Mixing in Chemical Reactors

- The three main reactor types developed thus far — batch, continuous-stirred-tank, and plug-flow reactors — are useful for modeling many complex chemical reactors.

- Up to this point we have neglected a careful treatment of the fluid flow pattern within the reactor.

- In this chapter we explore some of the limits of this approach and develop methods to address and overcome some of the more obvious limitations.

Scope of problem

- The general topic of mixing, even in the restricted context of chemical reactors, is an impossibly wide one to treat comprehensively.

- In this chapter, we will restrict ourselves to fluid-phase systems.

- One natural approach to describing mixing is to solve the equations of motion of the fluid.

- In fluid systems, the type of fluid flow is obviously important, and we should consider both laminar and turbulent flow, and various mechanisms of diffusion (molecular diffusion, eddy diffusion).

- Using fluid mechanics to describe all cases of interest is a difficult problem, both from the modeling and computational perspectives. Rapid developments in computational fluid dynamics (CFD), however, make this approach increasingly attractive [1].

Residence-time distribution

- A second, classical approach to describing mixing is to use simple tests to experimentally probe the system of interest.

- These empirical testing approaches do not use any of the structure of the equations of motion, but they can provide some rough features of the mixing taking place in the system under study.

- In this chapter we first develop this classical approach, and find out what kinds of understanding it can provide.

- We also identify some of the limitations of this approach. Nauman and Buffham provide a more in-depth treatment of many of the classical topics

covered in this chapter, and provide many further citations to the research literature [15].

Convection and diffusion

- One might intuitively expect that to enhance mixing and reduce spatial variation in concentration, one should seek conditions that maximize the rate of diffusion.

- Although this notion is correct for mixing on the finest length scales, it is generally much more important in macroscopic scale processes to decrease variations on the larger length scales.

- Mixing in this regime is enhanced primarily by improving the convection, and diffusion plays only a small role.

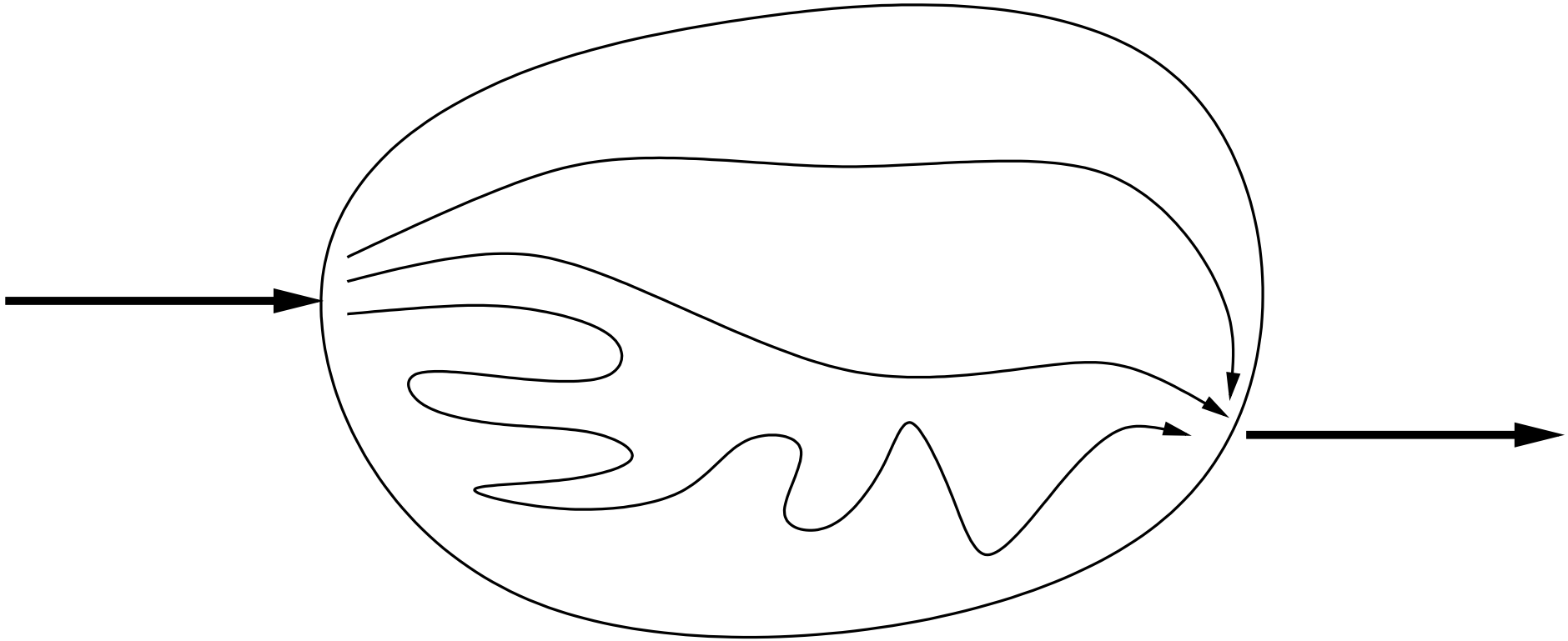
- In simple terms, one does not expect to appreciably decrease the time required to mix the cream in one's coffee by increasing the coffee temperature

(enhanced diffusion); one instead turns a spoon a few times (enhanced convection).

- On the finest length scales, mixing is accomplished readily for small molecules by the random process of molecular diffusion; in fact, the random molecular motions are the only effective mixing processes taking place on the finest length scales.

Residence-Time Distribution — Definition

- Consider an arbitrary reactor with single feed and effluent streams depicted in the following figure



- Without solving for the entire flow field, which might be quite complex, we would like to characterize the flow pattern established in the reactor at steady state.

- The residence-time distribution (RTD) of the reactor is one such characterization or measure of the flow pattern.

Gedanken Experiment

- Imagine we could slip some inert tracer molecules into the feed stream and could query these molecules on their exit from the reactor as to how much time they had spent in the reactor.

- We assume that we can add a small enough amount of tracer in the feed so that we do not disturb the established flow pattern.

- Some of the tracer molecules might happen to move in a very direct path to the exit; some molecules might spend a long time in a poorly mixed zone before finally finding their way to the exit.

- Due to their random motions as well as convection with the established flow, which itself might be turbulent, we would start recording a distribution of

residence times and we would create the residence-time probability density or residence-time distribution.

- If the reactor is at steady state, and after we had collected sufficient residence-time statistics, we expect the residence-time distribution to also settle down to a steady function.

Probability density

Let $p(\theta)$ represent the probability density or residence-time distribution, and $P(\theta)$ the integrated form so

$$p(\theta)d\theta, \quad \text{probability that a feed molecule spends time } \theta \text{ to } \theta + d\theta \text{ in the reactor} \tag{1}$$

$$P(\theta), \quad \text{probability that a feed molecule spends time zero to } \theta \text{ in the reactor} \tag{2}$$

The two versions of the probability function obviously contain the same in-

formation and are related by

$$P(\theta) = \int_0^\theta p(\theta')d\theta', \qquad p(\theta) = \frac{dP(\theta)}{d\theta}$$

Measuring the RTD

- As a thought experiment to define the RTD, querying tracer molecules on their exit from the reactor is a fine concept.

- But we plan to actually measure the RTD, so we require an implementable experiment with actual measurements.

- We cannot measure the time spent by a particular tracer molecule in the reactor; to us, all tracer molecules are identical. We can measure concentration of tracer molecules in the effluent, however, and that will prove sufficient to measure the RTD.

- Imagine an experiment in which we measure the concentration of tracer in the

feed and effluent streams over some time period, while the reactor maintains a steady flow condition.

- From the definition of the RTD in the previous section, the effluent tracer concentration at some time t is established by the combined exit of many tracer molecules with many different residence times.

Convolution integral

- The concentration of molecules that enter the reactor at time t' and spend time $t - t'$ in the reactor before exiting is given by $c_f(t')p(t - t')dt'$.

- These molecules are the ones leaving the reactor at time t that establish effluent concentration $c_e(t)$, so we have

$$c_e(t) = \int_{-\infty}^{t} c_f(t')p(t - t')dt' \tag{3}$$

- The inlet and outlet concentrations are connected through this convolution integral with the residence-time distribution.

- If we conduct the experiment so that the feed tracer concentration is zero before an initial time $t = 0$, then the integral reduces to

$$c_e(t) = \int_0^t c_f(t')p(t - t')dt', \qquad c_f(t) = 0, t \leq 0 \tag{4}$$

Tracer concentrations to RTD

- Notice we can change the variable of integration in Equation 4 to establish an equivalent representation

$$c_e(t) = \int_0^t c_f(t - t')p(t')dt' \tag{5}$$

  which is sometimes a convenient form.

- This connection between the inlet and outlet concentrations, and the RTD, allows us to determine the RTD by measuring only tracer concentrations.

- We next describe some of the convenient experiments to determine the RTD.

Step response

- In the step-response experiment, at time zero we abruptly change the feed tracer concentration from steady value c_0 to steady value c_f.

- For convenience we assume $c_0 = 0$. Because the feed concentration is constant at c_f after time zero, we can take it outside the integral in Equation 5 and obtain

$$c_e(t) = c_f \int_0^t p(t')dt' = c_f P(t)$$

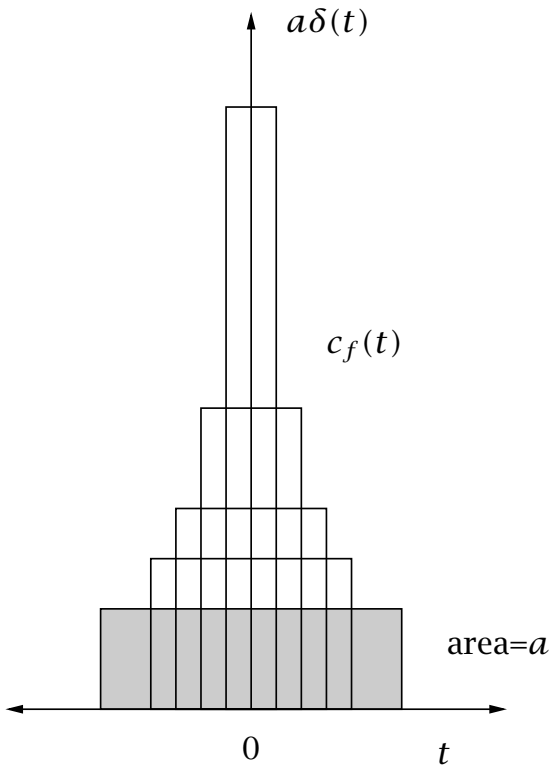
- So for a step-response experiment, the effluent concentration versus time provides immediately the integrated form of the residence-time distribution

$$P(\theta) = c_e(\theta)/c_f, \qquad \text{step response} \tag{6}$$

Pulse and impulse responses

- An impulse response is an idealized experiment, but is a useful concept. As we will see it provides the RTD directly rather than in the integrated form.

- To motivate the impulse-response experiment, imagine we abruptly change the inlet tracer concentration from zero to a large value and return it to zero after a short time as sketched in the following figure.



- Such a test is called a pulse test. The pulse test is no more difficult to implement than the step test; it is merely two step changes in feed concentration in rapid succession. In some ways it is a superior test to the step response, because by returning the tracer concentration to zero, we use less tracer in

the experiment and we cause less disruption of the normal operation of the reactor.

From pulse to impulse

- The impulse response is an idealized limit of the pulse response. Consider a family of pulse tests of shorter and shorter duration Δt, as sketched in the figure.

- We maintain constant total tracer addition by spiking the feed with higher and higher concentrations so that the product $c_f \Delta t = a$ is constant.

- The impulse response is the limit of this experiment as $\Delta t \longrightarrow 0$. We call this limiting feed concentration versus time function the delta function, $a\delta(t)$. It is also called the Dirac delta function or an impulse, hence the name, impulse response.

Impulse response

- The constant a is the amplitude of the delta function.

- The main property of the delta function is that, because it is so narrowly focused, it extracts the value of an integrand at a point in the interval of integration,

$$\int_{-\infty}^{\infty} g(t)\delta(t)dt = g(0), \qquad \text{all } g(t) \tag{7}$$

$$\int_{-\infty}^{\infty} \delta(t)dt = 1, \qquad \text{normalized} \tag{8}$$

- So if we can approximate $c_f(t) = a\delta(t)$, then we have from Equation 3

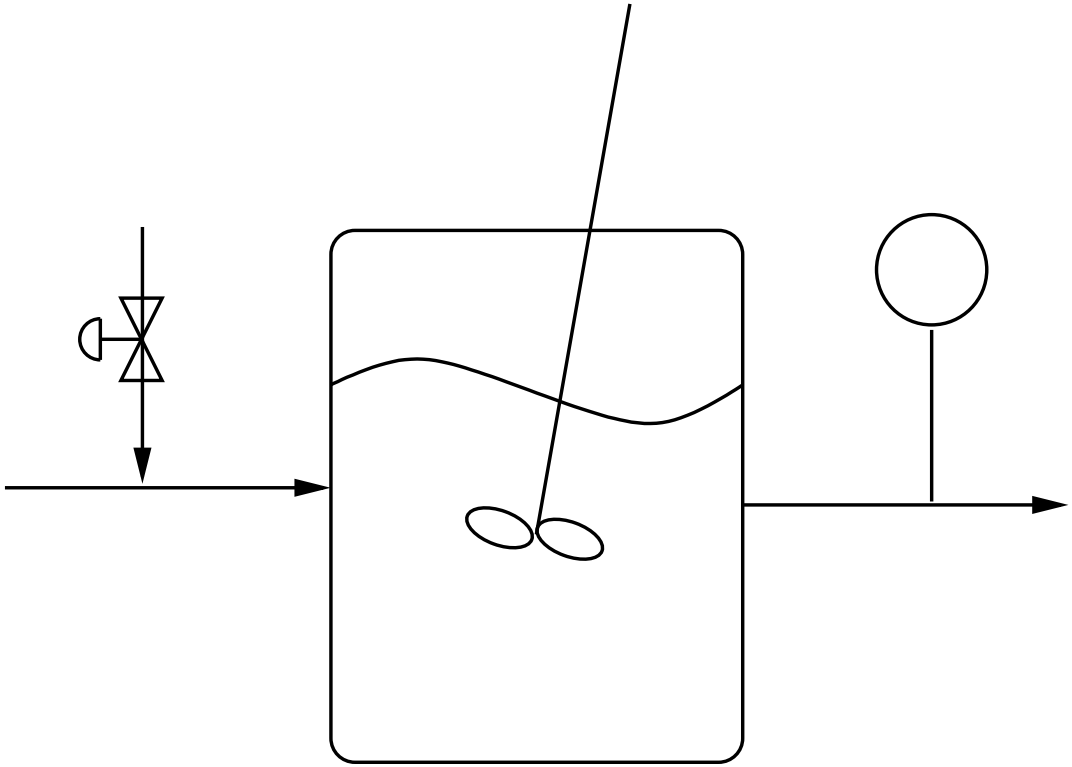
$$c_e(t) = a\int_{-\infty}^{t} \delta(t')p(t-t')dt' = ap(t)$$

- So for an experiment approximating an impulse, the effluent concentration versus time provides the residence-time distribution directly

$$p(\theta) = c_e(\theta)/a, \qquad \text{impulse response} \tag{9}$$

Continuous-Stirred-Tank Reactor (CSTR)

- We next examine again the well-stirred reactor.



- Consider the following step-response experiment: a clear fluid with flowrate Q_f enters a well-stirred reactor of volume V_R.

- At time zero we start adding a small flow of a tracer to the feed stream and measure the tracer concentration in the effluent stream.

- We expect to see a continuous change in the concentration of the effluent stream until, after a long time, it matches the concentration of the feed stream.

Mass balance

- Assuming constant density, the differential equation governing the concentration of dye in the reactor follows from Equation 4.38

$$\frac{dc}{dt} = \frac{Q_f}{V_R}(c_f - c), \qquad c(0) = 0 \tag{10}$$

  in which c is the concentration of the dye in the reactor and effluent stream.

- In Chapter 4, we named the parameter V_R/Q_f the "mean residence time" and gave it the symbol θ.

- For our purposes here, we have already reserved θ for the distribution of reactor residence times, so we define $\tau = V_R/Q_f$.

Solution to mass balance is the RTD

We already derived the solution to Equation 10, where

$$c(t) = (1 - e^{-t/\tau})c_f$$

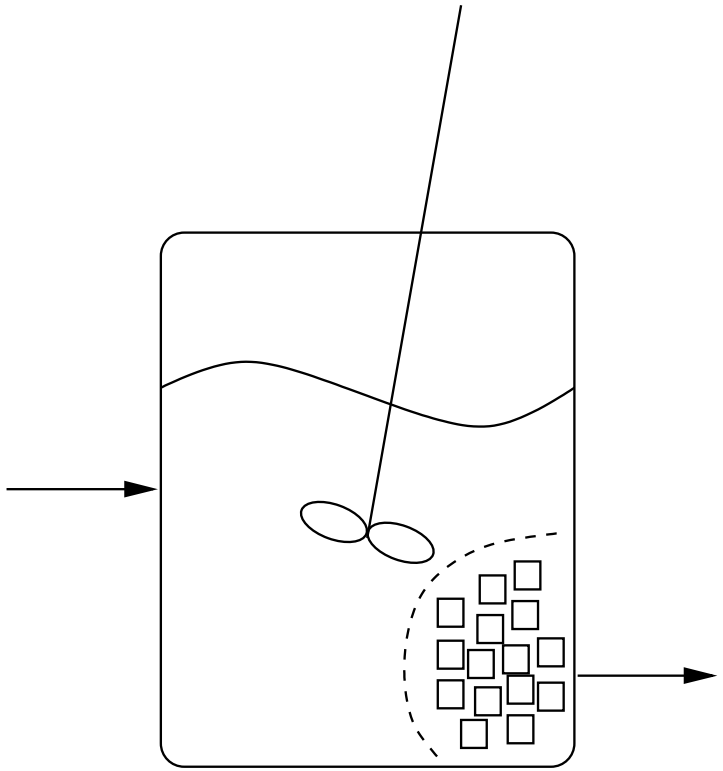
so we have immediately

$$P(\theta) = 1 - e^{-\theta/\tau} \tag{11}$$

which upon differentiation gives

$$p(\theta) = \frac{1}{\tau}e^{-\theta/\tau}, \qquad \text{CSTR residence-time distribution} \tag{12}$$

CSTR as a game of chance



- Imagine we divide the reactor into a number of volume elements.

- At each time instant, some group of volume elements is withdrawn from the reactor, and new volume elements enter from the feed stream.

- The well-mixed assumption is equivalent to the statement that all volume elements are equally likely to be withdrawn from the reactor.

- One can view the mixing as quickly (instantaneously in the case of perfect mixing) randomizing the locations of the volume elements so that each one is equally likely to be nearest to the exit when the next element is withdrawn in the effluent stream.

