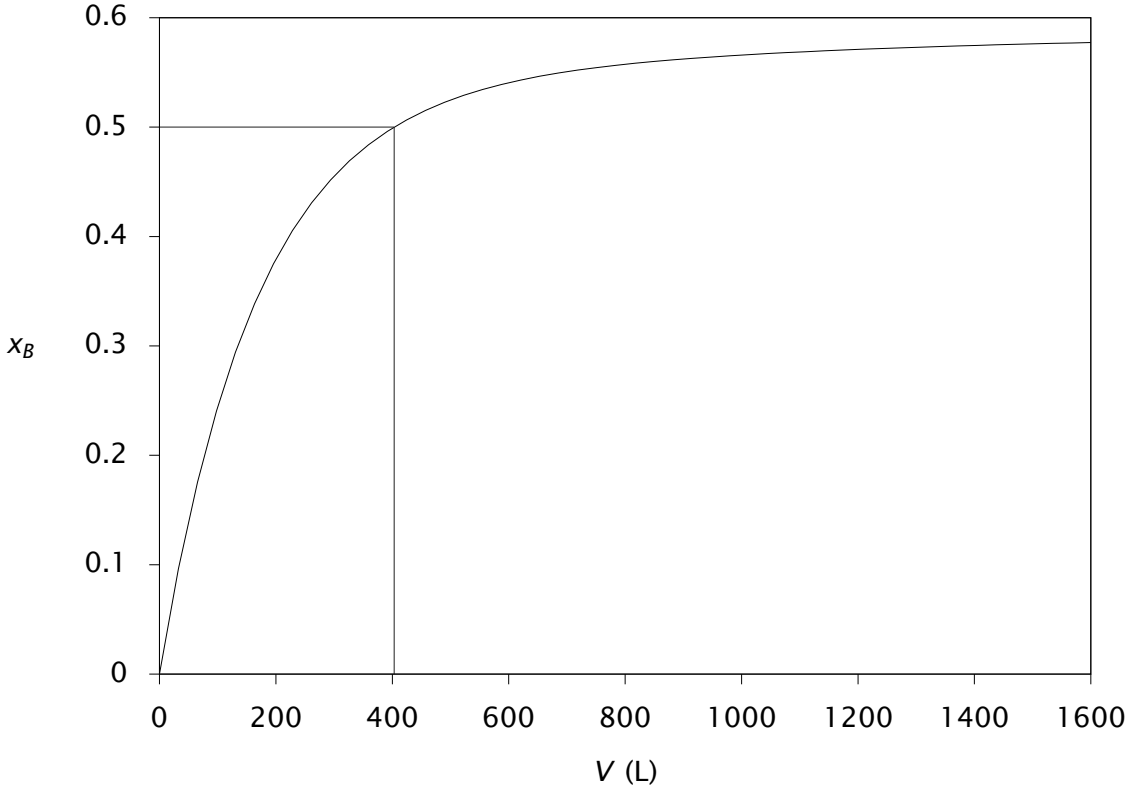


Figure 4.20: Benzene conversion versus reactor volume.