The new TV show, Survivor

- We have n volume elements, each with volume $V_n = V_R/n$.
- In time interval Δt, a volume of $Q_f \Delta t$ leaves with the effluent stream.
- The number of elements leaving in the time interval is therefore $Q_f \Delta t / V_n$ out of n, and the fraction of elements withdrawn is

$$f = \frac{Q_f \Delta t}{V_R} = \frac{\Delta t}{\tau}$$

- Now consider the probability that a particular volume element is still in the reactor after i time intervals. The probability of removal is f, so the probability of survival is $1 - f$.

- After i trials, each of which is independent, the probability of survival is the product $(1-f)^i$. Therefore the probability that an element has residence (survival) time $\theta = i\Delta t$ is

$$\tilde{p}(\theta) = \left(1 - \frac{\Delta t}{\tau}\right)^{\theta/\Delta t} \tag{13}$$

The continuous time limit

- We now take the limit as $\Delta t \to 0$. Recall from calculus

$$\lim_{x \to 0} (1 + ax)^{1/x} = e^{a}$$

- Taking the limit and using this result in Equation 13 gives

$$\tilde{p}(\theta) = e^{-\theta/\tau}$$

which, after normalization, is again the residence-time distribution of the CSTR.

- The normalization constant is computed by integration

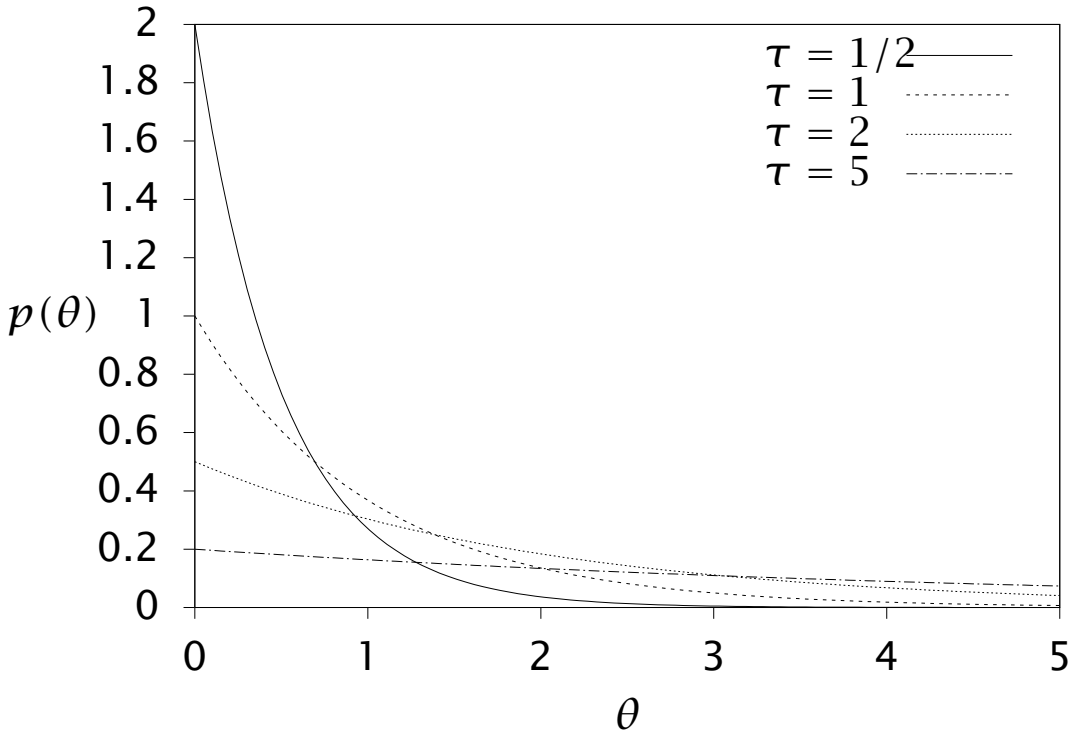
$$\int_0^\infty \tilde{p}(\theta)\, d\theta = \int_0^\infty e^{-\theta/\tau}\, d\theta = \tau$$

so the residence-time distribution is

$$p(\theta) = \frac{1}{\tau} e^{-\theta/\tau} \tag{14}$$

which is plotted in the next figure for a variety of mean residence times.

CSTR RTD


$\tau = 1/2$
$\tau = 1$
$\tau = 2$
$\tau = 5$
$p(\theta)$
θ
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
0
1
2
3
4
5

Mean of the CSTR RTD

- We next compute the mean of this distribution. An integration by parts produces

$$\begin{aligned}\overline{\theta} &= \int_0^\infty \theta\, p(\theta)\, d\theta = \frac{1}{\tau}\int_0^\infty \theta e^{-\theta/\tau}\, d\theta \\ &= \frac{1}{\tau}\left[-\tau\theta\, e^{-\theta/\tau} - (\tau)^2 e^{-\theta/\tau}\right]\Big|_0^\infty \\ &= \tau\end{aligned}$$

and we have established that the mean of the RTD for the CSTR is indeed $\tau = V_R/Q_f$.

CSTR RTD — Summary

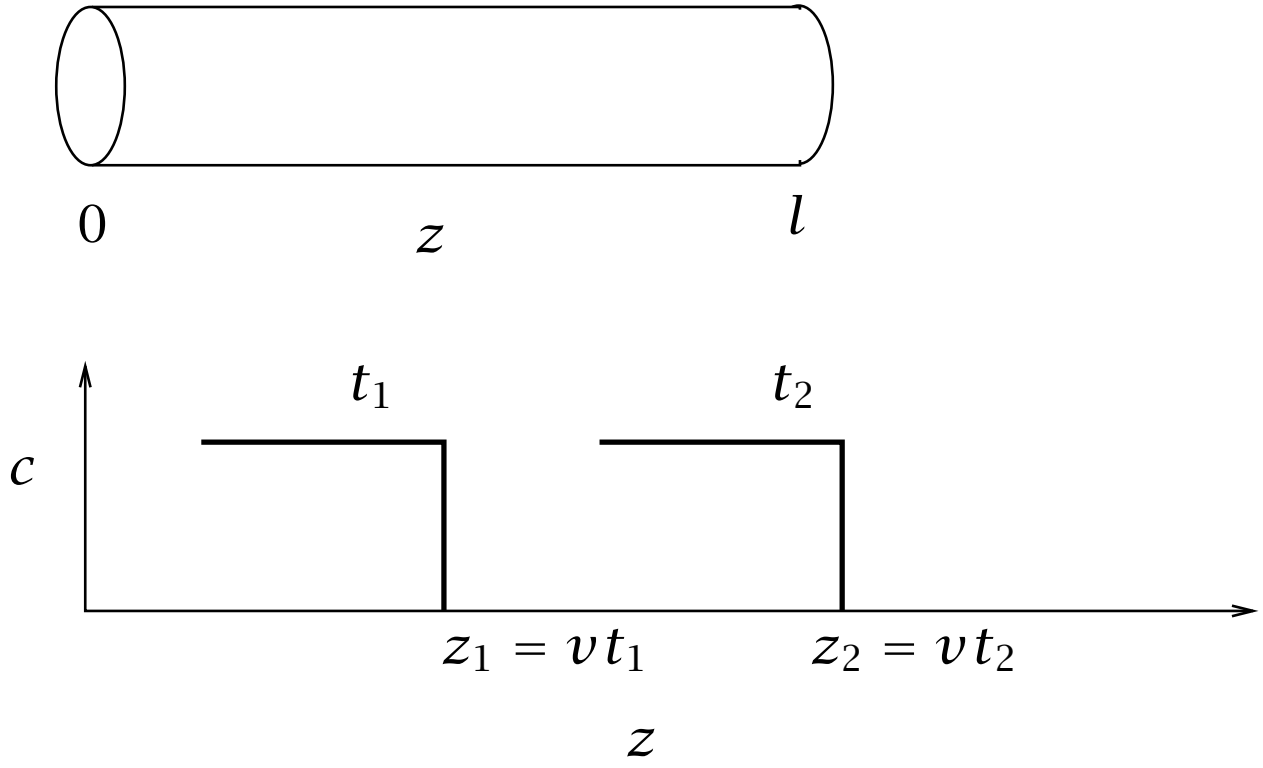
- We can therefore compactly write Equation 14 as

$$p(\theta) = \frac{1}{\overline{\theta}} e^{-\theta/\overline{\theta}} \tag{15}$$

- Notice the exponential distribution tells us that it is unlikely for a volume element to remain in this reactor for long because at each instant there is a constant probability that the element is withdrawn in the effluent.

Plug-Flow Reactor (PFR) and Batch Reactor

- The simple flow pattern in the PFR produces a simple residence-time distribution.



- Consider a step test in which the reactor is initially free of tracer and we increase the feed tracer concentration from zero to c_f at time zero.

Birds of a feather

- As shown in the figure, the tracer travels in a front that first reaches the reactor exit at time $t = l/v$, in which v is the velocity of the axial flow and l is the reactor length.

- From these physical considerations, we can write the reactor tracer concentration immediately

$$c(t,z) = \begin{cases} 0, & z - vt > 0 \\ c_f, & z - vt < 0 \end{cases} \tag{16}$$

- For $z - vt > 0$, the tracer front has not reached location z at time t so the tracer concentration is zero.

- For $z - vt < 0$, the front has passed location z at time t and the tracer concentration is equal to the feed value c_f.

The step function

- It is convenient to introduce the unit step or Heaviside function to summarize this result.

- The Heaviside function is defined as follows

$$H(t) = \begin{cases} 0, & t < 0 \\ 1, & t > 0 \end{cases} \tag{17}$$

- Because we are armed with the delta function, we can even consider differentiating this discontinuous function to obtain the relationship

$$\frac{dH(t)}{dt} = \delta(t) \tag{18}$$

Analysis of step test

- Equation 16 can then be summarized compactly by

$$c(t,z) = c_f H(t - z/v)$$

so the effluent tracer concentration is given by

$$c_e(t) = c_f H(t - l/v) = c_f H(t - V_R/Q_f) \tag{19}$$

and the integrated from of the residence-time distribution is therefore

$$P(\theta) = H(\theta - V_R/Q_f) \tag{20}$$

- We can differentiate this result using Equation 18 to obtain

$$p(\theta) = \delta(\theta - V_R/Q_f)$$

- In other words, all tracer molecules spend exactly the same time V_R/Q_f in the reactor. The mean of this distribution is then also V_R/Q_f, which is verified by using Equation 7

$$\overline{\theta} = \int_0^\infty \theta\delta(\theta - V_R/Q_f)d\theta = V_R/Q_f$$

  which shows that V_R/Q_f is the mean residence time for the PFR as well as the CSTR, even though the residence-time distributions of these two reactors are quite different.

PFR RTD — Summary

- We can compactly summarize the RTD for the plug-flow reactor by

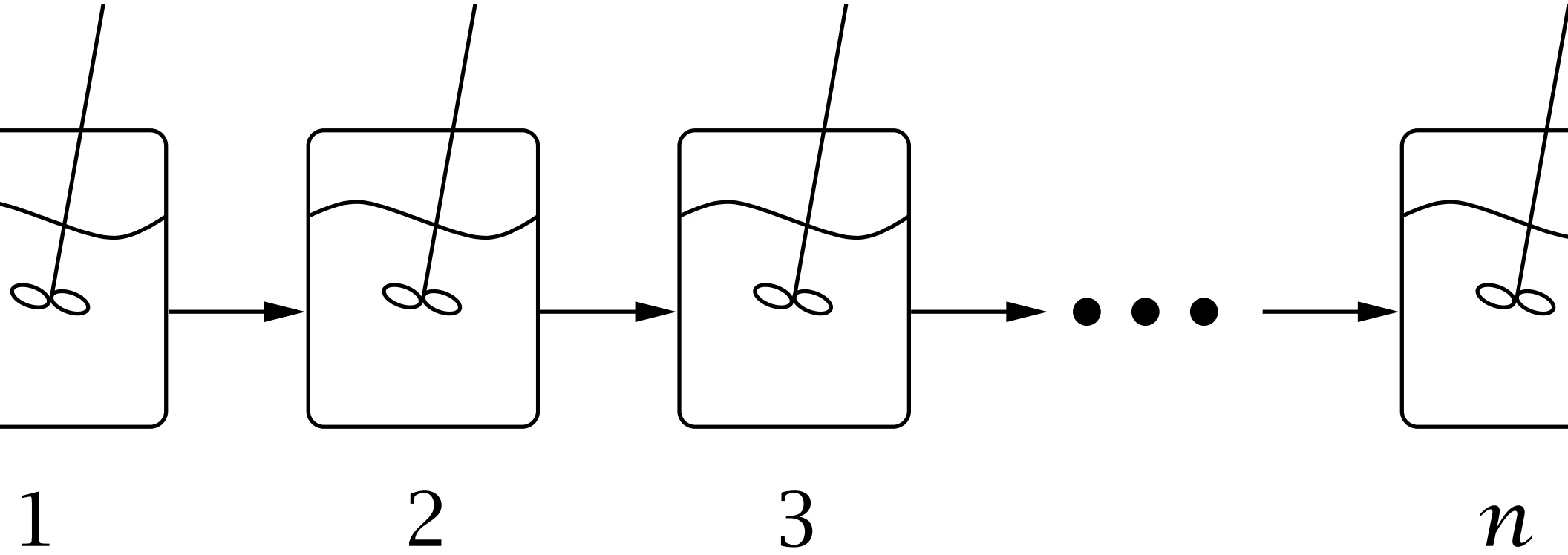
$$\boxed{\begin{aligned} p(\theta) &= \delta(\theta - \overline{\theta}) \qquad \text{PFR and} \\ P(\theta) &= H(\theta - \overline{\theta}) \qquad \text{batch reactors} \end{aligned}} \tag{21}$$

- Likewise, the RTD for a batch reactor is immediate. All material is charged to the reactor at time $t = 0$ and remains in the reactor until the final batch time, which we may call $\overline{\theta}$.

- Then Equations 21 also apply to the batch reactor.

CSTRs in series

Consider dividing the volume of a single CSTR into n equal-sized CSTRs in series

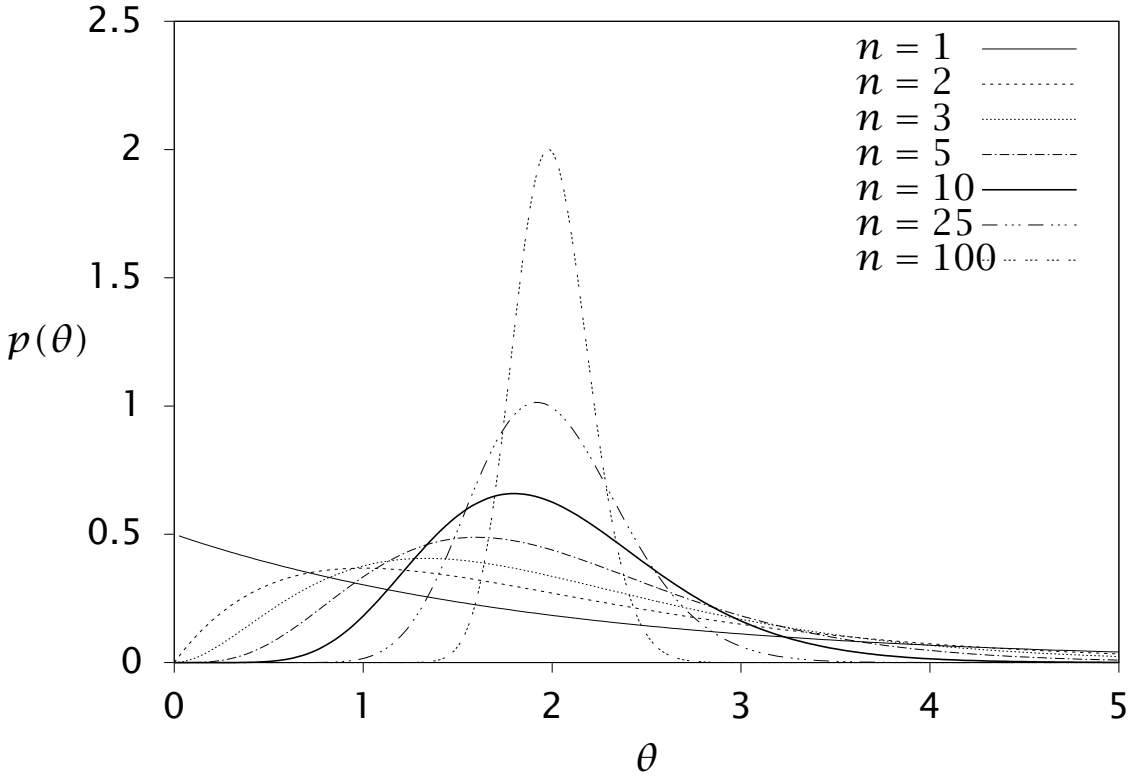


If the single CSTR has volume V_R and residence time $\tau = V_R/Q_f$, each of the CSTRs in series has volume V_R/n and residence time τ/n.

If we solve for the effluent concentration after an impulse at time zero, we can show

$$p(\theta) = \left(\frac{n}{\tau}\right)^n \frac{\theta^{n-1}}{(n-1)!} e^{-n\theta/\tau} \tag{22}$$

CSTRs in series



Notice the residence-time distribution becomes more narrowly focused at τ as n increases. In fact Equation 22 for large n is another approximation for $\delta(\theta - \tau)$.