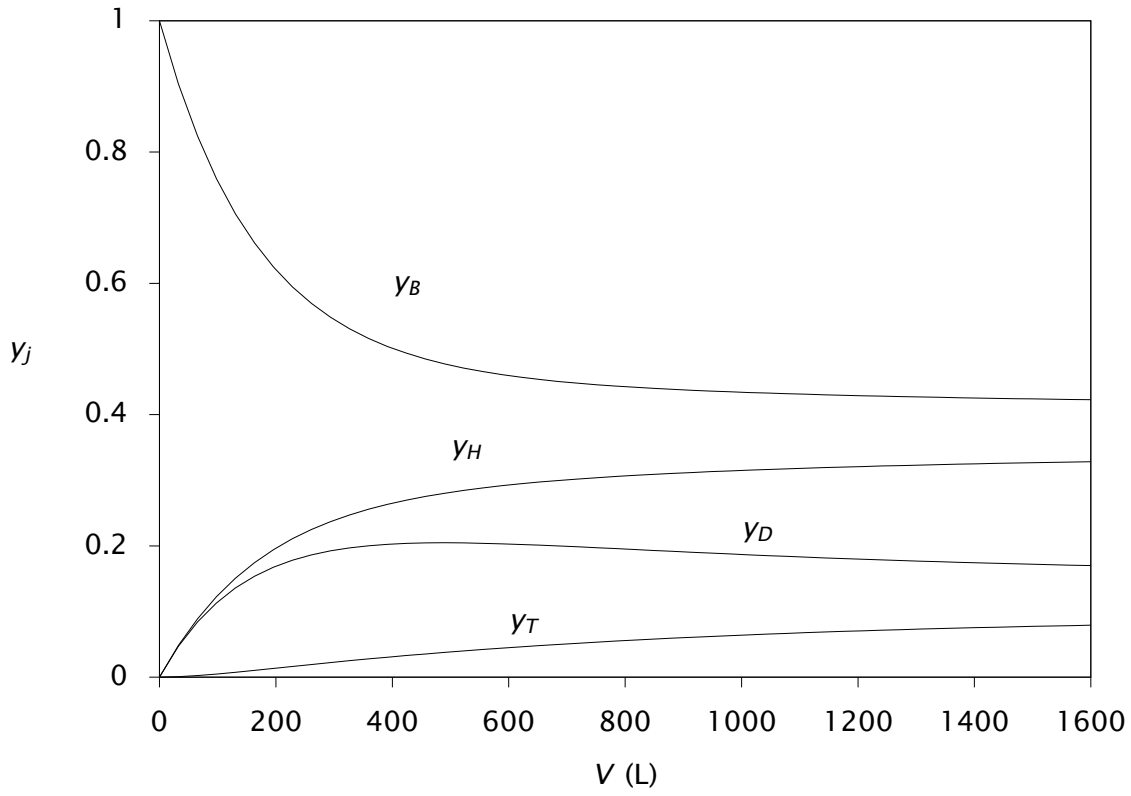


Figure 4.21: Component mole fractions versus reactor volume.

Ethane pyrolysis in the presence of NO

- See the text for another worked PFR example.

Some PFR-CSTR Comparisons

- We have two continuous reactors in this chapter: the CSTR and the PFR.
- Let's compare their steady-state efficiencies in converting reactants to products.
- For simplicity, consider a constant-density, liquid

$$\mathrm{A} \xrightarrow{k} \mathrm{B} \qquad r = kc_A^n$$

- For this situation, the steady-state PFR material balance is given by Equation 4.74

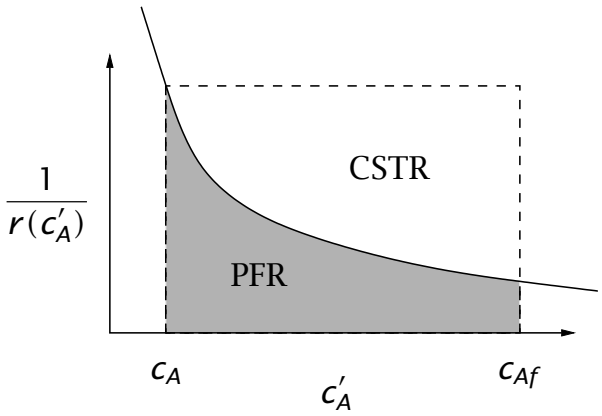
$$\frac{dc_A}{d\tau} = -r(c_A)$$

Some PFR-CSTR Comparisons

- We rearrange and solve for the time required to change from the feed condition c_{Af} to some exit concentration c_A

$$\tau = \int_{c_{Af}}^{c_A} \frac{1}{r(c'_A)} dc'_A$$

- The area under the curve $1/r(c'_A)$ is the total time required to achieve the desired concentration change.

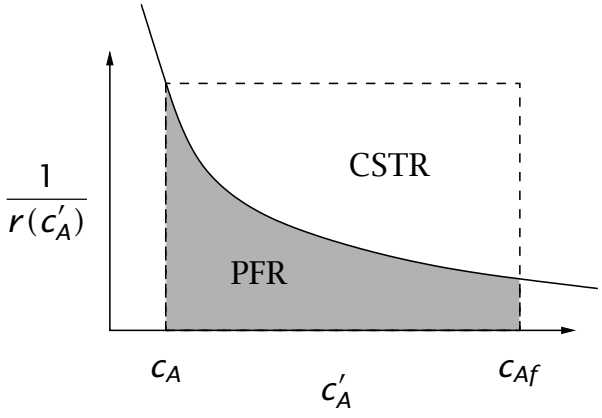


Some PFR-CSTR Comparisons

- To achieve this same concentration change in the CSTR, we start with Equation 4.40, and solve for τ giving

$$\tau = \frac{c_{Af} - c_A}{r(c_A)}$$

- This result also can be interpreted as an area. Notice that this area is the height, $1/r(c_A)$, times the width, $c_{Af} - c_A$, of the rectangle.