Integrated form of CSTRs in series

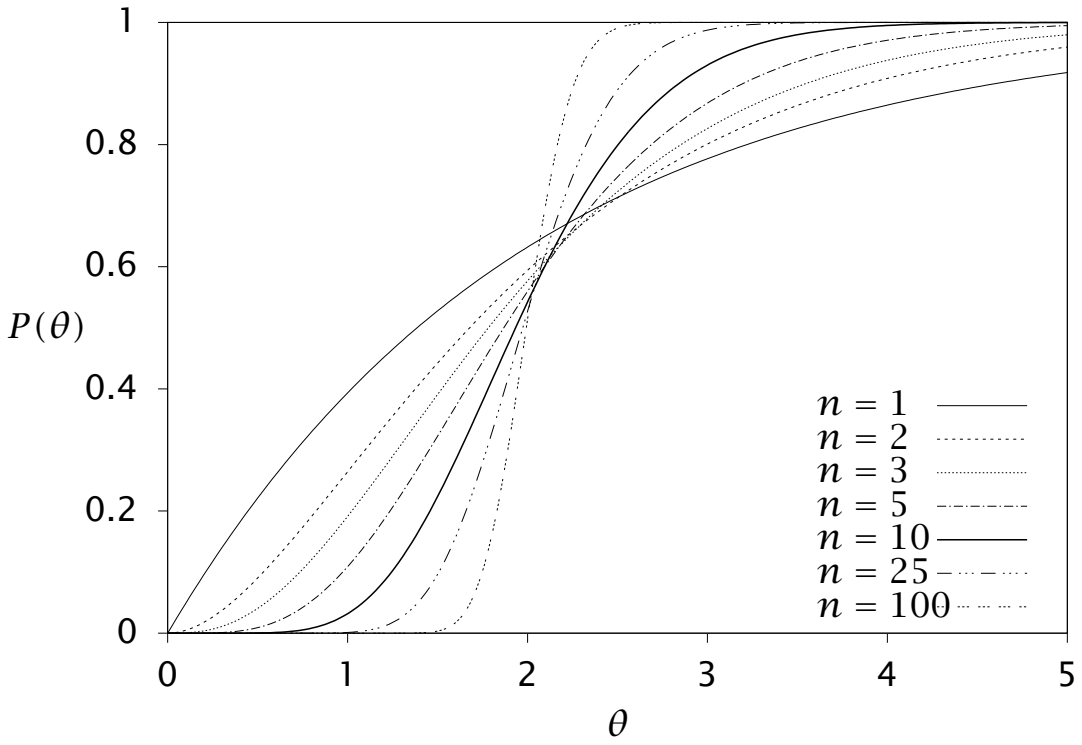
If we integrate Equation 22 we obtain

$$P(\theta) = \frac{\gamma(n, n\theta/\tau)}{\Gamma(n)} \tag{23}$$

You can perform integration by parts on Equation 22 to obtain a series representation

$$P(\theta) = 1 - \left(1 + \frac{n\theta/\tau}{1!} + \frac{(n\theta/\tau)^2}{2!} + \cdots + \frac{(n\theta/\tau)^{n-1}}{(n-1)!}\right) e^{-n\theta/\tau} \tag{24}$$

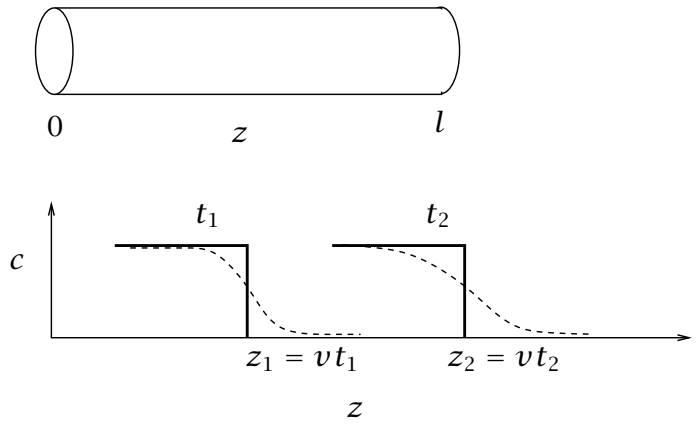
Integrated form of CSTRs in series



Dispersed Plug Flow

- Ideal plug flow may not be realized in many packed-bed reactors. We develop next a model that allows for deviations from plug flow.

- In the PFR a change in the feed concentration travels as a perfect front. But measurements in actual packed-bed reactors may show a fair amount of spreading or dispersion as this front travels through the reactor.



Dispersed Plug Flow

- The dispersed plug-flow model given in Equation 25 allows for this spreading phenomenon.

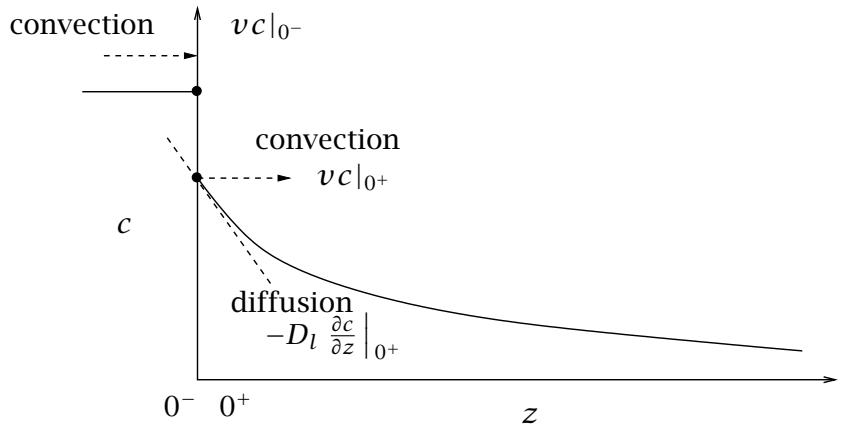
- A diffusion-like term has been added to the mass balance. The coefficient, D_l, is called the dispersion coefficient.

$$\underbrace{\frac{\partial c}{\partial t}}_{\text{accumulation}} = \underbrace{-v\frac{\partial c}{\partial z}}_{\text{convection}} + \underbrace{D_l\frac{\partial^2 c}{\partial z^2}}_{\text{diffusion}} \tag{25}$$

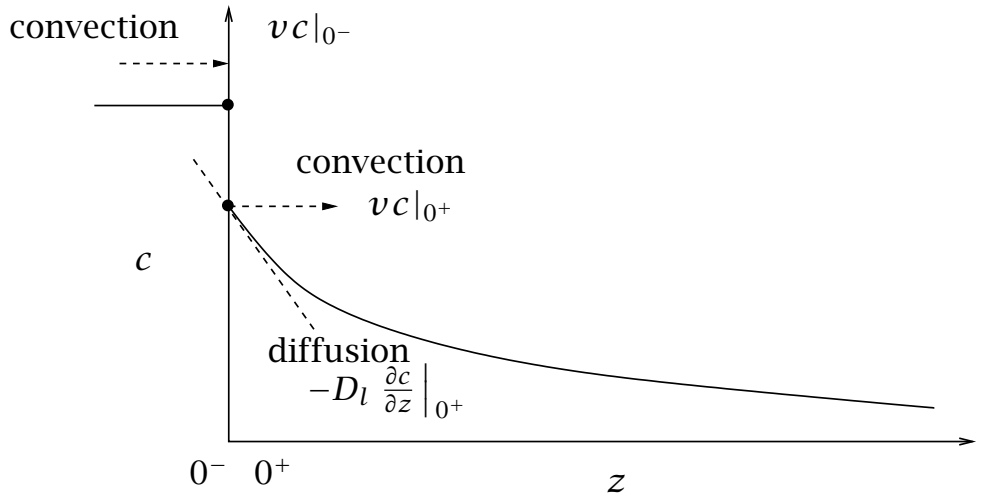
2nd derivative and boundary conditions

- Given diffusion in the tube, the inlet boundary condition is no longer just the feed condition, $c(0) = c_f$, that we used in the PFR.

- To derive the boundary condition at the inlet, we write a material balance over a small region containing the entry point, and consider diffusion and convection terms.



Inlet boundary condition



$$vc|_{0^-} = vc|_{0^+} - D_l \left.\frac{\partial c}{\partial z}\right|_{0^+} \qquad z = 0$$

Danckwerts boundary conditions

- The diffusion term introduces a second-order derivative in Equation 25, so we now require two boundary conditions.

- We specify a zero slope condition at the tube exit.

$$
\begin{aligned}
v c|_{0^-} &= v c|_{0^+} - D_l \left.\frac{\partial c}{\partial z}\right|_{0^+} && z = 0 \\
\frac{\partial c}{\partial z} &= 0 && z = l
\end{aligned}
\tag{26}
$$

- These two boundary conditions have become known as Danckwerts boundary conditions [4], but they were derived at least 45 years prior to Danckwerts in a classic paper by Langmuir [13].

It is now convenient to introduce a coordinate moving with a scaled velocity

$$x = \frac{z - vt}{\sqrt{4D_l t}} = \frac{\overline{z} - t/\tau}{\sqrt{4Dt/\tau}} \tag{27}$$

in which

$$D = \frac{D_l}{vl} = \frac{D_l \tau}{l^2}, \qquad \text{dimensionless dispersion number}$$

Transforming variables from z and t in Equation 25 to x gives

$$\frac{d^2c}{dx^2} + 2x\frac{dc}{dx} = 0 \tag{28}$$

Rather than use the Danckwerts boundary conditions, we can approximate the

behavior with the following simplified boundary conditions

$$c = 1, \qquad x = -\infty$$
$$c = 0, \qquad x = \infty \tag{29}$$

These boundary conditions correspond to stating that $c = 0$ for z, t values corresponding to arbitrarily long times before the step change arrives, and that $c = 1$, for z, t values corresponding to arbitrarily long times after the step change has passed. See Exercise 8.10 for comparing the dispersed PFR RTD with Danckwerts boundary conditions to the one we calculate here with the simplified boundary conditions.

The solution to Equation 28 with boundary conditions listed in Equations 29 is

$$c(x) = 1/2 \left[1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \right]$$

The integral can be expressed in terms of the error function, which is defined

as

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \tag{30}$$

Substituting in the original variables and setting $\overline{z} = 1$ to obtain the response at the reactor outlet as a function of time gives

$$c(\overline{z} = 1, t) = 1/2 \left[1 - \text{erf} \left(\frac{1 - t/\tau}{\sqrt{4Dt/\tau}} \right) \right] \tag{31}$$

and we have calculated the integrated form of the RTD for the dispersed PFR with simplified boundary conditions

$$P(\theta) = 1/2 \left[1 - \text{erf} \left(\frac{1 - \theta/\tau}{\sqrt{4D\theta/\tau}} \right) \right] \tag{32}$$

Equation 32 is plotted in Figure 1 for $\tau = 2$ and various dispersion numbers D.

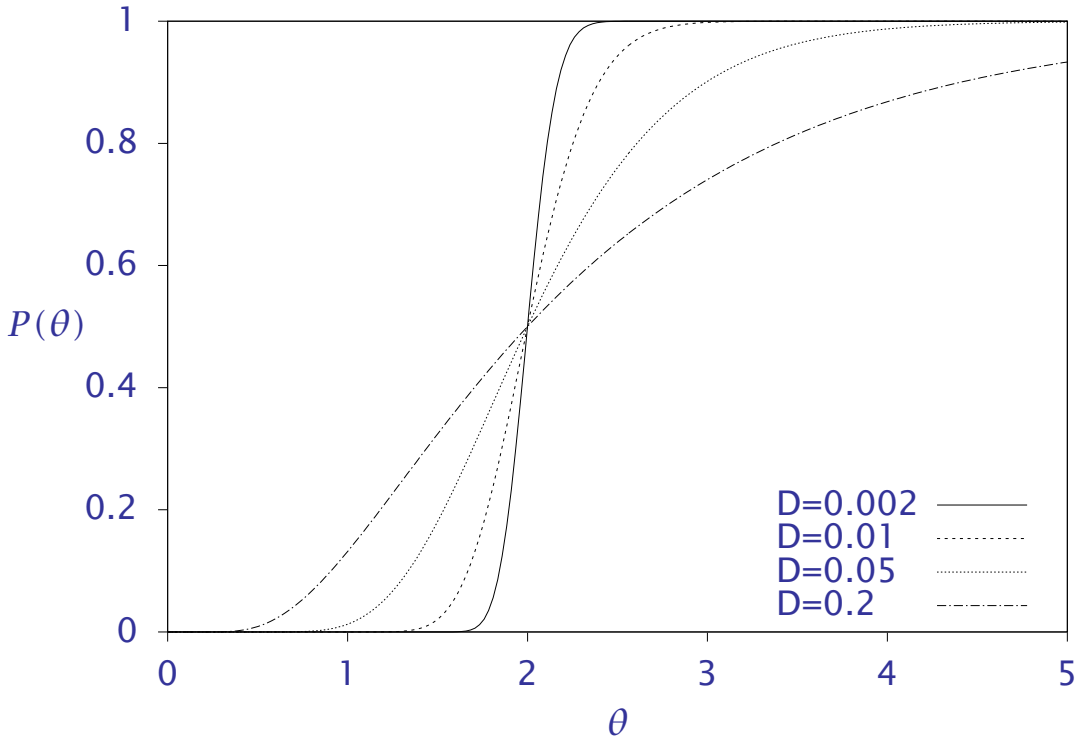


Figure 1: $P(\theta)$ versus θ for plug flow with dispersion number D, $\tau = 2$.

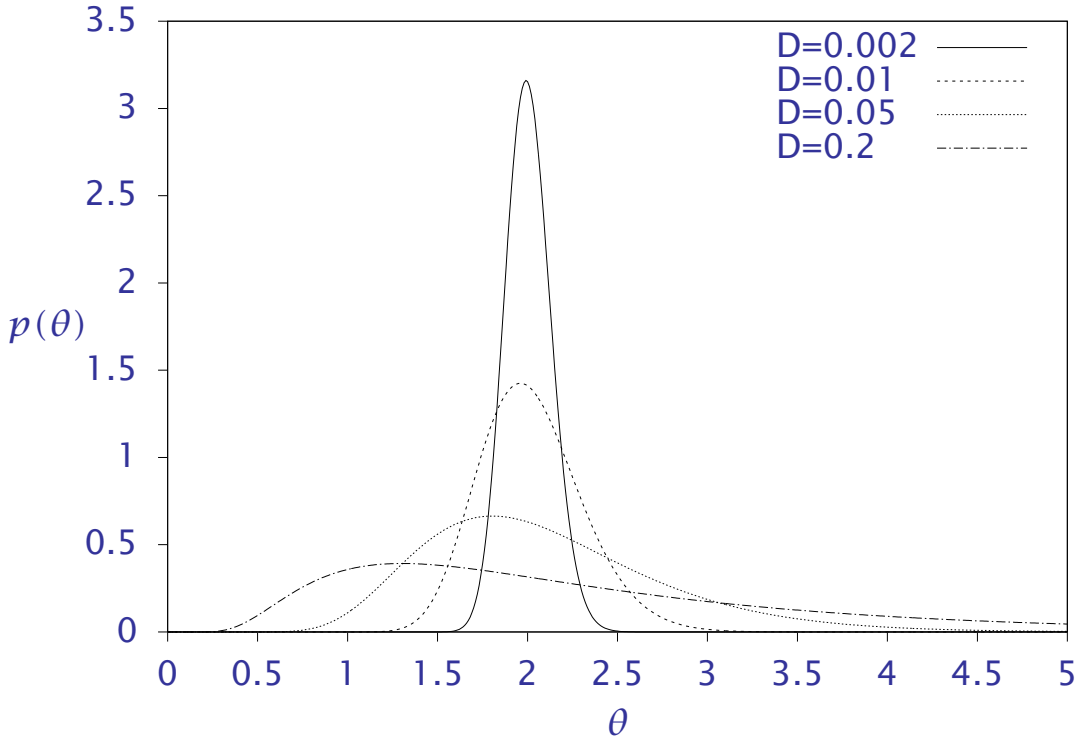


Figure 2: Residence-time distribution $p(\theta)$ versus θ for plug flow with dispersion number D, $\tau = 2$.

We can differentiate Equation 32 to obtain the dispersed plug-flow RTD

$$p(\theta) = \frac{1}{4\tau\sqrt{\pi D}} \frac{1 + \tau/\theta}{\sqrt{\theta/\tau}} \exp\left(-\left(\frac{1 - \theta/\tau}{\sqrt{4D\theta/\tau}}\right)^2\right) \tag{33}$$

This RTD is plotted in Figure 2.

The dispersion number, D, is related to another dimensionless group, the mass-transfer analog of the inverse of the Péclet number,

$$\mathrm{Pe} = \frac{vl}{D_A}, \qquad \frac{1}{\mathrm{Pe}} = \frac{D_A}{vl}$$

which measures the rate of diffusion compared to the rate of convection. The key difference is the Péclet number contains the molecular diffusivity, D_A, and the dispersion number contains the effective axial dispersion coefficient, D_l. Levenspiel makes a compelling case that these two quantities have different origins

and motivations and deserve different names. To further complicate matters, the inverse of the Péclet number is often called the Bodenstein number in European literature. Weller [20] provides an interesting discussion of the history of the literature on the Bodenstein number, which does not appear to have been defined or used by Bodenstein, but was defined and used by Langmuir [13].

Dispersed plug flow with reaction.

We modify Equation 25 for dispersed plug flow to account for chemical reaction,

$$\frac{\partial c_j}{\partial t} = -v\frac{\partial c_j}{\partial z} + D_{jl}\frac{\partial^2 c_j}{\partial z^2} + R_j \tag{34}$$

Danckwerts boundary conditions, as given in Equations 26, can be applied without change.

Up to this point in the text, we have solved *exclusively steady-state* profiles in tubular reactors. Obviously tubular reactors experience a start-up transient like every other reactor, and this time-dependent behavior is also important and interesting. Calculating the transient tubular-reactor behavior involves solving the partial differential equation (PDE), Equation 34, rather than the usual ODE for the steady-state profile. Appendix A describes the method we use for this purpose, which is called orthogonal collocation.

Example 8.1: Transient start-up of a PFR

Compute the transient behavior of the dispersed plug-flow reactor for the isothermal, liquid-phase, second-order reaction

$$2\mathrm{A} \longrightarrow \mathrm{B}, \qquad r = kc_A^2 \tag{35}$$

The reactor is initially filled with solvent. The kinetic and reactor parameters are given in Table 1.

Parameter	Value	Units
k	0.5	L/mol·min
c_{Af}	1	mol/L
D_{Al}	0.01	m^2/min
v	0.5	m/min
l	1	m

Table 1: Mass-transfer and kinetic parameters for Example 8.1.