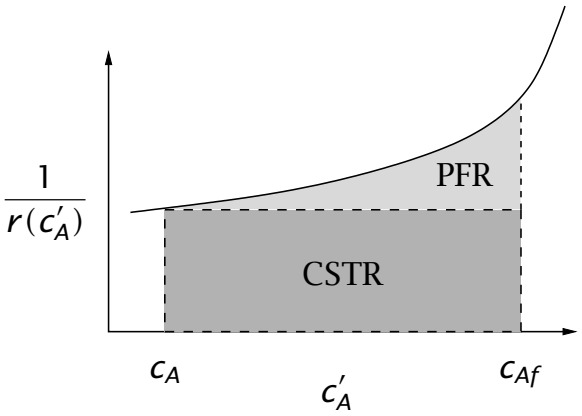


Some PFR-CSTR Comparisons

- If $1/r(c_A)$ is a *decreasing* function of c_A, or, equivalently, $r(c_A)$ is an *increasing* function of c_A, to achieve the same conversion, the PFR time (or volume, $V_R = Q_f \tau$) is less than the CSTR time (volume).
- The PFR reaction rate varies with length. The rate is high at the entrance to the tube where the concentration of A is equal to the feed value, and decreases with length as the concentration drops. At the exit of the PFR, the rate is the lowest of any location in the tube.
- Now considering that the entire volume of the CSTR is reacting at this *lowest* rate of the PFR, it is intuitively obvious that more volume is required for the CSTR to achieve the same conversion as the PFR.

Some PFR-CSTR Comparisons

- If the reaction order is positive (the usual case), the PFR is more efficient. If the reaction order is negative, the CSTR is more efficient.



The PFR versus CSTR with separation

- The PFR achieves higher conversion than an equivalent volume CSTR for the irreversible reaction with first-order kinetics

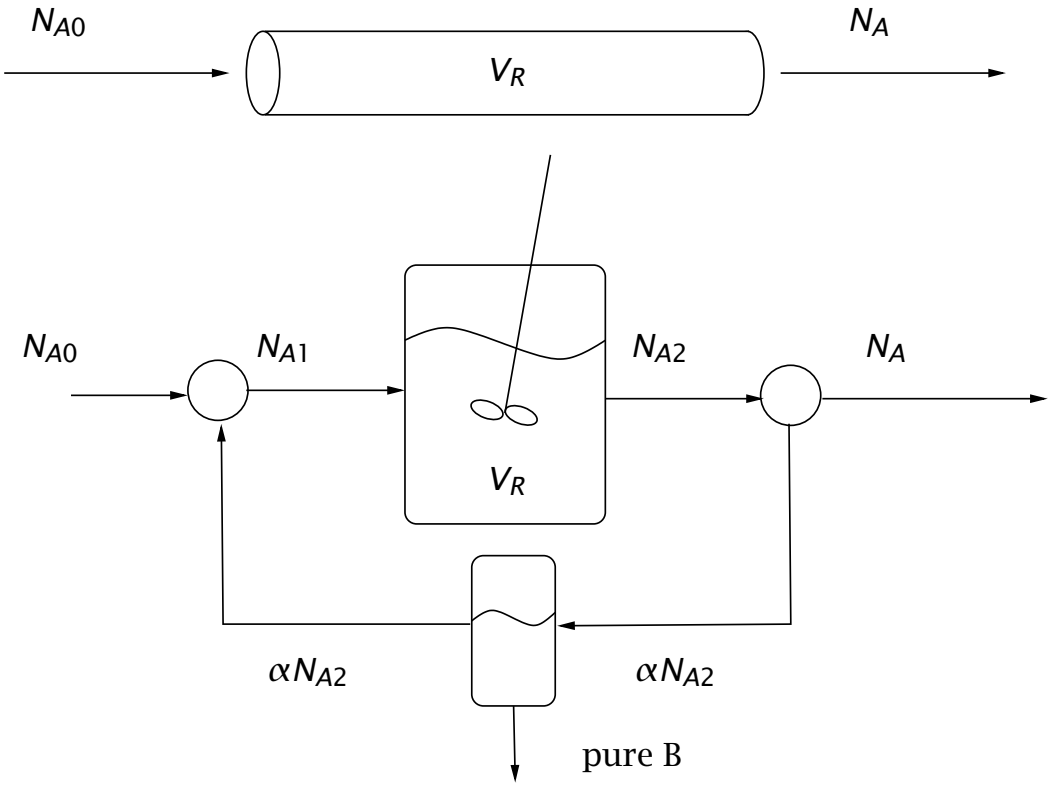
$$\mathrm{A} \longrightarrow \mathrm{B} \qquad r = kc_A$$

- Consider the case in which we add separation.
- Find a single CSTR and separator combination that achieves the same conversion as the PFR.

The PFR versus CSTR with separation

- The issue is to increase the CSTR achievable conversion using separation.
- Education in chemical engineering principles leads one immediately to consider recycle of the unreacted A as a means to increase this conversion.

The PFR versus CSTR with separation



- In the text, we show how to find the recycle flowrate so this system achieves the PFR conversion.

CSTR Equivalence Principle.

- This example was motivated by a recent result of Feinberg and Ellison called the CSTR Equivalence Principle of Reactor-Separator Systems [2].
- 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.

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.
- 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.

Stochastic Simulation of Chemical Reactions

- 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.

Stochastic Simulation of Chemical Reactions

- Assume we have only a hundred molecules moving randomly in the gas phase

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}$$
$$\mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

  in a constant-volume batch reactor.
- 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 the deterministic model's c_j, which is real.