Solution

The mass balance for component A is

$$\frac{\partial c_A}{\partial t} = -v\frac{\partial c_A}{\partial z} + D_{Al}\frac{\partial^2 c_A}{\partial z^2} - 2kc_A^2 \tag{36}$$

The boundary conditions are

$$v c_{Af} = v c_A|_{0^+} - D_{Al} \left.\frac{\partial c_A}{\partial z}\right|_{0^+}, \qquad z = 0 \tag{37}$$

$$\frac{\partial c_A}{\partial z} = 0, \qquad z = l \tag{38}$$

Finally, an initial condition is required

$$c_A(z,t) = 0, \qquad t = 0$$

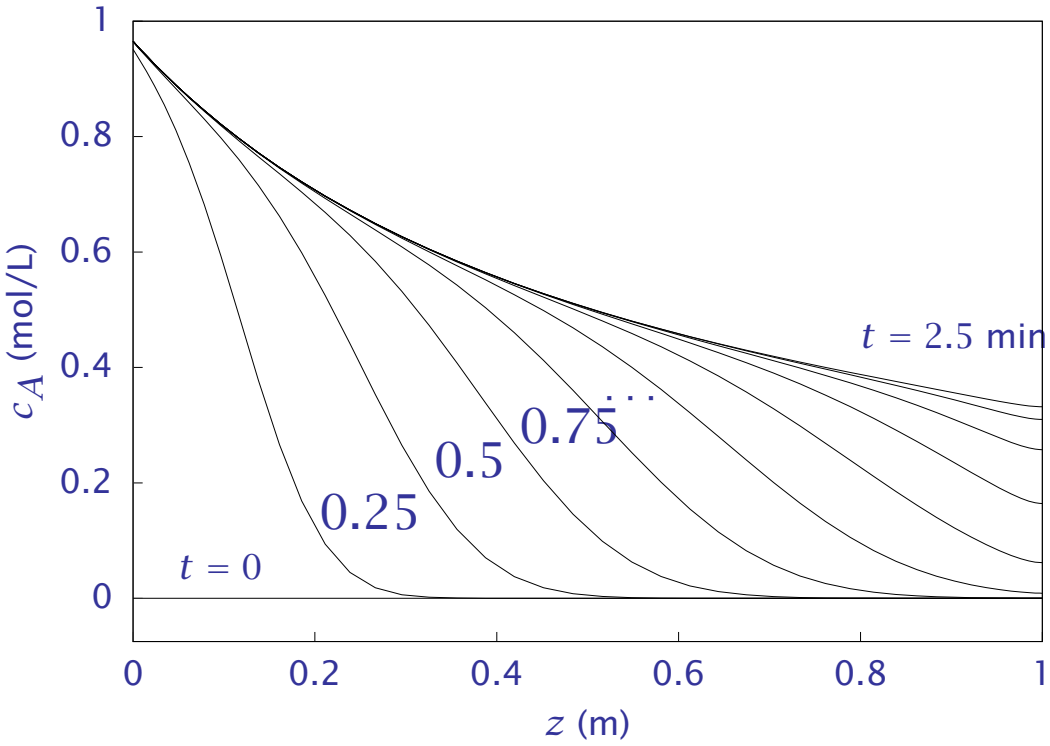


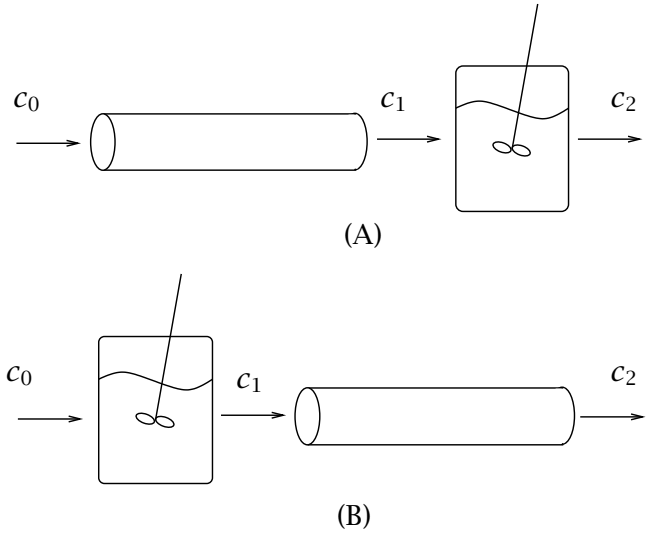
Figure 3: Start-up of the tubular reactor; $c_A(z,t)$ versus z for various times, $0 \leq t \leq 2.5$, $\Delta t = 0.25$.

Figure 3 shows the transient profiles. We see the reactor initially has zero A concentration. The feed enters the reactor and the A concentration at the inlet

rises rapidly. Component A is transported by convection and diffusion down the reactor, and the reaction consumes the A as it goes. After about $t = 2.5$, the concentration profile has reached its steady value. Given the low value of dispersion in this problem, the steady-state profile is close to the steady-state PFR profile for this problem. □

Example — order matters

- Consider two arrangements of a PFR and CSTR of equal volume in series as shown below



- What are the residence-time distributions for the two reactor systems? What are the overall conversions for the two systems?

Solution

- Consider a unit step test for the CSTR–PFR arrangement. The outlet concentration for the CSTR is given by

$$c_1(t) = 1 - \exp(-t/\tau)$$

- That feed concentration to the PFR is then simply delayed by τ time units to give for the CSTR–PFR arrangement.

$$p(\theta) = (1 - \exp(-(t-\tau)/\tau))\, H(t-\tau)$$

Reverse order

- Next consider a unit step test into the PFR–CSTR arrangement. For this case the intermediate stream is given by a delayed step input

$$c_1(t) = H(t-\tau)$$

- With this feed into the CSTR, the effluent is merely the CSTR response to a unit step change after we shift the starting time of the step forward τ time units,

$$c_2(t) = (1 - \exp(-(t-\tau)/\tau))\, H(t-\tau)$$

- so again for this case

$$p(\theta) = (1 - \exp(-(t-\tau)/\tau))\, H(t-\tau)$$

- and the two residence-time distributions are equal.

Conversion for the two arrangements

- The steady-state conversions for both arrangements are also simply calculated. For a single CSTR, the steady-state inlet and outlet concentrations are related by

$$c_o/c_i = \frac{-1 + \sqrt{1 + 4k\tau c_i}}{2k\tau c_i} = C(c_i)$$

- For a single PFR, the inlet and outlet concentrations are related by

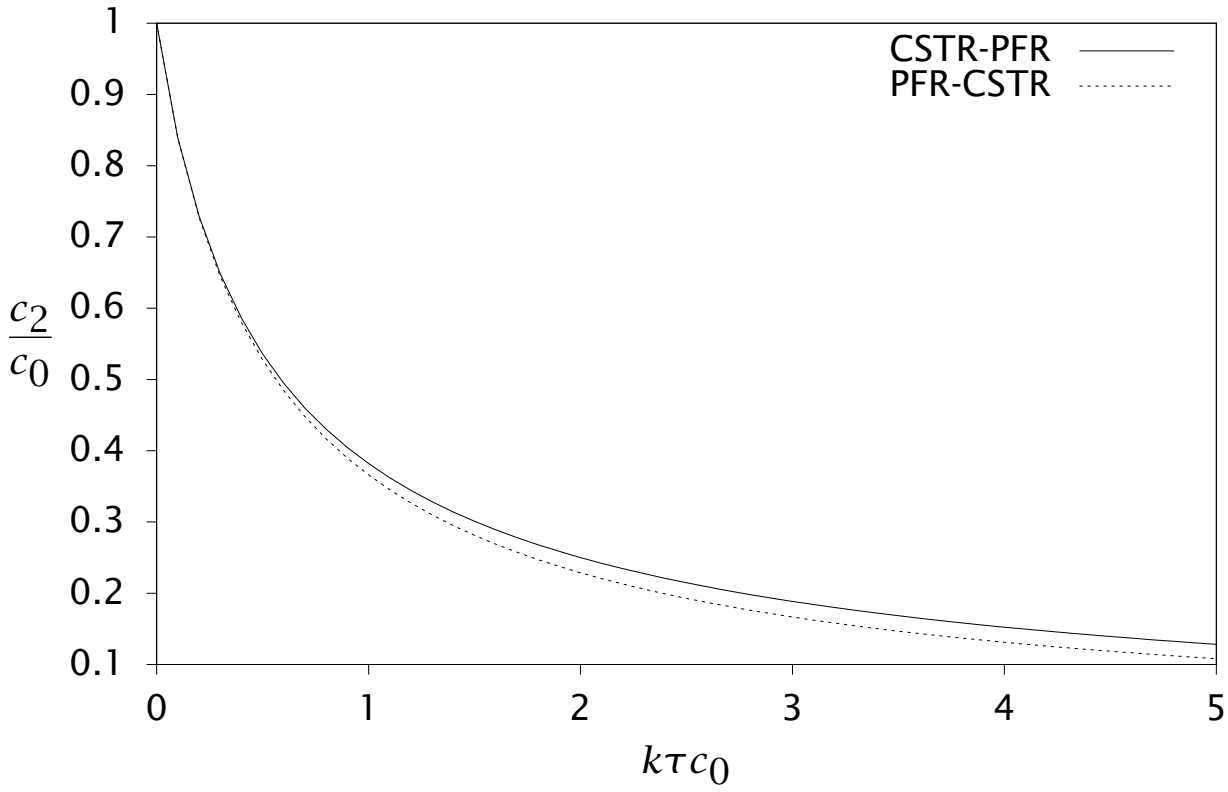
$$c_o/c_i = \frac{1}{1 + k\tau c_i} = P(c_i)$$

- So we wish to compare $P(C(c_0))$ for the CSTR–PFR case and $C(P(c_0))$ for PFR–CSTR case.

- Because we are not even told $k\tau c_0$, we check over a range of values.

Outcome of the calculation

- The figure displays the result. We see that the conversions are *not* the same and that *the PFR–CSTR gives higher conversion* (lower outlet concentration) than the CSTR–PFR for all values of $k\tau c_0$ for a second-order reaction.


CSTR-PFR
PFR-CSTR
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
$\frac{c_2}{c_0}$
0
1
2
3
4
5
$k\tau c_0$

Limits of Reactor Mixing

We have seen in the previous section that complete knowledge of the reactor residence-time distribution is insufficient to predict the reactor performance. Although we have characterized completely the time tracer molecules spend in the reactor, we have not characterized their surrounding environment in the reactor during this time.[1] In the literature these two effects are sometimes termed **macromixing:** the distribution of residence times of molecules moving with the flow; and **micromixing:** the exchange of material between different volume elements during their residence times. Although we may find it instructive to separate these two phenomena in the simple reactor mixing models under dis-

[1] If someone were to characterize your learning in this course by measuring your hours spent in the classroom (RTD), they would hopefully obtain a positive correlation between learning and residence time. But we would naturally want to evaluate the environment inside the classroom during these hours if we were going to make more accurate predictions of learning. We would want to know if the instructor was prepared for lecture and saying reasonable things, if the students were attentive or asleep, and so on.

cussion, in actual reactors this separation may be unrealistic. Accurate prediction of reactor performance may require solution or approximate solution of the equations of motion for the fluid, including material transport due to diffusion.

In defense of the simple mixing models, however, they do provide another important insight. We can determine the limits of achievable mixing consistent with a measured reactor residence-time distribution. These mixing limits do provide some insight into the limits of achievable reactor performance, although this connection remains an active area of research as discussed in section .

Complete Segregation

Imagine we know a reactor RTD, $p(\theta)$, either through direct measurement in a tracer experiment or solution of the equations of motion or some other means. We know from Example that this constraint does not tell us the complete state of mixing in the reactor. We define next the two extreme limits of mixing consistent with the given RTD. These ideas were laid out in influential papers by Danckwerts and Zwietering. The first limit is called complete segregation; it is the limit of no mixing between volume elements. We can realize this limit by considering the ideal reactor depicted in Figure 4.

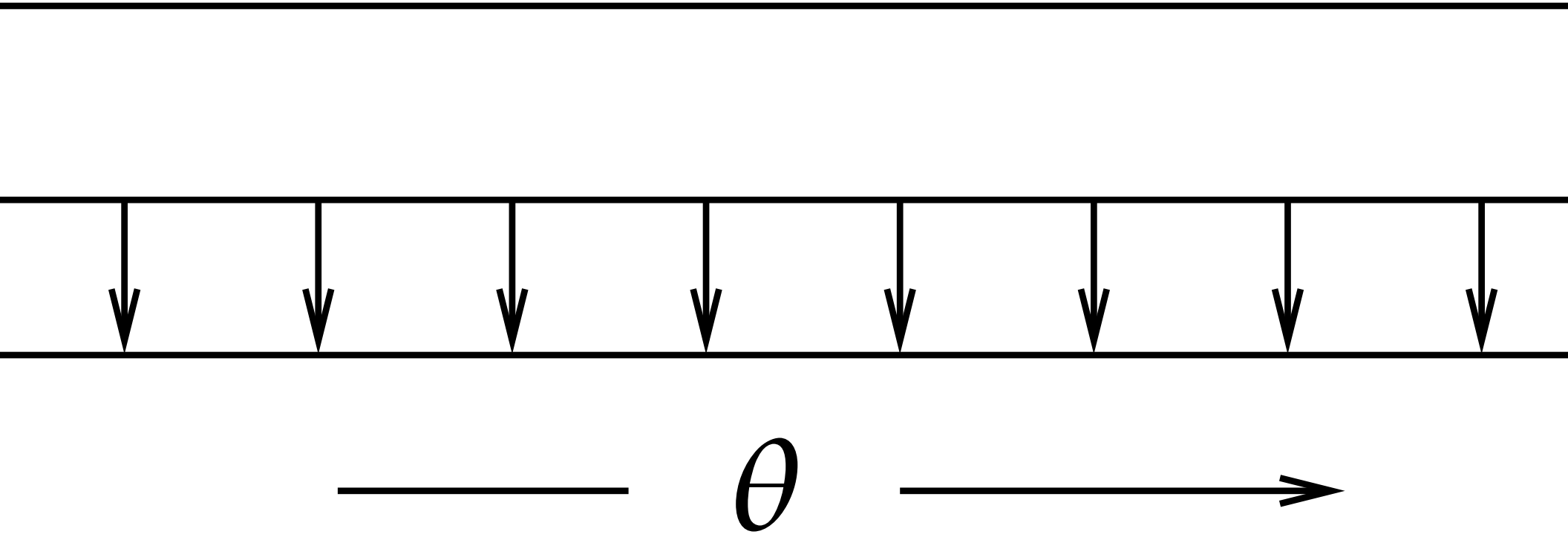


Figure 4: Completely segregated flow as a plug-flow reactor with side exits; outlet flows adjusted to achieve given RTD.

As we progress down the plug-flow reactor, the residence time θ of the material reaching that location increases. We can imagine withdrawing from the

reactor at each location or θ a fraction of the flow corresponding to the required RTD value $p(\theta)$, although this might be difficult to achieve in practice. A PFR with this removal rate then has the specified RTD. No material in two volume elements with different residence times is ever exchanged because the plug flow has zero backmixing. This last point is perhaps more clear if we redraw the reactor configuration as an equivalent bank of PFRs of different lengths without side exits, as in Figure 5.A [19].

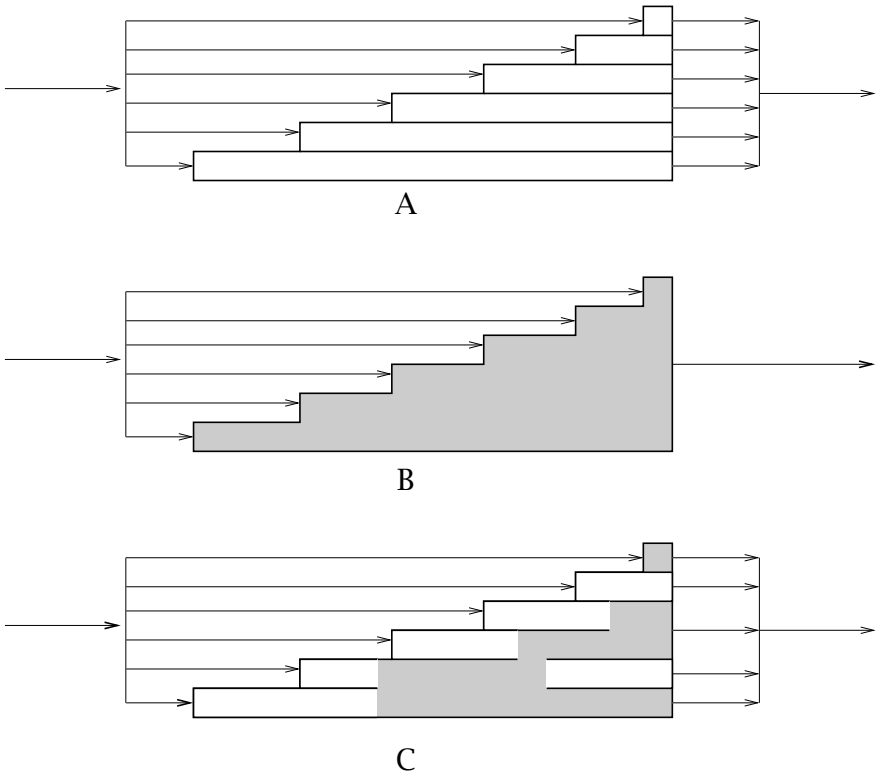


Figure 5: Alternate representation of completely segregated flow (A), maximum mixed flow (B), and an intermediate mixing pattern (C).

Each tube has a single θ value according to its length. We feed the fraction $p(\theta)$ of the total flow into each tube of residence time θ so as to achieve

the given RTD for the composite reactor system. This reactor system is called completely segregated because there is no exchange of material between the various tubes. Each tube acts as its own private reactor that processes material for a given amount of time and then discharges it to be mixed with the other reactors at the exit.

It is a simple matter to predict the behavior of this completely segregated reactor. We assume a single reaction and constant density throughout the following discussion. Each tube of specified length or volume V can be assigned a residence time according to $\theta = V/Q$. Let $c(\theta)$ represent the concentration of a reactant in a volume element that has spent time θ in the reactor. Because the reactor is segregated, each tube satisfies the constant density PFR equation, Equation 4.112,

$$\frac{dc}{d\theta} = R(c), \qquad c(0) = c_f \tag{39}$$

The concentration of the effluent stream is then simply computed by multiplying the concentration of each tube by the fraction of the total feed passing through

that tube

$$c_s = \int_0^\infty p(\theta)c(\theta)d\theta \tag{40}$$

in which $c(\theta)$ comes from the solution of Equations 39. It is often convenient to remove the explicit integration required by Equation 40. Let $c_s(\theta)$ represent the effect of combining streams with residence times less than or equal to θ, so

$$c_s(\theta) = \int_0^\theta p(\theta)c(\theta)d\theta$$

From this definition it is clear that $c_s(\theta)$ satisfies the following differential equation and initial condition

$$\frac{dc_s}{d\theta} = p(\theta)c(\theta), \qquad c_s(0) = 0$$

and the reactor effluent concentration is the limit of $c_s(\theta)$ as $\theta \longrightarrow \infty$. We can combine the two differential equations for convenient numerical solution of the

segregated case

$$\boxed{\begin{aligned} \frac{dc}{d\theta} &= R(c) & c(0) &= c_f \\ \frac{dc_s}{d\theta} &= p(\theta)c(\theta) & c_s(0) &= 0 \end{aligned}} \tag{41}$$

Notice that this is an initial-value problem, but, in general, we require the solution at $\theta = \infty$ to determine the effluent concentration of the reactor. Differential equations on semi-infinite domains are termed singular, and require some care in their numerical treatment as we discuss next. On the other hand, if the residence-time distribution is zero beyond some maximum residence time, θ_{max}, then it is straightforward to integrate the initial-value problem on $0 \leq \theta \leq \theta_{\text{max}}$.

Numerical solution.

We can solve Equation 41 as an initial-value problem as written with an ODE solver. Because of the semi-infinite domain, we would need to check the solution for a sequence of increasingly large θ values and terminate the ODE solver when the value of $c_s(\theta)$ stops changing. Alternatively, we can map the semi-infinite domain onto a finite domain and let the ODE solver do the work for us. Many transformations are possible, such as $z = \exp(-\theta)$, but experience suggests a strongly decreasing function like the exponential causes the right-hand side to go to infinity at $z = 1$, and we simply exchange one singularity for another. A more gentle transformation and its inverse are

$$z = \frac{\theta}{1+\theta}, \qquad \theta = \frac{z}{1-z}$$

Using this change of variable, we rewrite the derivative as

$$\frac{dc}{d\theta} = \frac{dc}{dz}\frac{dz}{d\theta} = (1-z)^2\frac{dc}{dz}$$

Using this result, we transform Equation 41 to

$$\boxed{\begin{aligned} \frac{dc}{dz} &= \frac{R(c)}{(1-z)^2} & c(0) &= c_f \\ \frac{dc_s}{dz} &= \frac{p(z/(1-z))\,c}{(1-z)^2} & c_s(0) &= 0 \end{aligned}} \tag{42}$$

Most modern ODE solvers allow the user to specify critical stopping values. These are values of the variable of integration beyond which the ODE solver will not step. We would specify $z = 1$ as a critical value because the right-hand side is not defined past $z = 1$. At the value $z = 1$, we would specify the right-hand sides are zero because the reaction will have equilibrated at $z = 1, \theta = \infty$

so $R(c) = 0$, and $p(\theta) = 0$ at $\theta = \infty$. Again, some care with must be taken because the denominators are also going to zero. If the ODE solver terminates successfully, that usually indicates the transformation was successful. It is useful to plot $c(z)$ to make sure the $z = 1$ end does not exhibit some unusual behavior.

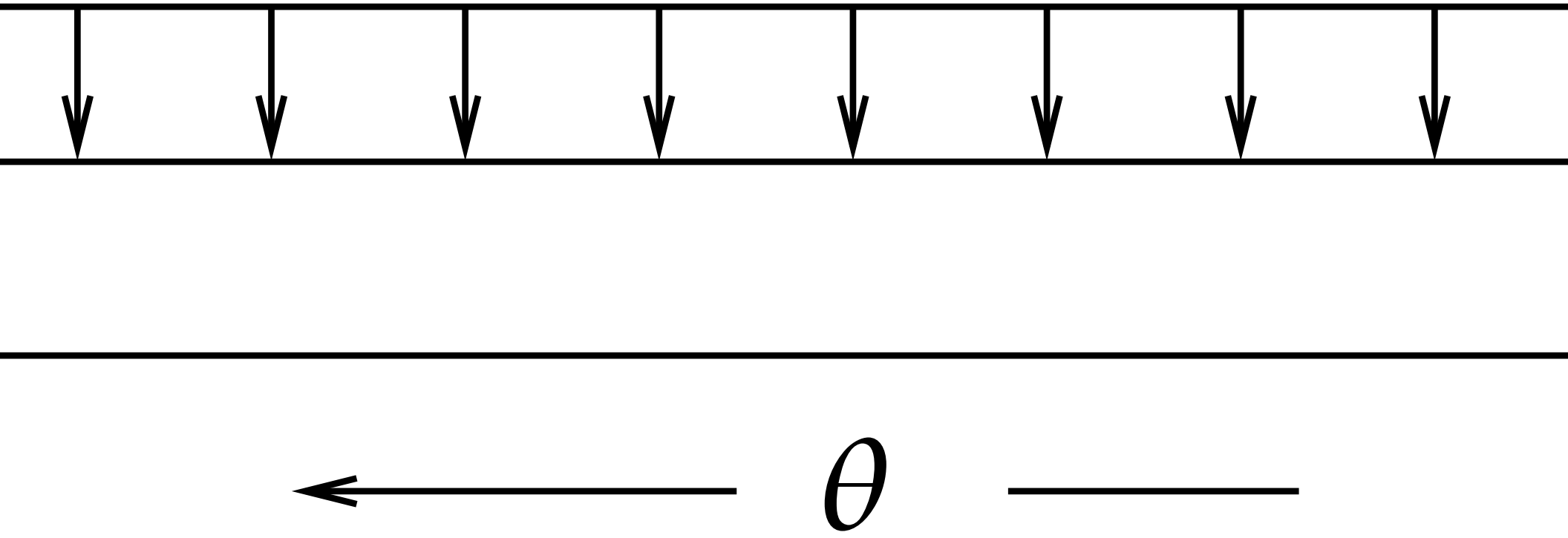


Figure 6: Maximum mixed flow as a plug-flow reactor with side entrances; inlet flows adjusted to achieve a given RTD.

Maximum Mixedness

We realize the opposite mixing limit, maximum mixedness, by reversing the flow in the segregated reactor as shown in Figure 6 [21]. The feed stream is distributed along the length of the PFR and injected at the appropriate rate at various side entrances corresponding to different θ "locations" to achieve the required RTD. Notice that because the flow has been reversed compared to the segregated case, the θ locations increase from zero at the exit of the tube to large values at the entrance to the tube. We allow an infinitely long tube if we wish to allow RTDs such as the CSTR defined on a semi-infinite domain. Reactors with these specified sidestream addition policies are conceptually important in understanding recent research on achievable reactor performance as discussed in Section .

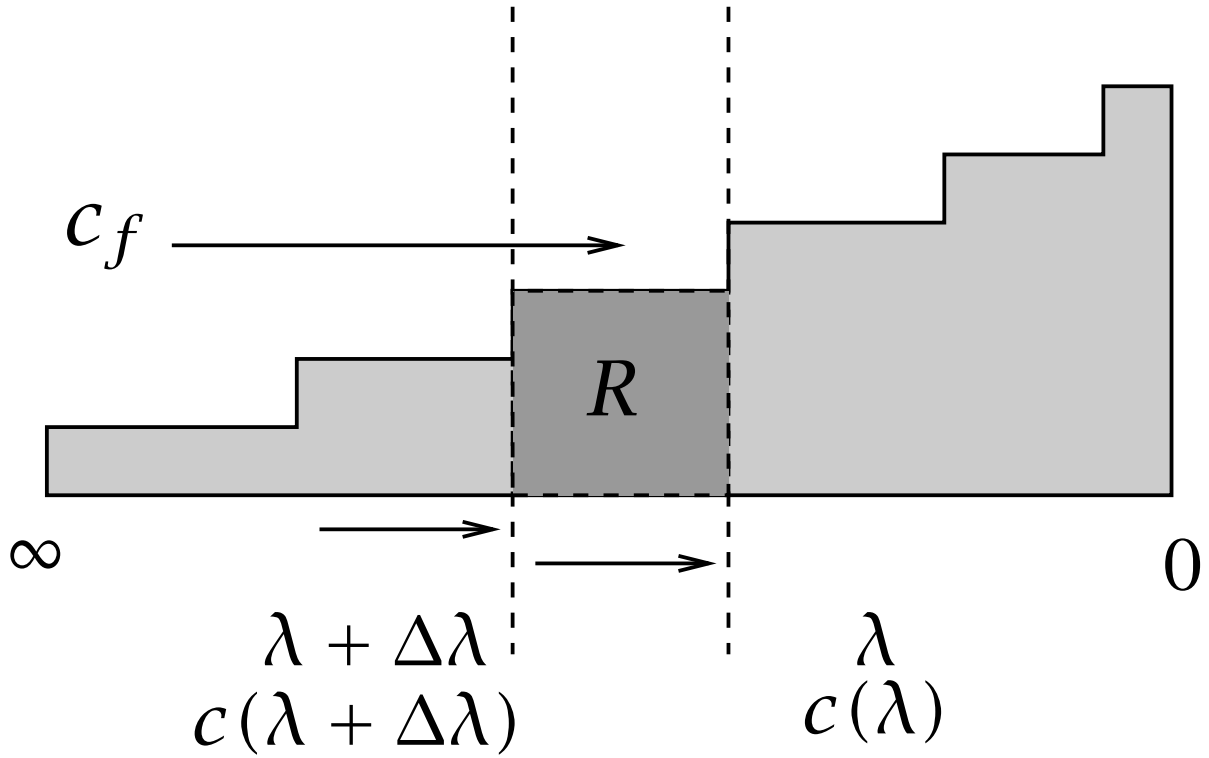


Figure 7: Volume element in the state of maximum mixedness.

Consider the equivalent representation of maximum mixedness in Figure 5.B. The shading means that the material at these locations is completely mixed with the material from the other tubes at these same locations [19]. Notice that

we have aligned the exits of the tubes in Figure 5. Therefore when we mix material between tubes, we are mixing material not with common time spent in the reactor but rather with a common time-to-go λ. Indeed, the mixing process at a given location is mixing material with different times spent in the reactor. It is not possible to mix material with different times-to-go without changing their exit times for the following reason. If we mix two groups of molecules with different times-to-go, λ_1, λ_2, the mixture must later be separated again so that the molecules may exit the reactor at the specified times λ_1 and λ_2. Such a separation is not possible because molecules are not distinguishable based on their times-to-go in the reactor. We face the equivalent problem if we mix two identical, pure-component gases initially on opposite sides of a partition. After mixing, we have no process to separate them again based on their initial locations because the molecules are identical. Such a separation process would violate the second law of thermodynamics.

We next derive the differential equation that governs the maximum mixedness reactor [21]. Consider an expanded view of the reactor in a state of maxi-

mum mixedness shown in Figure 5.B. As depicted in Figure 7, feed with flowrate $Qp(\theta)d\theta$ is added to each tube having residence time θ to achieve the desired RTD. So if we consider a volume element to be a mixed section of the composite reactor between times-to-go λ and $\lambda + \Delta\lambda$, the material balance for this element consists of the following terms:

entering at $\lambda + \Delta\lambda$: $$Q\left(\int_{\lambda+\Delta\lambda}^{\infty} p(\lambda')d\lambda'\right)c(\lambda+\Delta\lambda) \tag{43}$$

leaving at λ: $$Q\left(\int_{\lambda}^{\infty} p(\lambda')d\lambda'\right)c(\lambda) \tag{44}$$

feed addition: $$Q\left(p(\lambda)\Delta\lambda\right)c_f \tag{45}$$

production: $$\underbrace{Q\left(\int_{\lambda}^{\infty} p(\lambda')d\lambda'\right)\Delta\lambda}_{\text{volume of reactor element}}\ \underbrace{R(c(\lambda))}_{\text{rate per volume}} \tag{46}$$

Considering the reactor is at steady state, we set the accumulation to zero and

obtain

$$c(\lambda+\Delta\lambda)\int_{\lambda+\Delta\lambda}^{\infty} p(\lambda')d\lambda' - c(\lambda)\int_{\lambda}^{\infty} p(\lambda')d\lambda' + c_f p(\lambda)\Delta\lambda + R(c)\Delta\lambda\int_{\lambda}^{\infty} p(\lambda')d\lambda' = 0$$

We can combine the first two integral terms and divide by $\Delta\lambda$ to obtain

$$\frac{c(\lambda+\Delta\lambda)-c(\lambda)}{\Delta\lambda}\int_{\lambda+\Delta\lambda}^{\infty} p(\lambda')d\lambda' - c(\lambda)p(\lambda) + c_f p(\lambda) + R(c)\int_{\lambda}^{\infty} p(\lambda')d\lambda' = 0$$

Taking the limit as $\Delta\lambda \to 0$ and rearranging gives

$$\frac{dc}{d\lambda} = \frac{p(\lambda)}{\int_{\lambda}^{\infty} p(\lambda')d\lambda'}\left(c(\lambda)-c_f\right) - R(c)$$

Equivalently we can express the integral in terms of the integrated form of the RTD and write

$$\boxed{\frac{dc}{d\lambda} = \frac{p(\lambda)}{1 - P(\lambda)} \left(c(\lambda) - c_f \right) - R(c)} \tag{47}$$

We wish to calculate the reactor effluent concentration, which is given by $c(\lambda)$ at $\lambda = 0$. As in the segregated reactor case, this first-order differential equation is singular; we wish to integrate from $\lambda = \infty$, the entrance to the longest tube, to the combined tube exits at $\lambda = 0$. A boundary condition is required at $\lambda = \infty$. For c to remain bounded as $\lambda \longrightarrow \infty$, we stipulate the boundary condition

$$\frac{dc}{d\lambda} = 0, \qquad \lambda = \infty$$

Provided we know the limit $p(\lambda)/(1-P(\lambda))$ as $\lambda \longrightarrow \infty$, we can solve Equation 47 directly for the boundary condition on c at $\lambda = \infty$; we call this value c_∞. Note that $c_\infty \neq c_f$.

Numerical solution.

We wish to transform the $\lambda \in (\infty, 0)$ interval into $z \in (0, 1)$. The analogous transformation to the segregated reactor is

$$z = \frac{1}{1+\lambda}, \qquad \lambda = \frac{1-z}{z}$$

The derivative becomes

$$\frac{dc}{d\lambda} = \frac{dc}{dz}\frac{dz}{d\lambda} = -z^2\frac{dc}{dz}$$

in which the minus sign arises because we are changing the direction when integrating in the transformed z variable. Equation 47 then becomes

$$\boxed{\frac{dc}{dz} = -\frac{1}{z^2}\left[\frac{p((1-z)/z)}{1-P((1-z)/z)}\left(c - c_f\right) - R(c)\right] \qquad c(0) = c_\infty} \tag{48}$$

and we integrate from $z = 0$ to $z = 1$. Again, a critical stopping value should be set at $z = 1$ to avoid an undefined right-hand side. We set the right-hand side to zero at $z = 0$ because we determined the value of c_∞ such that the bracketed term in Equation 48 was zero. Again, care should be exercised at $z = 0$ because the denominator goes to zero at $z = 0(\lambda = \infty)$. Plotting $c(z)$ and examining the $z = 0$ end for unusual behavior is recommended.

Example 8.2: Two CSTRs in series

We illustrate the results of these sections with an example taken from Zwietering [21].

Given the RTD of two equal-sized CSTRs in series for a single, second-order, irreversible reaction, compute the reactor effluent concentration for the following cases: segregated flow, maximum mixedness and two ideal CSTRs.

Solution

The residence-time distribution for two CSTRs in series is given by Equations 22 and 24 for $n = 2$,

$$p(\theta) = \frac{4\theta}{\tau^2} e^{-2\theta/\tau}$$

$$1 - P(\theta) = (1 + 2\theta/\tau) e^{-2\theta/\tau}$$

in which $\tau = V_R/Q_f$ and V_R is the total volume of the CSTRs. The balance for the maximum mixedness case becomes

$$\frac{dc}{d\lambda} = \frac{4\lambda}{\tau(\tau + 2\lambda)}(c - c_f) + kc^2$$

Defining dimensionless variables, $\overline{c} = c/c_0$ and $\overline{\lambda} = \lambda/\tau$, the equation becomes

$$\frac{d\overline{c}}{d\overline{\lambda}} = \frac{4\overline{\lambda}}{2\overline{\lambda}+1}(\overline{c}-1) + K\overline{c}^2 \tag{49}$$

in which $K = kc_0\tau$. Notice that all the physical constants of the reactor combine into the single dimensionless constant K. If we apply the zero slope condition at $\lambda = \infty$, we obtain the quadratic equation

$$2(\overline{c}_\infty - 1) + K\overline{c}_\infty^2 = 0$$

which can be solved for $\overline{c}_\infty$. Again we have an equation on a semi-infinite interval, which we can transform via

$$z = \frac{1}{1+\overline{\lambda}}, \qquad \overline{\lambda} = \frac{1-z}{z}$$

in which $\overline{\lambda} \in (\infty, 0)$ is transformed to $z \in (0, 1)$. The transformed derivative satisfies

$$\frac{d\overline{c}}{d\overline{\lambda}} = \frac{d\overline{c}}{dz}\frac{dz}{d\overline{\lambda}} = -z^2\frac{d\overline{c}}{dz}$$

so the final differential equation is

$$\begin{aligned} \frac{d\overline{c}}{dz} &= -\frac{1}{z^2}\left[\frac{4(1-z)/z}{2(1-z)/z+1}(\overline{c}-1) + K\overline{c}^2\right] \\ \overline{c}(0) &= \overline{c}_\infty \end{aligned}$$

The effluent of the maximum mixed reactor is given by the solution $\overline{c}(z)$ at $z = 1$. Figure 8 displays the solution to this differential equation for a range of K values.

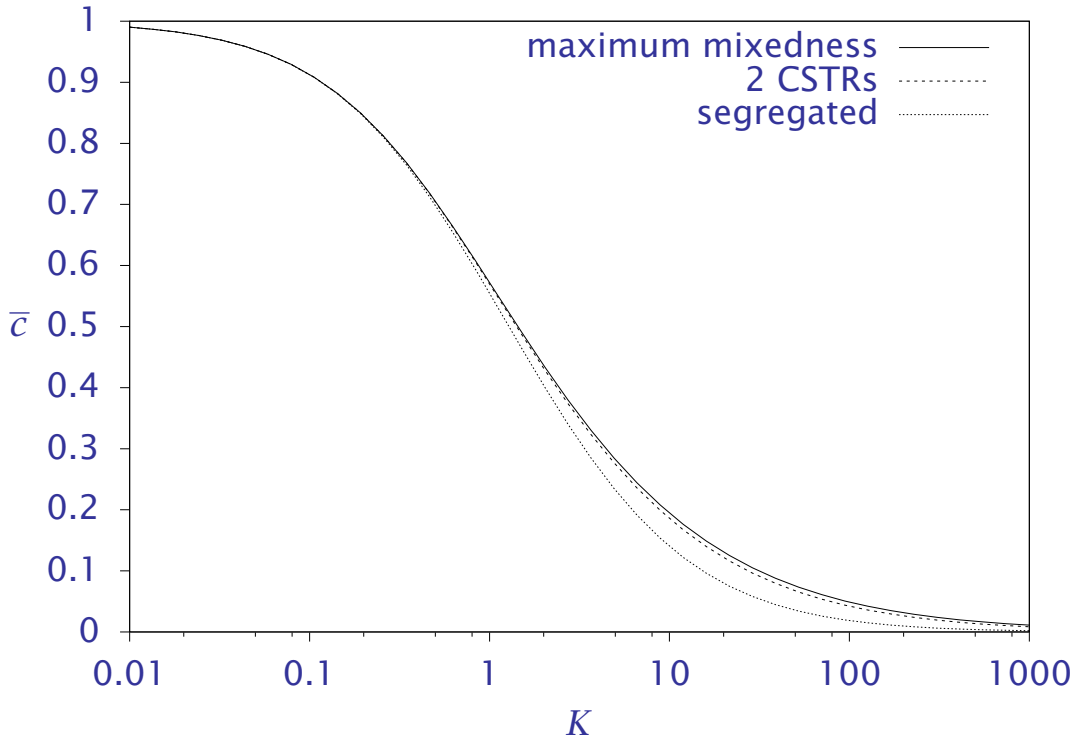


Figure 8: Dimensionless effluent concentration $\overline{c} = c/c_0$ versus dimensionless rate constant $K = k\tau c_0$ for second-order reaction; the RTD for all cases is given by 2 CSTRs in series.