Stochastic Simulation of Chemical Reactions

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.

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 $r_{\text{tot}} = \sum_i r_i$.

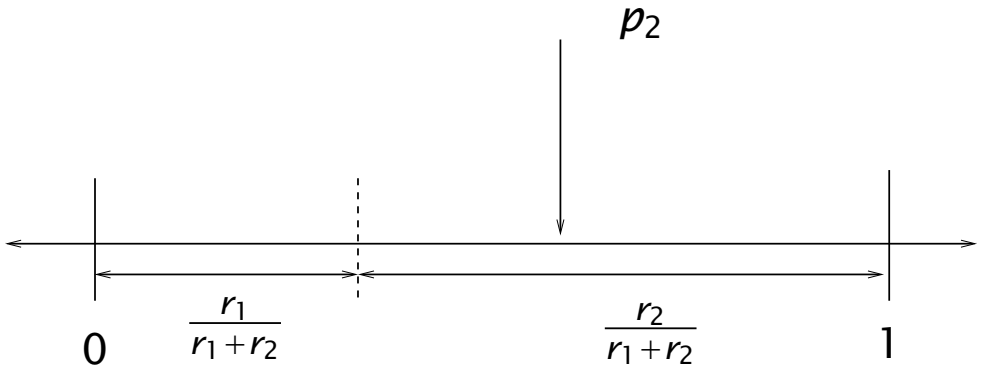
Stochastic Simulation of Chemical Reactions

1. 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

$$\tilde{t} = -\ln(p_1)/r_{\text{tot}} \tag{4.85}$$

Stochastic Simulation of Chemical Reactions

1. 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.



Stochastic Simulation of Chemical Reactions

1. Update the simulation time $t(n+1) = t(n) + \tilde{t}$. Update the species numbers for the single occurrence of the mth reaction via

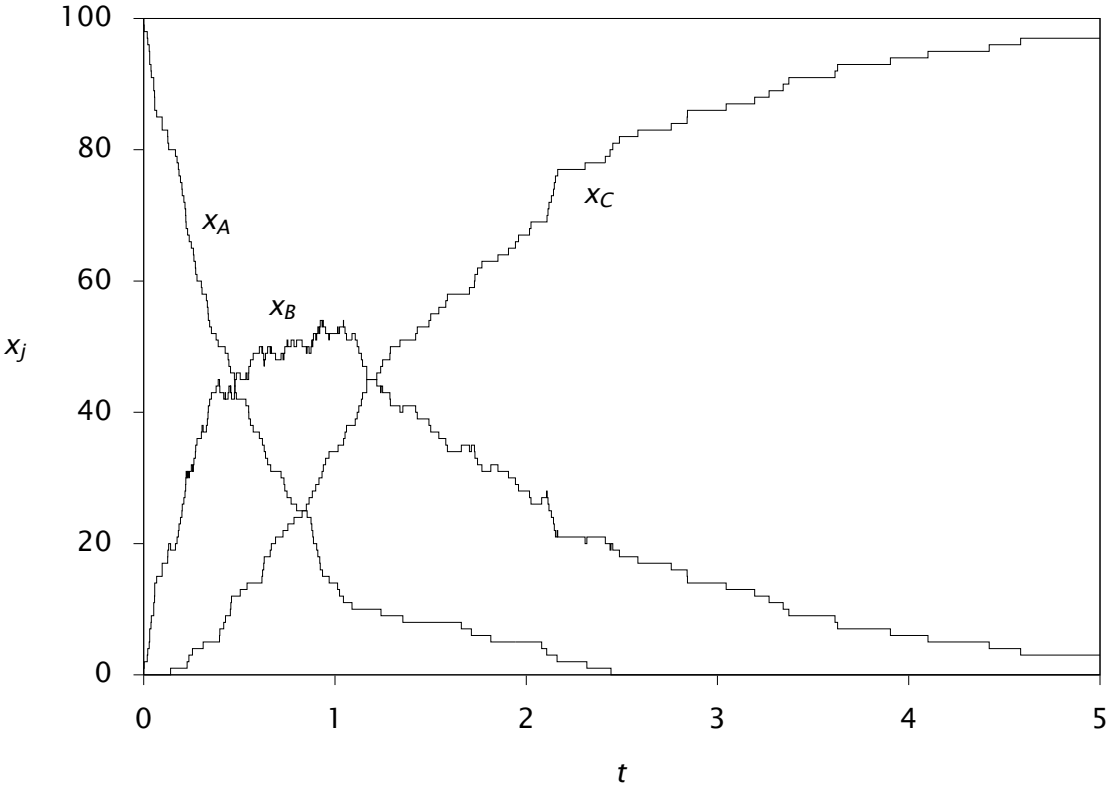
$$x_j(n+1) = x_j(n) + \nu_{mj}, \qquad j = 1, \ldots n_s$$

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

Stochastic Simulation of Chemical Reactions

- If r_{tot} is the total probability for reaction, $e^{-r_{tot}\tilde{t}}$ is the probability that a reaction has not occurred during time interval $\tilde{t}$.
- We will derive this fact in Chapter 8 when we develop the residence-time distribution for a CSTR.
- The next figure shows the results of this algorithm when starting with $x_A = 100$ molecules.