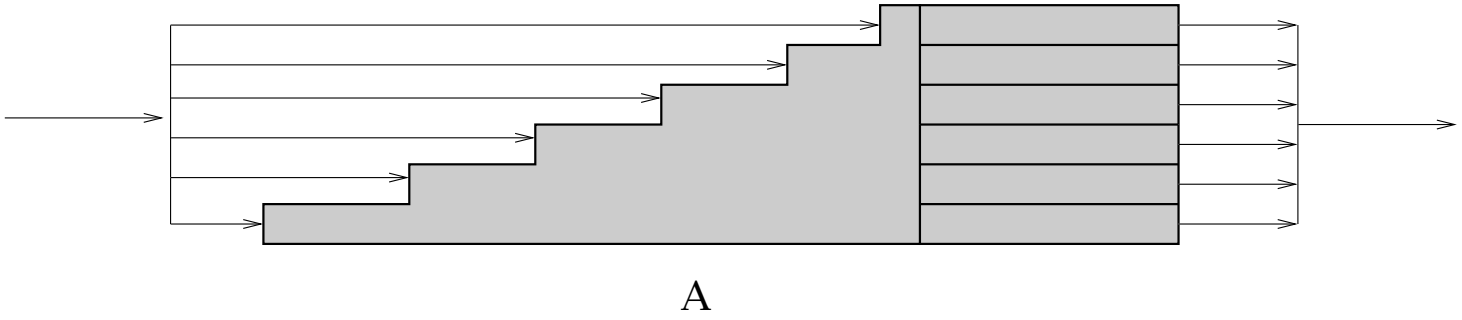
□

Intermediate conditions of mixing.

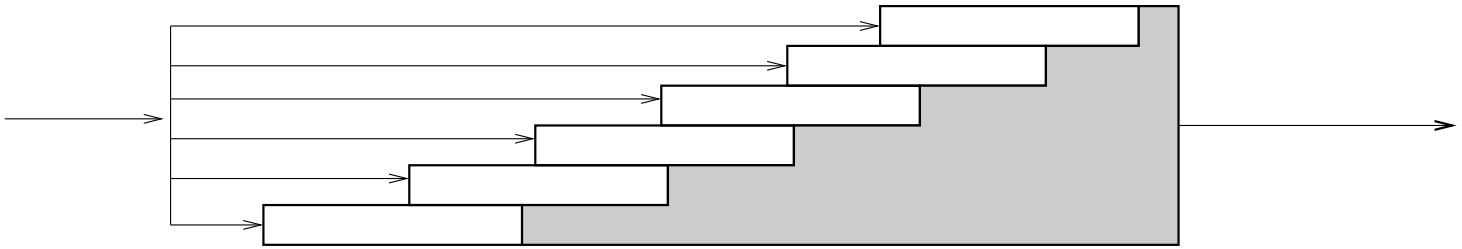
Weinstein and Adler [19] also proposed an interesting general conceptual mixing model by allowing a general mixing pattern between the various tubes as depicted in Figure 5.C.

The segregated reactor depicted in Figure 4 and Figure 5.A is sometimes referred to as late mixing or mixing as late as possible. The material remains segregated until it reaches the common exit where the segregated streams are finally mixed in the reactor effluent. The situation depicted by the maximum mixedness reactor of Figure 6 and Figure 5.B is sometimes called early mixing. The material is mixed at the earliest possible times as it travels down the tubes; no segregated streams remain to be combined at the reactor exit.

Consider again the two reactors in Example . The conceptual mixing pattern is sketched in Figure 9.



A



B

Figure 9: CSTR followed by PFR (A) and PFR followed by CSTR (B) as examples of complete and partial mixing; RTDs for the two configurations are equal.

The reactors have identical RTDs. Comparing these two reactor configurations, the reactor with the CSTR preceding the PFR is in the condition of maxi-

mum mixedness because the CSTR is the condition of maximum mixedness and the feed to the PFR is therefore well mixed, so the different portions of the RTD in the PFR section have identical compositions, and could be considered well mixed or segregated. The PFR preceding the CSTR is not in the condition of maximum mixedness, nor is it segregated. As shown in Figure 9, it displays an intermediate state of mixing, similar to case C in Figure 5. We show in Section that because the reaction rate is second order, complete mixing gives the lowest conversion possible consistent with the given RTD. This conclusion is consistent with the calculation performed in Example in which the CSTR–PFR arrangement had lower conversion than the PFR–CSTR.

Mass Transfer and Limits of Reactor Mixing

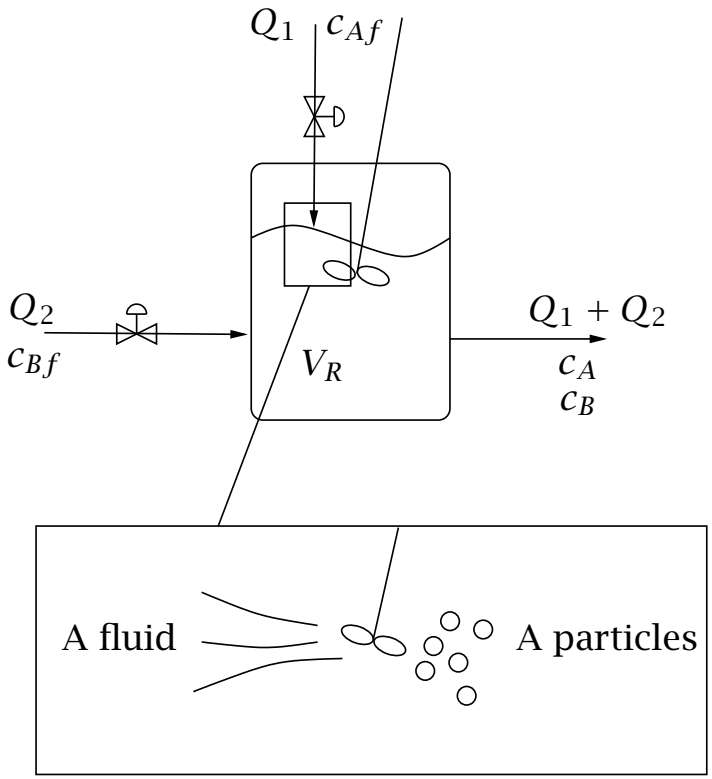


Figure 10: Adding two liquid-phase feed streams to a stirred tank; the stirrer is modeled as shearing the liquid A feed stream into small, uniformly sized particles of A and randomly distributing them in the continuous phase containing B.

Consider the following physical picture to help in our understanding of segregated flow and maximum mixedness. Figure 10 shows the classic situation in which we mix two liquid-phase feed streams in a stirred tank for the second-order reaction

$$A + B \longrightarrow C \tag{50}$$

We model the action of the stirrer as shearing the fluid A stream into small, uniformly sized "particles" of component A dispersed in the continuous phase containing component B dissolved in a solvent. The size of the A "particles" is one measure of how well the stirrer is working. This physical picture, although idealized, is motivated by several types of real reactors, such as suspension and emulsion polymerization reactors. Ottino provides a well-illustrated discussion of the detailed results of fluid shear [16, pp.1–17]. We assume these "particles" of component A move rapidly about the reactor with the fluid flow. We therefore have an ideal CSTR residence-time distribution; if we inject tracer with the A

stream or the B stream, we would see the classic step response for the CSTR. In other words, the macromixing is excellent, and determining the residence-time distribution would not indicate anything except an ideally mixed reactor.

Parameter	Value	Units
k	1	L/mol·min
k_{mA}	1.67×10^{-4}	cm/min
k_{mB}	1.67×10^{-4}	cm/min
$\alpha = Q_1/Q_2$	1	
c_{Af}	1	mol/L
c_{Bf}	1	mol/L
$\overline{\theta} = V_R/(Q_1 + Q_2)$	10	min

Table 2: Mass-transfer and kinetic parameters for micromixing problem.

Now we model the micromixing. Let the mass transfer between the particles and the continuous phase be described by a mass-transfer coefficient, so the

mass balance for components A and B inside the particles is given by

$$V\frac{dc_A}{d\theta} = k_{mA}(\overline{c}_A - c_A)S - kc_Ac_BV \qquad c_A(0) = c_{Af}$$
$$V\frac{dc_B}{d\theta} = k_{mB}(\overline{c}_B - c_B)S - kc_Ac_BV \qquad c_B(0) = 0 \tag{51}$$

in which θ is the time the particle has been in the reactor, V and S are the particle volume and area, respectively, and k_{mA} and k_{mB} are the A and B mass-transfer coefficients. The variables $\overline{c}_A$ and $\overline{c}_B$ are the continuous-phase concentrations of A and B. The initial conditions follow from the fact that the particles are initially formed from the pure A feed stream. Only as θ increases do they have time to communicate with the continuous phase. To determine the A and B concentrations in the continuous phase, we write the overall, steady-state mass balances for both components

$$0 = Q_1 c_{Af} - Q_1 \int_0^\infty c_A(\theta) p(\theta) d\theta - Q_2 \overline{c}_A - \frac{V_R}{1+\alpha}\left[\alpha \int_0^\infty k c_A c_B p(\theta) d\theta + k \overline{c}_A \overline{c}_B\right]$$

$$0 = Q_2 c_{Bf} - Q_1 \int_0^\infty c_B(\theta) p(\theta) d\theta - Q_2 \overline{c}_B - \frac{V_R}{1+\alpha}\left[\alpha \int_0^\infty k c_A c_B p(\theta) d\theta + k \overline{c}_A \overline{c}_B\right] \tag{52}$$

We use orthogonal collocation on $z = \theta/(1+\theta)$ to solve Equations 51 simultaneously with Equations 52 [18]. Orthogonal collocation is described briefly in Appendix A. The kinetic and mass-transfer parameters are given in Table 2 We compute the total A and B concentration in the effluent by summing over both particle and continuous phases

$$c_{At} = \frac{\alpha}{1+\alpha} \int_0^\infty c_A(\theta) p(\theta) d\theta + \frac{1}{1+\alpha} \overline{c}_A$$

$$c_{Bt} = \frac{\alpha}{1+\alpha} \int_0^\infty c_B(\theta) p(\theta) d\theta + \frac{1}{1+\alpha} \overline{c}_B$$

We next study the effect of particle size. Figure 11 shows $c_A(\theta)$ for particle sizes ranging from 0.1 μm to 1.0 cm. We see that if the stirrer is able to produce A particles of 1.0 μm or less, then the reactor is essentially in the state of maximum mixedness, or, equivalently, operates as an ideally mixed CSTR. At the other extreme, if the A particles are larger than about 1.0 mm, then the reactor operates essentially as a segregated-flow reactor. Segregated flow essentially reduces the reaction rate to zero because the A and B species cannot come into contact.

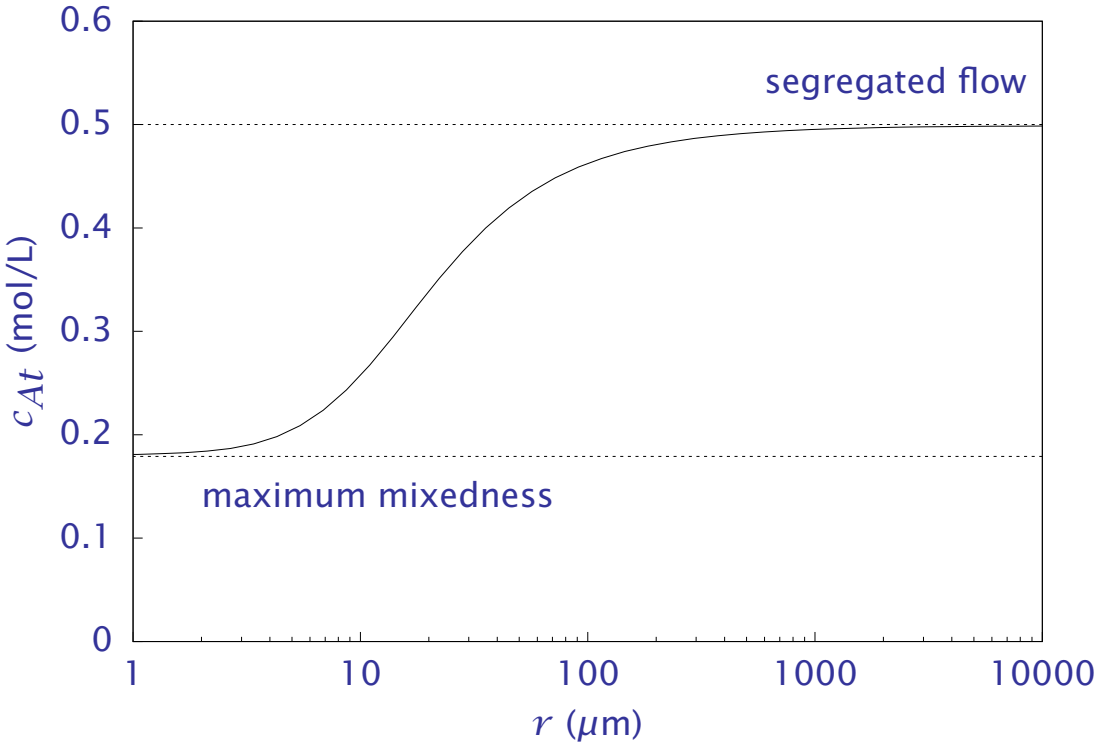


Figure 11: Total concentration of A in the reactor effluent versus particle size.

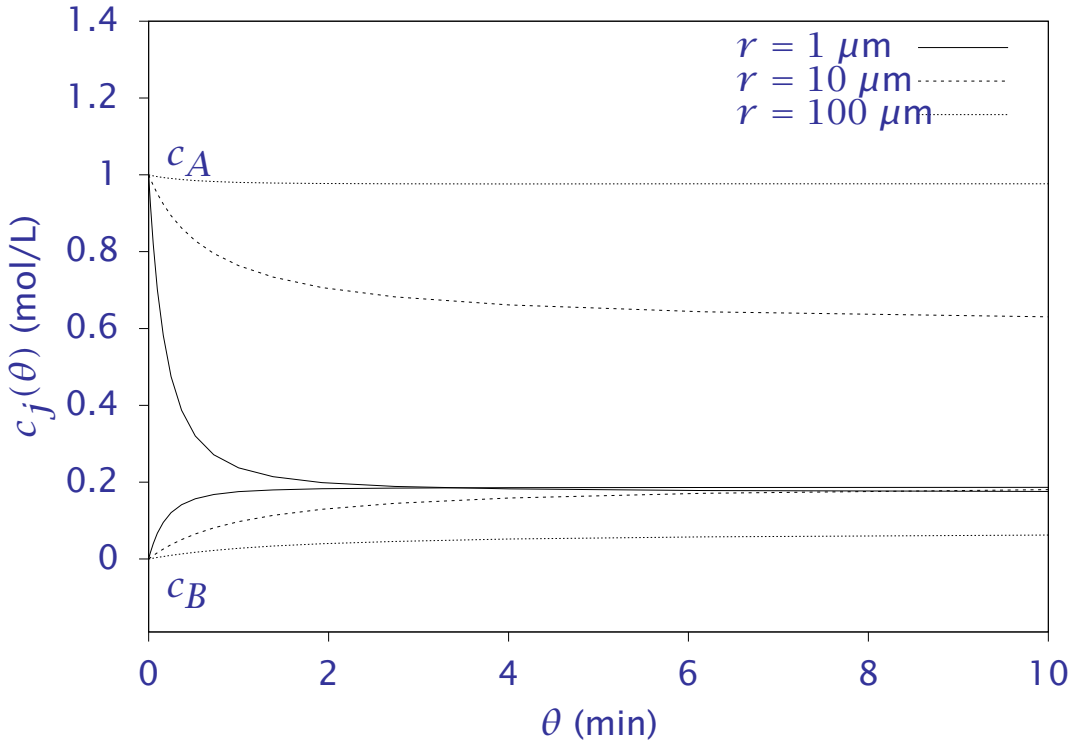


Figure 12: Particle concentrations of A and B versus particle age for three different-sized particles.

Figure 12 provides a detailed look inside the particles for $r = 1$, 10 and 100 μm. For $r = 1$ μm, the A and B concentrations in the particles rapidly

change from the feed values to the continuous phase values as they spend time in the reactor. This equilibration with the continuous phase is rapid because the particles are small, the total surface area and rate of mass transfer are therefore large. This case is close to maximum mixedness. For $r = 100$ μm, the particles are 100 times larger, and the total surface area and rate of mass transfer are small. Therefore, these particles remain at the inlet feed conditions for a large time. They are washed out of the reactor before they can produce hardly any reaction rate. This case corresponds to essentially complete segregation.

Summarizing, this example is instructive for two reasons. First the residence-time distribution corresponds to a perfect CSTR regardless of particle size. Residence-time distribution measures the reactor macromixing, which is excellent. The particle size governs the micromixing. Small particles have large mass-transfer rates and equilibrate with the continuous phase and the particles in the reactor with different ages leading to the case of maximum mixedness. Large particles have small mass-transfer rates and do not exchange much material with the continuous phase nor therefore with particles of other ages. This

case corresponds to segregated flow, which leads to essentially zero rate of reaction. Particles of intermediate size then describe the reactors in intermediate states of mixing.

Limits of Reactor Performance

A Single Convex (Concave) Reaction Rate

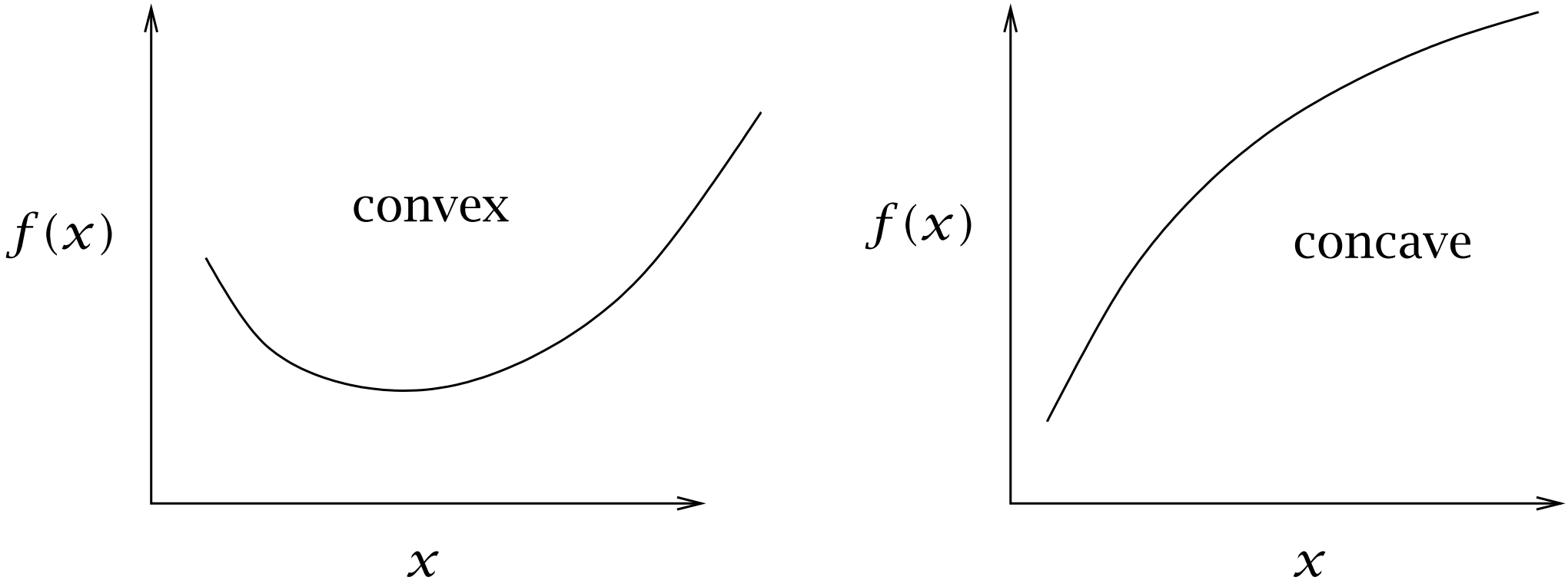


Figure 13: Differentiable convex and concave functions.

To generalize the results of Examples and 8.2, we define convex and concave functions. As presented in the introductory calculus course, the simplest version pertains to functions having at least two derivatives. In that case, a function is convex (concave upward) if its second derivative is everywhere greater than or equal to zero. A function is concave (concave downward) if its second derivative is everywhere less than or equal to zero, as shown in Figure 13

$$\frac{d^2 f(x)}{dx} \geq 0, \qquad f \text{ convex}$$

$$\frac{d^2 f(x)}{dx} \leq 0, \qquad f \text{ concave}$$

For example, the nth-order reaction-rate expression $r = c^n$, is *convex if* $n \geq 1$ and *concave if* $n \leq 1$. Note that first-order rate functions are both convex and concave.

The general result for the single reaction is

Given a single reaction with convex (concave) reaction rate expression, the highest (lowest) conversion for a given RTD is achieved by the segregated reactor and the lowest (highest) conversion is achieved by the maximally mixed reactor.

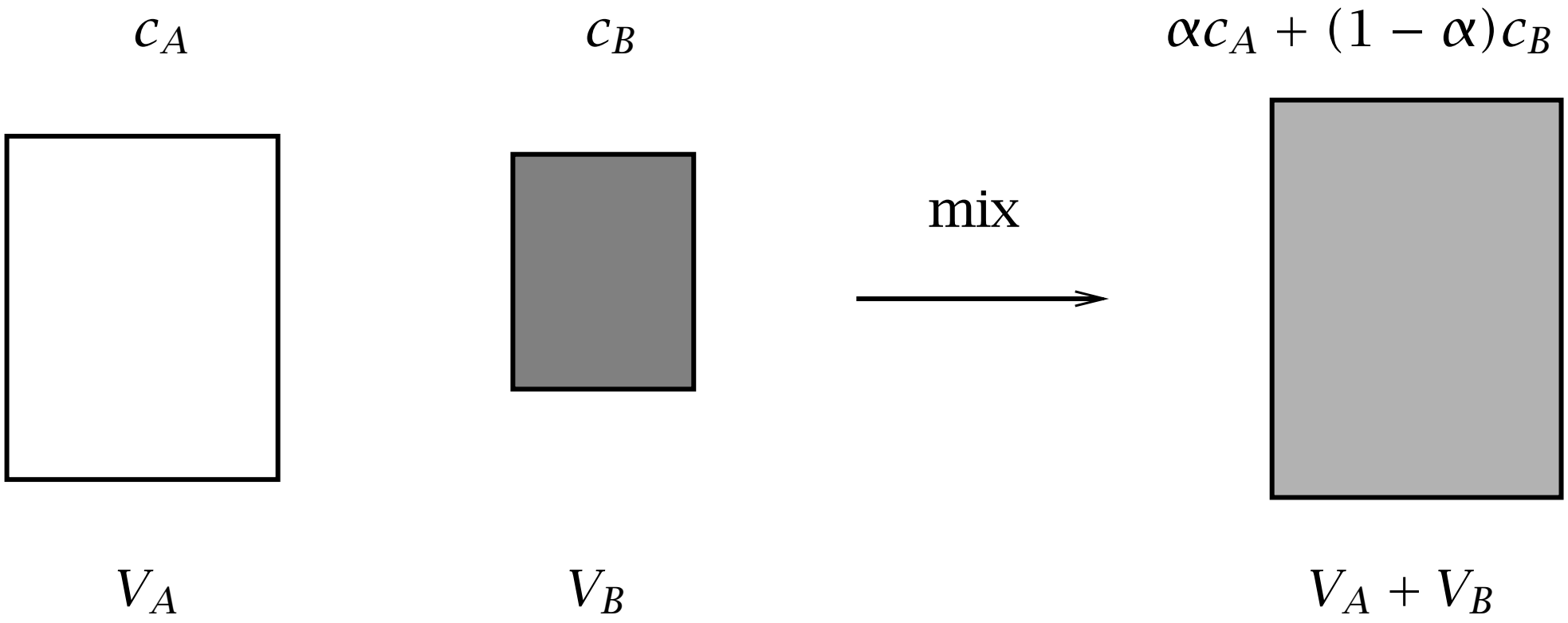


Figure 14: Two volume elements before and after mixing.

This nonobvious result is a significant generalization of the numerical Examples and 8.2, and Exercise 8.6, and requires justification. The argument presented next first appeared in Chauhan et al. [3]; Nauman and Buffham [15]

also provide a detailed discussion.

Step 1.

To start, consider the two volume elements shown in Figure 14. Note that in this discussion c_A and c_B represent concentration of the *same reactant species* in volume elements or tubes A and B. When the volume elements are segregated the total reaction rate r_s is simply

$$r_s = r(c_A)V_A + r(c_B)V_B$$

so that the segregated rate per volume is

$$r_s = \alpha r(c_A) + (1 - \alpha)r(c_B), \qquad 0 \leq \alpha \leq 1$$

in which α is the volume fraction of element A

$$\alpha = \frac{V_A}{V_A + V_B}$$

On the other hand, if we mix the contents, the concentration is

$$c_m = \frac{c_A V_A + c_B V_B}{V_A + V_B} = \alpha c_A + (1 - \alpha) c_B$$

The total reaction rate per volume after mixing is therefore

$$r_m = r(c_m)$$

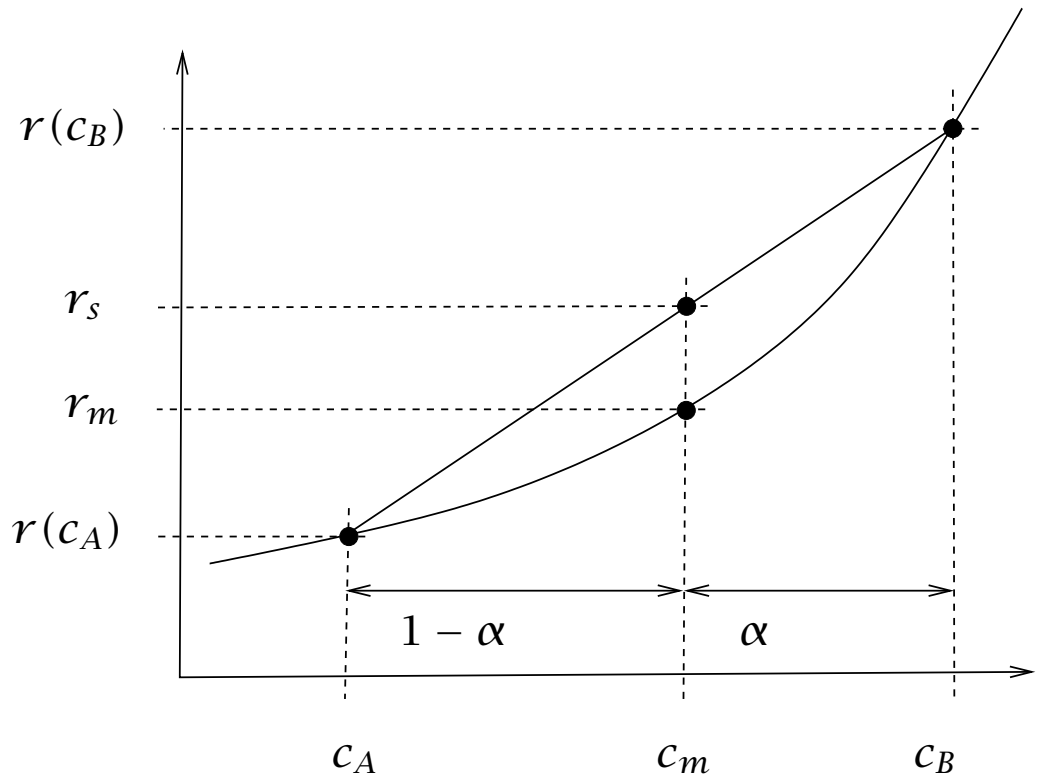


Figure 15: Convex rate expression and the effect of mixing; rate of the mean (r_m) is less than the mean of the rate (r_s).

As shown in Figure 15, for all c_A, c_B and α, *if we mix the two volume elements, we lower the overall reaction rate.* The opposite conclusion applies if we have a

concave rate expression. The rate of the mean r_m is less than the mean of the rate r_s for convex reactions, or

$$r(\alpha c_A + (1-\alpha)c_B) \leq \alpha r(c_A) + (1-\alpha)r(c_B), \qquad \text{all } c_A, c_B, 0 \leq \alpha \leq 1$$

This result is the key to understanding what happens in the general reactor. In fact, this statement can be taken as the definition of convexity (Exercise 8.13).

Step 2.

Now consider two tubes as shown in Figure 16, which we may choose to mix or maintain segregated as material proceeds down their lengths.

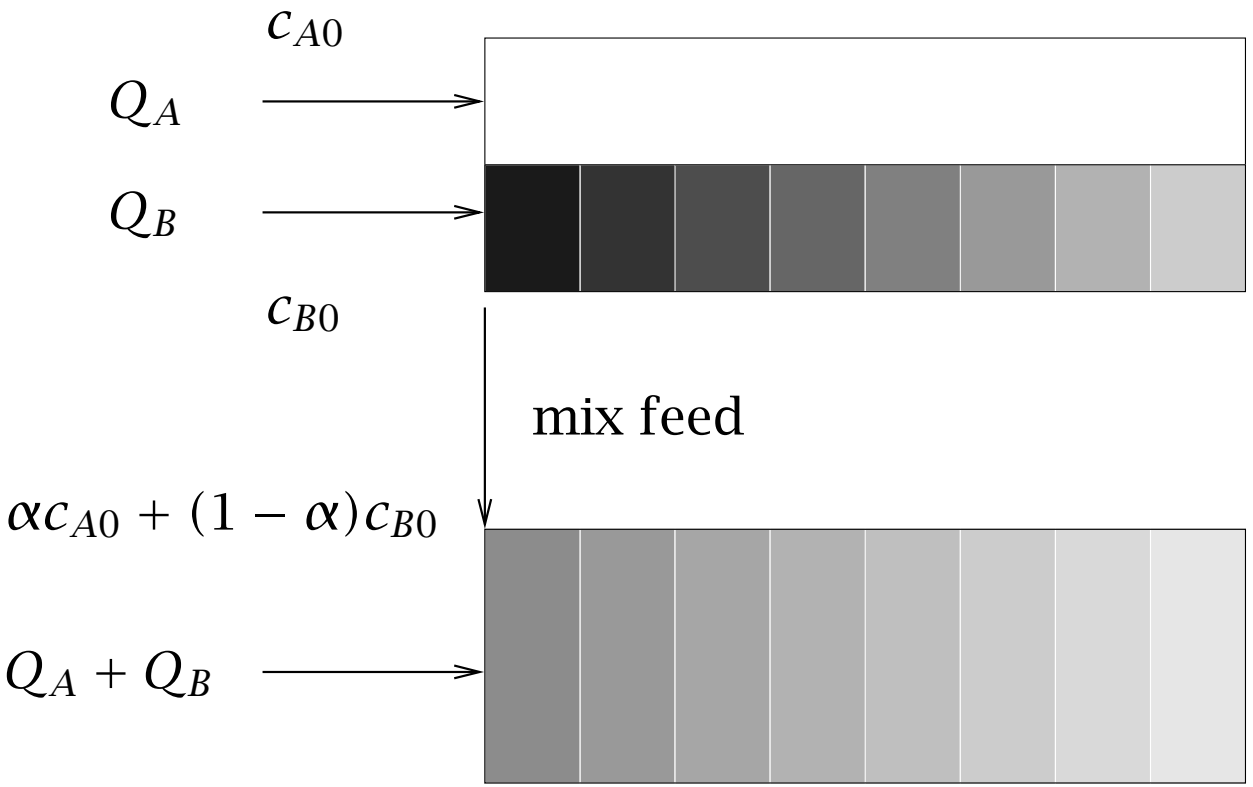


Figure 16: Two tubes before and after mixing the entering feed; averaging the two segregated tubes produces c_s; the mixed feed tube produces c_m.

Again assume a single reaction takes place and the reaction-rate expression is a convex function of a single reactant species. Without loss of generality

assume the stoichiometric coefficient for the limiting species is negative one. For constant density, the material balances for the segregated tubes are

$$\frac{dc_A}{d\theta} = -r(c_A), \qquad c_A(0) = c_{A0}$$
$$\frac{dc_B}{d\theta} = -r(c_B), \qquad c_B(0) = c_{B0}$$

in which $\theta = V/Q_f$. We can track the mean concentration for the segregated case c_s by simply summing the molar flows for tubes A and B divided by the total flow

$$c_s = \alpha c_A + (1-\alpha)c_B \tag{53}$$

in which α is now the flowrate fraction in tube A

$$\alpha = \frac{Q_A}{Q_A + Q_B}$$

We also can write a differential equation for c_s by simply differentiating Equa-

tion 53

$$\frac{dc_s}{d\theta} = -\left[\alpha r(c_A) + (1-\alpha) r(c_B)\right], \qquad c_s(0) = \alpha c_{A0} + (1-\alpha) c_{B0} \tag{54}$$

Consider now the mixed case. If the tubes are mixed at some point, which we may call $\theta = 0$, then the material balance for the concentration after that point is

$$\frac{dc_m}{d\theta} = -r(c_m), \qquad c_m(0) = \alpha c_{A0} + (1-\alpha) c_{B0} \tag{55}$$

Our goal now is to show $c_m \geq c_s$ for all reactor positions, θ, and all feed concentrations and flowrates, c_{A0}, c_{B0} and α. We know at $\theta = 0$

$$\frac{dc_m}{d\theta} = -\left[r(\alpha c_{A0} + (1-\alpha) c_{B0})\right] \geq -\left[\alpha r(c_A) + (1-\alpha) r(c_B)\right] = \frac{dc_s}{d\theta}$$

If the initial derivatives have this relationship we know, for at least some small distance down the tube, $c_m \geq c_s$ as shown in Figure 17.

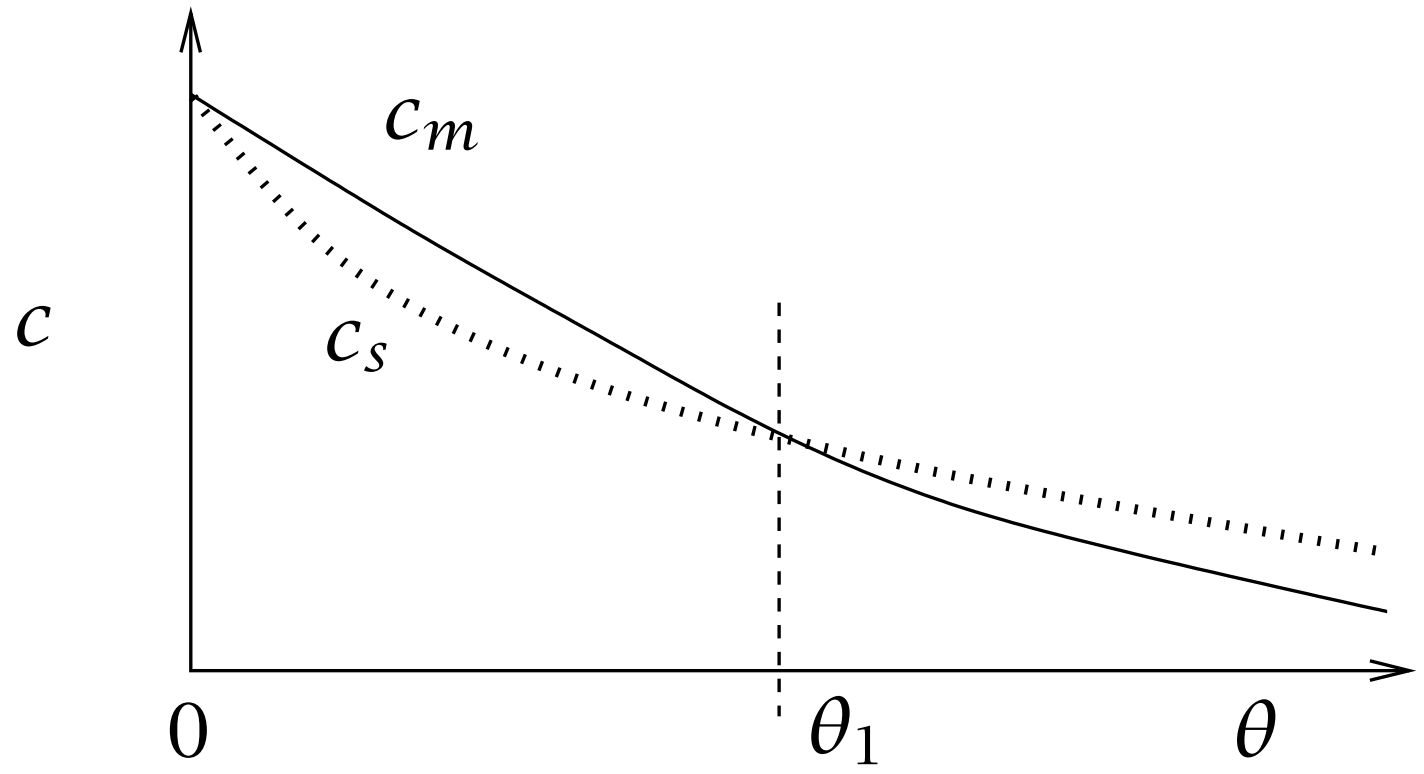


Figure 17: Mean segregated and mixed concentrations versus θ; curves crossing at θ_1 is a contradiction.

How do we know, however, that the curves do not cross each other at some later time? Assume this crossing can happen as shown in Figure 17, and we

establish a contradiction. Let θ_1 be the first such crossing time. At θ_1, c_A and c_B have some well-defined values and $c_s = \alpha c_A + (1-\alpha)c_B$. We have assumed that $c_m = c_s$ at θ_1 so the differential equation for c_m, Equation 55, gives

$$\frac{dc_m}{d\theta} = -\left[r(\alpha c_A + (1-\alpha)c_B)\right], \qquad \theta = \theta_1$$

The differential equation for c_s still applies and Equation 54 gives

$$\frac{dc_s}{d\theta} = -\left[\alpha r(c_A) + (1-\alpha)r(c_B)\right], \qquad \theta = \theta_1$$

Comparing the right-hand sides of these two differential equations and using the convexity of $r(c)$, we conclude

$$\frac{dc_m}{d\theta} \geq \frac{dc_s}{d\theta}, \qquad \theta = \theta_1$$

But this relationship contradicts the assumption that the c_s and c_m curves cross

each other. Therefore there can be no time θ_1 at which the curves cross and we conclude

$$c_m(\theta) \geq c_s(\theta), \qquad \text{all } \theta$$

This argument and result apply equally well for all c_{A0}, c_{B0} and α.