Stochastic Simulation of Chemical Reactions



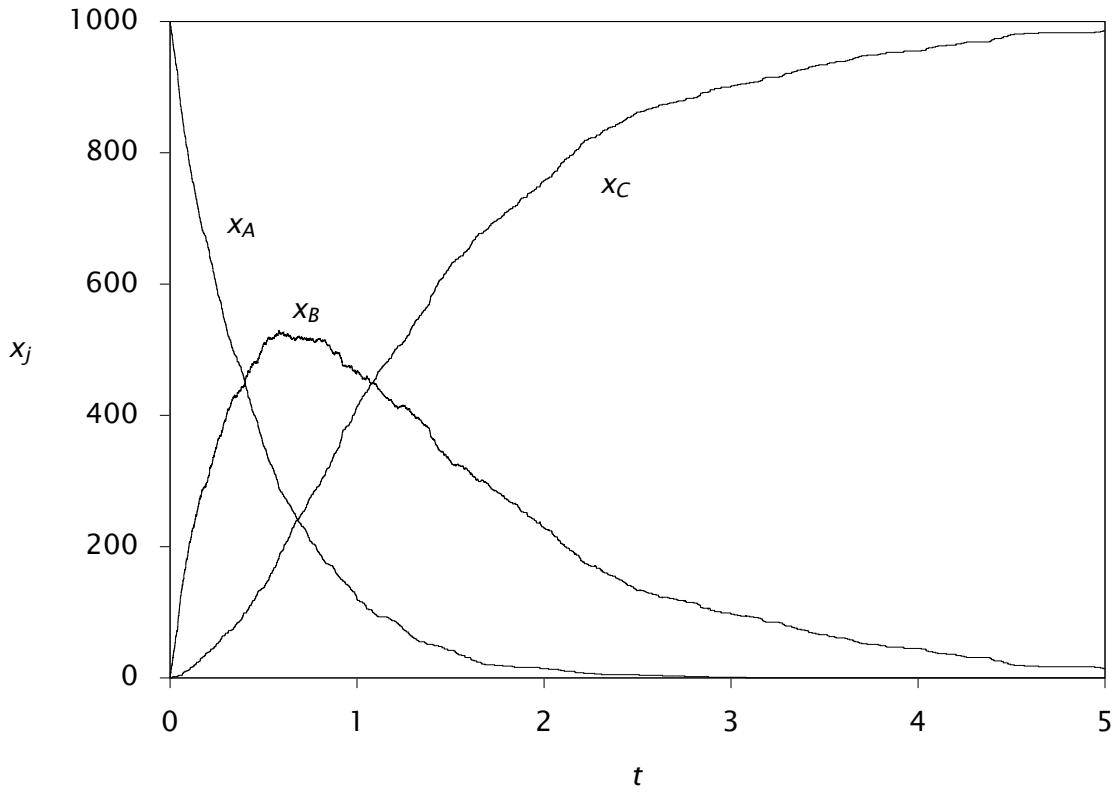
Stochastic Simulation of Chemical Reactions

- 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.
- 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.

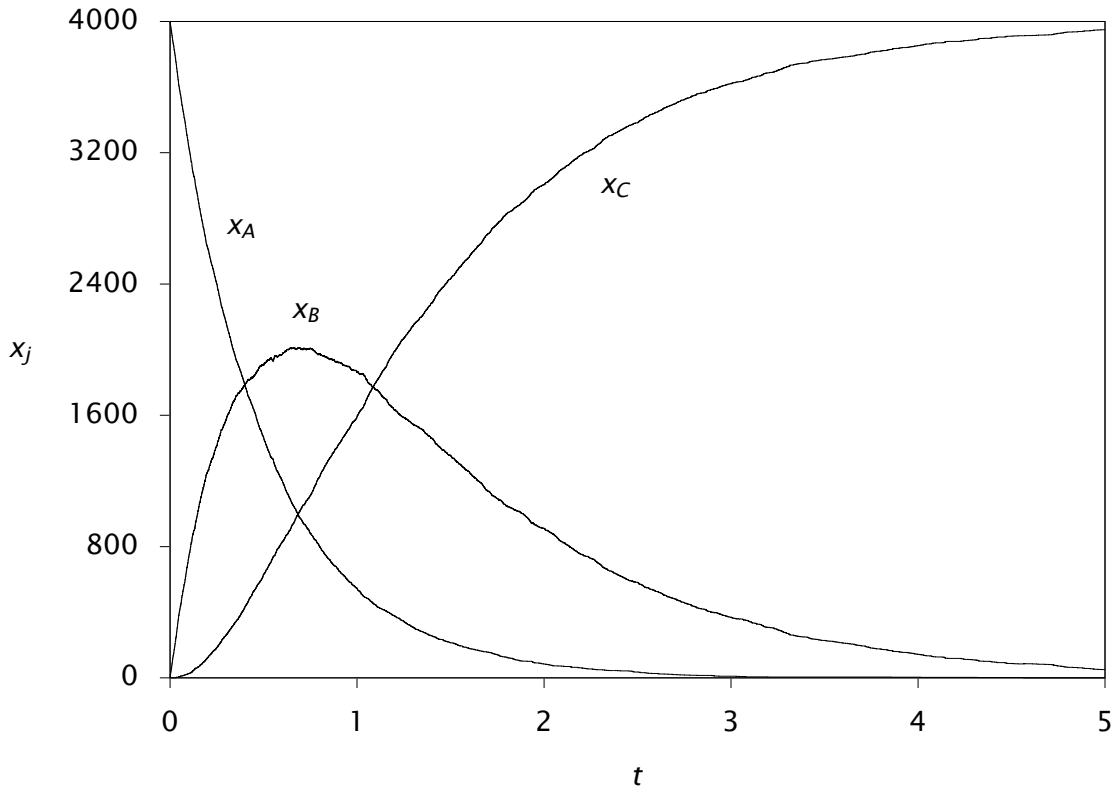
Stochastic Simulation of Chemical Reactions

- 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 the next figures.

Stochastic Simulation of Chemical Reactions



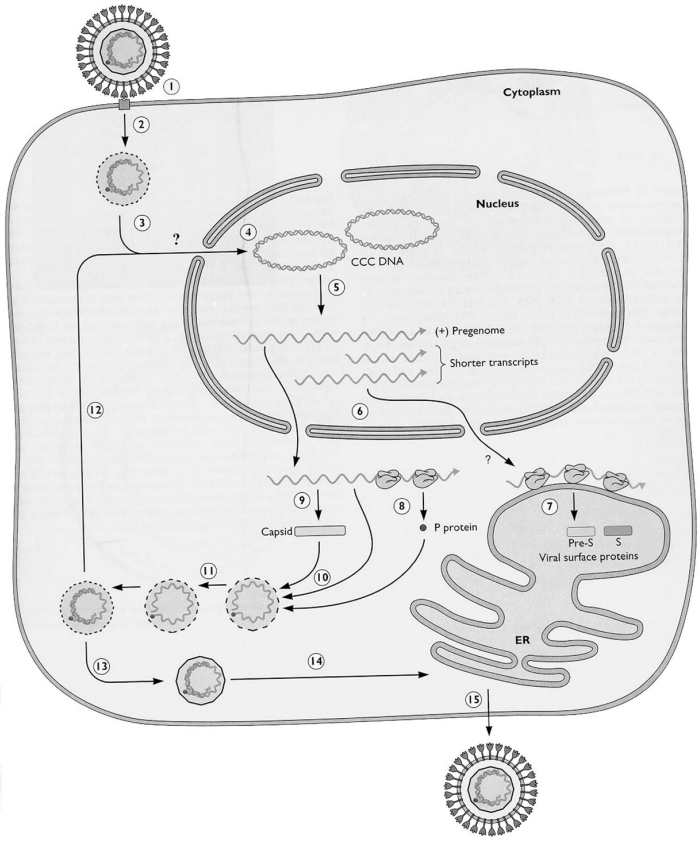
Stochastic Simulation of Chemical Reactions



Stochastic Simulation of Chemical Reactions

- We see the random fluctuations become less pronounced. Notice that even with only 4000 starting molecules, the results compare very favorably with the deterministic simulation shown previously.
- Another striking feature of the stochastic approach is the trivial level of programming effort required to make the simulations.
- The biggest numerical challenge is producing the pseudorandom numbers and many well-developed algorithms are available for that task.
- The computational time required for performing the stochastic simulation may, however, be large.

Hepatitis B virus modeling



Hepatitis B virus modeling

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

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

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

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

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

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

Hepatitis B virus modeling

- The reaction rates and production rates for Reactions 4.86–4.91 are given by

$$\begin{bmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \\ r_5 \\ r_6 \end{bmatrix} = \begin{bmatrix} k_1 x_A \\ k_2 x_B \\ k_3 x_A \\ k_4 x_A \\ k_5 x_C \\ k_6 x_B x_C \end{bmatrix} \qquad \begin{bmatrix} R_A \\ R_B \\ R_C \end{bmatrix} = \begin{bmatrix} r_2 - r_4 \\ r_1 - r_2 - r_6 \\ r_3 - r_5 - r_6 \end{bmatrix} \tag{4.94}$$

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

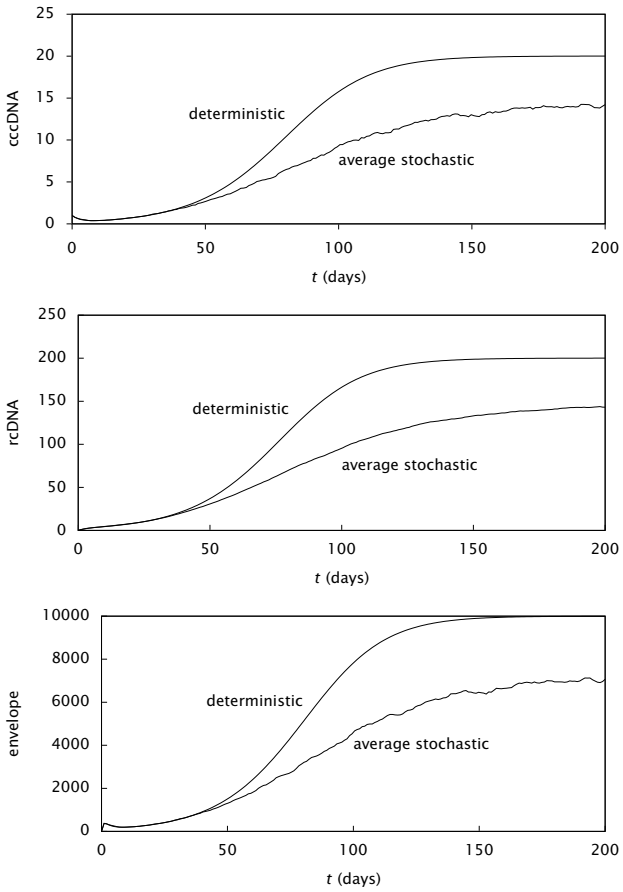
Hepatitis B virus modeling

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

$$\begin{bmatrix} x_A & x_B & x_C \end{bmatrix}^T = \begin{bmatrix} 1 & 0 & 0 \end{bmatrix}^T \tag{4.92}$$

$$\boldsymbol{k}^T = \begin{bmatrix} 1 & 0.025 & 1000 & 0.25 & 2 & 7.5 \times 10^{-6} \end{bmatrix} \tag{4.93}$$

Average stochastic is not deterministic. I



Hepatitis B virus modeling

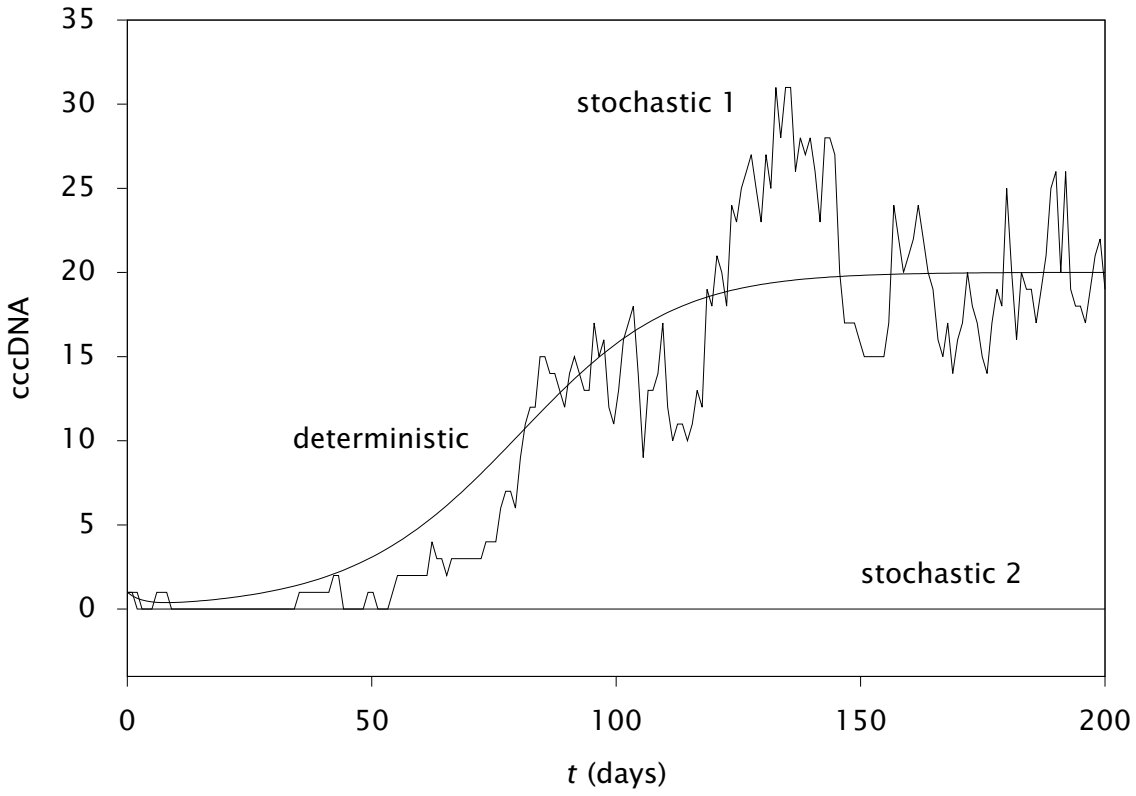


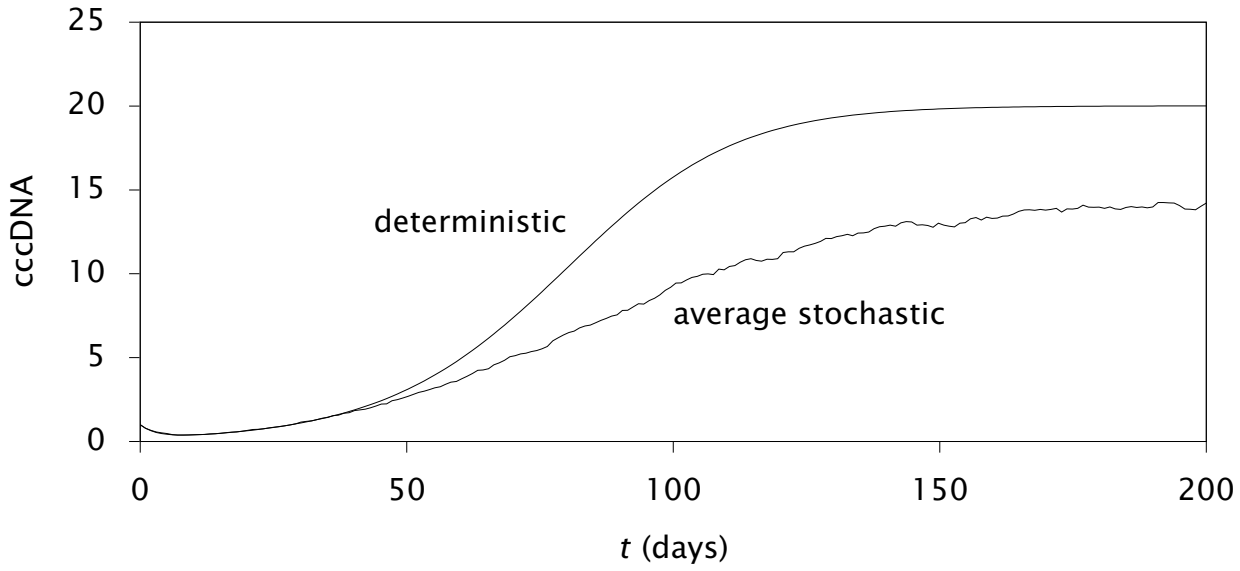
Figure 4.35: Species cccDNA versus time for hepatitis B virus model; two representative stochastic trajectories.

Hepatitis B virus modeling

- The simulation of the deterministic model and an average of 500 stochastic simulations are *not* the same.
- 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.

Average stochastic is not deterministic.

- In fact, it occurs for 125 of the 500 simulations. So the *average* stochastic simulation consists of 75% trajectories that fluctuate about the deterministic trajectory and 25% trajectories that go to zero.



Summary

- We have introduced four main reactor types in this chapter.
- the batch reactor
- the continuous-stirred-tank reactor (CSTR)
- the semi-batch reactor
- the plug-flow reactor (PFR).

Summary

BATCH	$\frac{d(c_j V_R)}{dt} = R_j V_R$	(4.95)
constant volume	$\frac{dc_j}{dt} = R_j$	(4.96)
CSTR	$\frac{d(c_j V_R)}{dt} = Q_f c_{jf} - Q c_j + R_j V_R$	(4.97)
constant density	$\frac{dc_j}{dt} = \frac{1}{\tau}(c_{jf} - c_j) + R_j$	(4.98)
steady state	$c_j = c_{jf} + R_j \tau$	(4.99)
SEMI-BATCH	$\frac{d(c_j V_R)}{dt} = Q_f c_{jf} + R_j V_R$	(4.100)
PFR	$\frac{\partial c_j}{\partial t} = -\frac{\partial (c_j Q)}{\partial V} + R_j$	(4.101)
steady state	$\frac{d(c_j Q)}{dV} = R_j$	(4.102)
constant flowrate	$\frac{dc_j}{d\tau} = R_j, \quad \tau = V/Q_f$	(4.103)

Summary

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

Summary

- 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.
- 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.

Summary

- 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 nth-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.

Summary

- The stochastic model uses basic probability to compute reaction rate. A given reaction's probability of occurrence is assumed proportional to the number of possible combinations of reactants for the given stoichiometry.
- Two pseudorandom 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.

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