Step 3.

Finally, consider a segregated reactor with arbitrary residence-time distribution as depicted in Figure 5.C. We select any pair of tubes, mix them, make the same argument that we made in Step 2, and replace the segregated tubes with mixed tubes that achieve lower conversion than the original system. We continue in this fashion, and after we pairwise mix all the segregated tubes with mixed tubes, we achieve the reactor of maximum mixedness in Figure 5.B. and the lowest possible conversion. Note this pairing and mixing procedure does not affect the RTD.

The General Case

One might expect that the limits of reactor mixing determine directly the limits of reactor performance for more general kinetic schemes as well as the single convex or concave rate expression of the last section. Unfortunately nature is more subtle. We present next an example that dispels this notion, and then discuss what is known about the limits of reactor performance. This example is based on one presented by Glasser, Hildebrandt and Godorr [8]. Levenspiel [14] shows how to find the optimal reactor configuration for this type of example.

Example 8.3: Optimal is neither segregated nor maximally mixed

Consider the rate expression

$$r(c) = \frac{c}{1 + 5c^2} + 0.05c \tag{56}$$

which is plotted in Figure 18.

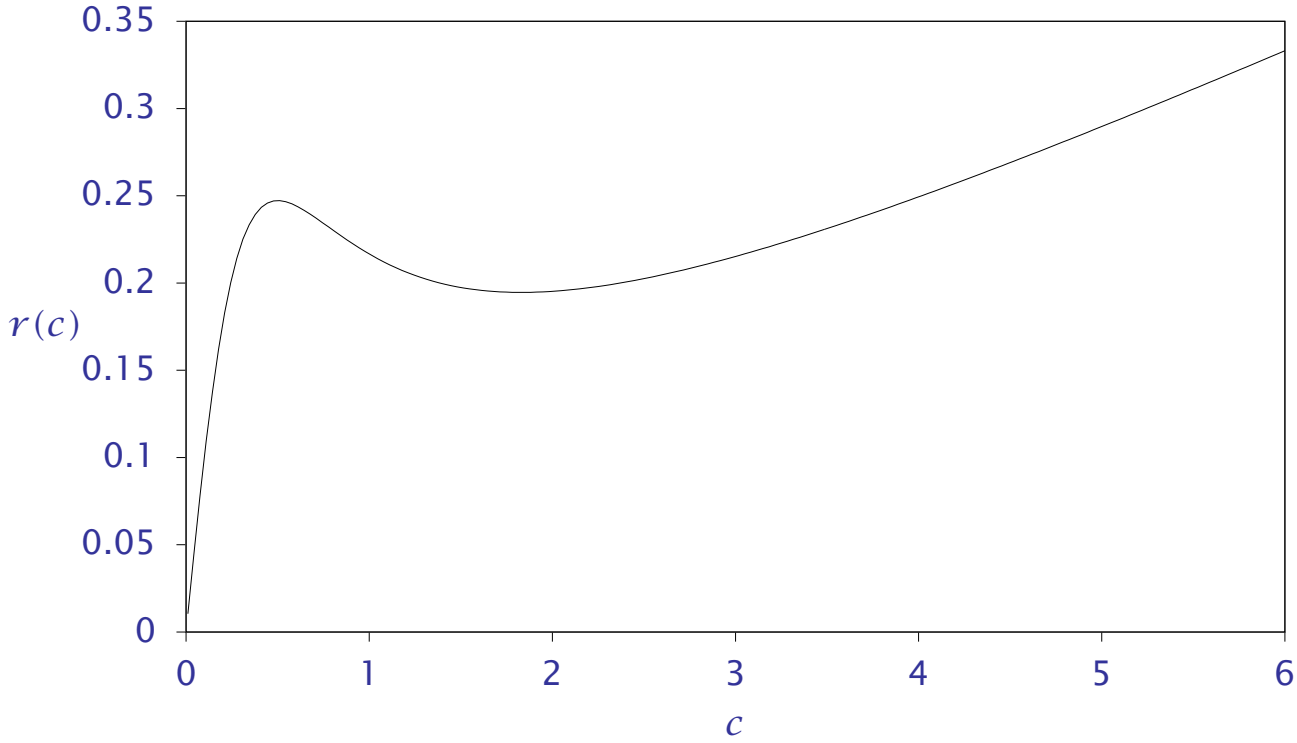


Figure 18: Reaction rate versus concentration of limiting reactant; rate expression is neither convex nor concave.

For a feed concentration of 5, find the combination of CSTRs and PFRs that

achieve 95% conversion with the smallest total reactor volume. Determine the RTD for this reactor configuration. What conversion is achieved in a segregated reactor with this RTD? What conversion is achieved in a maximally mixed reactor with this RTD?

Solution

As we mentioned in Chapter 4, the smallest volume can be achieved with a series combination of CSTRs and PFRs. First we plot the inverse of the rate as shown in Figure 19.

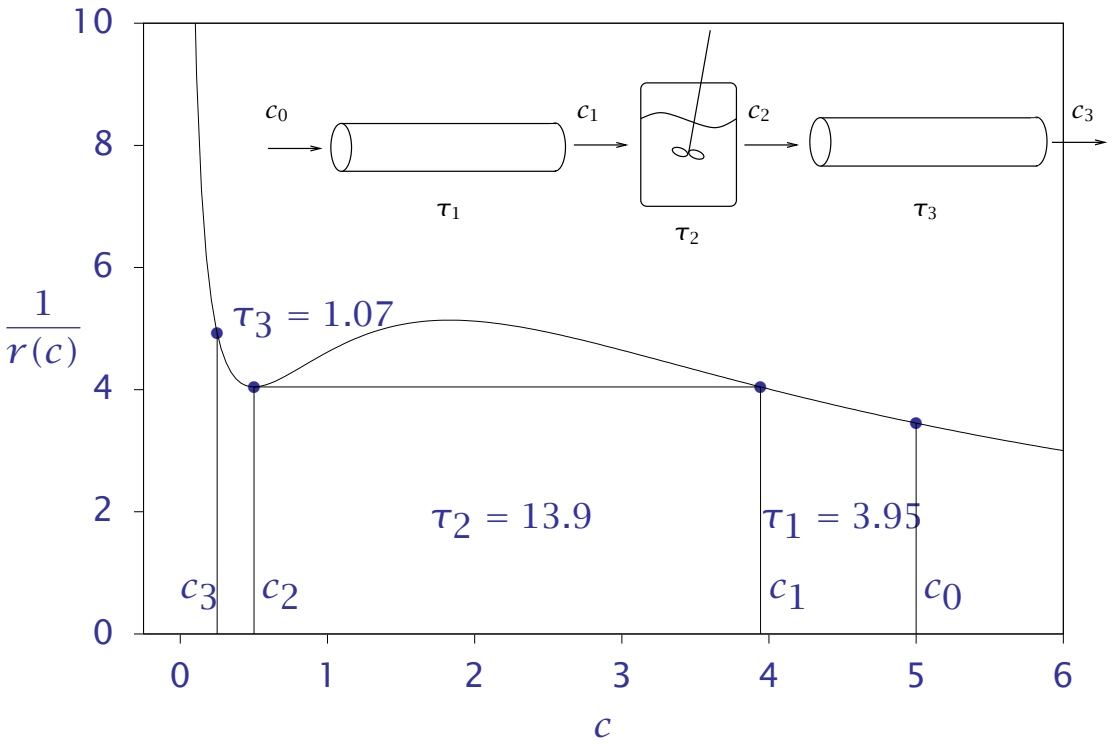


Figure 19: Inverse of reaction rate versus concentration; optimal sequence to achieve 95% conversion is PFR–CSTR–PFR.

Then we find any minima in the inverse rate function and construct CSTRs from those values until we intersect the inverse rate curve. In the remaining

sections of the curve where the inverse rate is a decreasing function of concentration, we use PFRs. Examining the plotted $1/r$ function in Figure 19, we see the optimal configuration is a PFR–CSTR–PFR; this configuration is sketched in Figure 19. We can calculate the sizes of the reactors as follows. We know from the problem statement that $c_0 = 5, c_3 = 0.25$. We next find the point where $dr(c)/dc = 0$. Notice these are also the places where $d(1/r(c))/dc = 0$. Setting the derivative of Equation 56 to zero gives a quadratic equation with two roots: 0.501 and 1.83. We choose the one corresponding to the minimum in $1/r$, which gives

$$c_2 = 0.501, \qquad 1/r(c_2) = 4.045$$

Next we find the concentration c_1 such that $1/r(c_1) = 1/r(c_2)$. This results in a cubic equation, which we solve numerically. Then the residence time is given by $\theta_2 = 1/r(c_2)(c_1 - c_2)$ which gives

$$c_1 = 3.94, \qquad \theta_2 = 13.9$$

To size the PFRs we simply use the PFR design equation and obtain

$$\theta_1 = -\int_{c_0}^{c_1} \frac{1}{r(c)} dc = 3.95, \qquad \theta_3 = -\int_{c_2}^{c_3} \frac{1}{r(c)} dc = 1.07$$

These results are displayed in Figure 19. Because we have a series of CSTRs and PFRs, we can write the RTD immediately

$$p(\theta) = \frac{1}{\theta_2} \exp\left[-\frac{\theta - (\theta_1 + \theta_3)}{\theta_2}\right] H(\theta - (\theta_1 + \theta_3))$$

which is plotted in Figure 20.

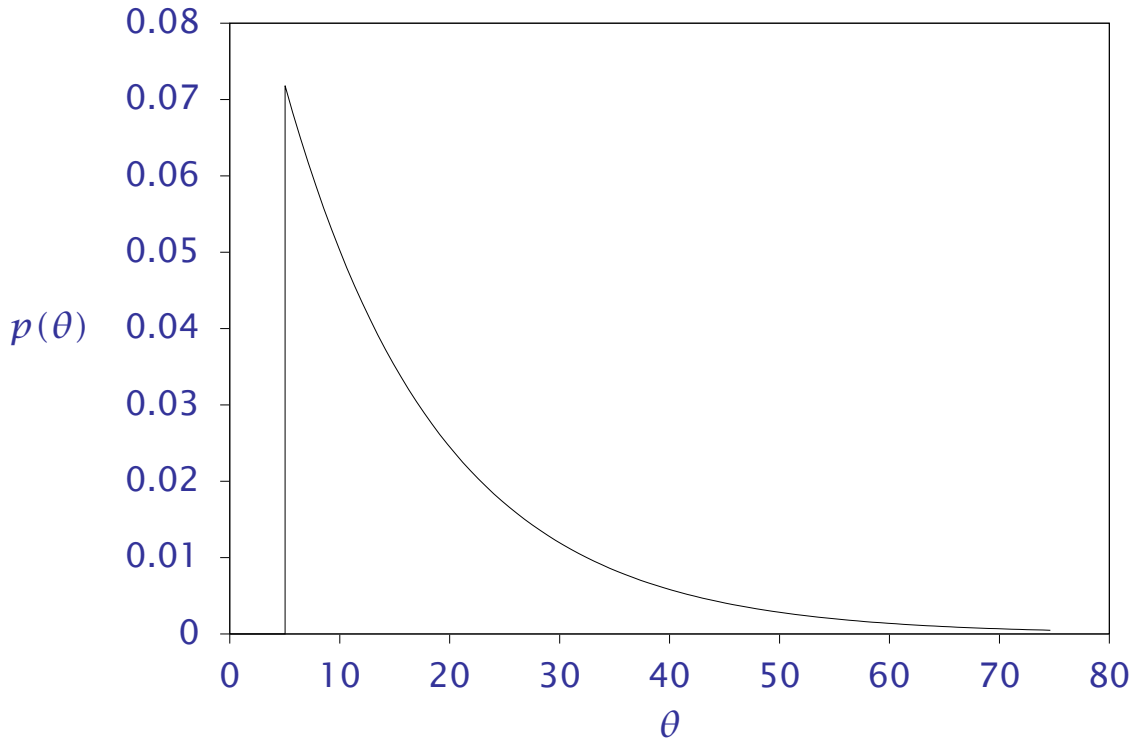


Figure 20: Residence-time distribution for the optimal reactor configuration.

With the RTD in hand, we can compute both the maximally mixed, Equation 48, and segregated, Equation 42, reactor cases. The results of those two calculations are summarized in the following table

Reactor	Conversion
optimal	0.95
segregated	0.68
maximally mixed	0.75

We see that these two mixing limits do *not* bound the performance of the actual reactor sequence with the given RTD. In fact, they are off by more than 20%. Even with a single reaction, if the rate expression is neither convex nor concave, we cannot bound the performance of an actual reactor between the segregated and maximally mixed mixing limits. □

The attainable region.

The primary use of the classical mixing models, such as the segregated reactor and the maximally mixed reactor, is to build insight into the effects of mixing on reactor behavior under the constraint of a fixed, and presumably measurable, RTD. As we have seen in Example 8.3, however, if we are mainly interested in determining bounds on achievable reactor states (conversions, yields, etc.), these simple mixing models are insufficient. In this section we would like to provide a brief overview of what is known about finding sharp bounds on reactor performance. The general problem can be defined in this way.

> Given a feed stream of known composition and a set of chemical reactions with known rate expressions, determine the set of all possible steady-state species concentrations that can be achieved by *any* combination of chemical reactors.

This set was proposed by Horn almost 40 years ago and named the **attainable region** [10]. Because the set is defined for *all possible reactor combinations*, it seems conceptually difficult to formulate a procedure by which we can calculate this set. We should also note that by considering all reactor combinations, we are also considering all possible residence-time distributions, which is a considerable generalization from the single RTD that was considered in the mixing discussion in previous sections. In spite of the seeming difficulty in finding the attainable region, excellent, recent research progress has been made. Feinberg provides a nice summary overview of the history and many recent developments [5].

Glasser and Hildebrandt revived recent interest in this problem [9, 8]. Feinberg and Hildebrandt [7] characterized the boundary of the attainable region, which is of importance because it bounds the possible steady-state concentrations. They showed, for example, that the extreme points of the attainable region boundary are made up entirely of plug-flow reactor trajectories. They also showed that combinations of PFRs, CSTRs, and what are called differen-

tial side-stream reactors (PFRs with addition of feed along the side of the tube), provide the means to find all of the attainable region extreme points.

In addition to properties and conceptual characterization of the attainable region, researchers have proposed computational procedures to approximate the attainable region and solve reactor synthesis problems. Some of these are based on proposing a superstructure of reactor types and numbers, and optimizing an objective function among the possible reactors [11]. Because the superstructure does not enumerate all possibilities, the solution may not be close to the true attainable region. A person skilled in reactor design may be able to choose reactor numbers and types well and overcome this general difficulty on specific reaction networks of interest.

Some computational methods are based on finding the boundary of the attainable region using the reactor types that characterize the attainable region extreme points. Hybrid methods involving superstructures and geometric considerations have also been proposed [12].

Manousiouthakis has recently proposed an infinite dimensional state-space approach (IDEAS) that requires only PFRs, CSTRS and mixing. The advantage of this approach is that one solves only convex, linear optimization problems. The disadvantage is the problems are infinite dimensional and require a finite dimensional approximation for calculation. A full analysis of the convergence properties of the finite dimensional approximation is not yet available, but the approach shows promise on numerical examples [2].

If we wish to allow separation as well as chemical reaction, and almost all industrial designs would fall into this category, then the problem switches from a pure reactor synthesis problem to a reactor-separator synthesis problem. The CSTR equivalence principle of Chapter 4 is an example of the strikingly simple and general results that recently have been achieved for the reactor-separator synthesis problem [6].

Forecasting is always risky business, but given the rapid pace of recent progress, it seems likely that new and highly useful results on pure reactor and

reactor-separator synthesis problems will be forthcoming. These ideas and results may have immediate industrial impact, and certainly fall within the scope of the course in reactor analysis and design.

Examples in Which Mixing is Critical

Returning to the topic of mixing, we would like to close the chapter by presenting a few more chemical mechanisms for which reactor mixing can play a critical role.

Mixing two liquid-phase streams in a stirred tank

- A classic mixing problem arises when we must bring two liquid-phase feed streams together to perform the second-order reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{C} \tag{57}$$

  in the presence of the undesirable side reaction

$$\mathrm{A} \xrightarrow{k_2} \mathrm{D} \tag{58}$$

- If the rate of the second degradation reaction is fast compared to the rate of mixing of the two feed streams, we can anticipate problems. To under-

stand what happens in this situation, consider the mixing model depicted in Figure 21.

A simple mixing model

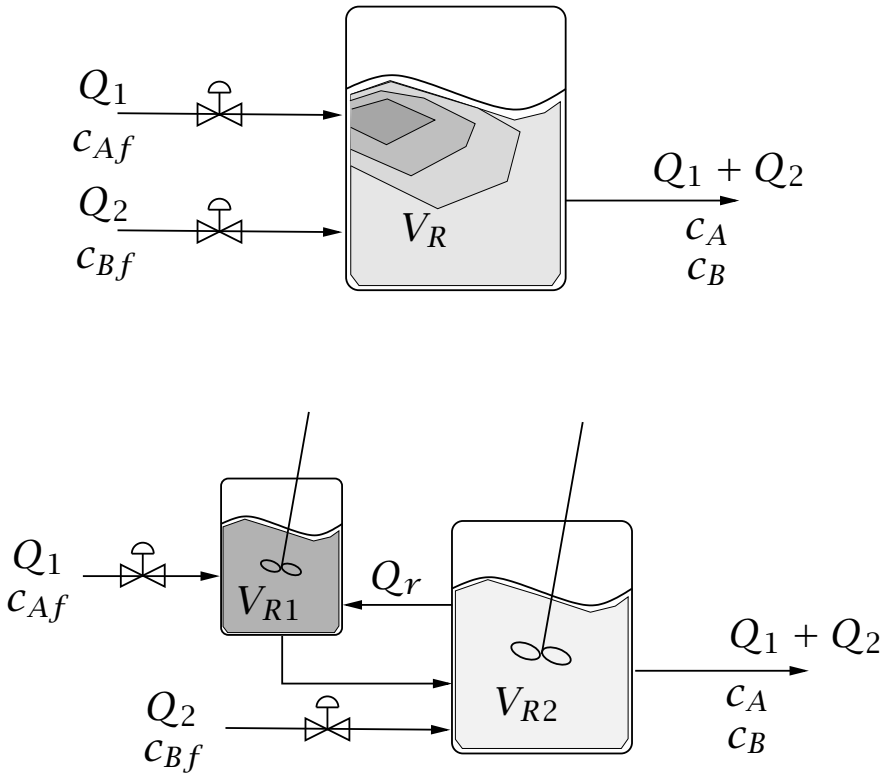


Figure 21: Imperfect mixing (top reactor) leads to formation of an A-rich zone, which is modeled as a small CSTR feeding a second CSTR (bottom two reactors).

Modeling the imperfect mixing

- Component A is assumed to be the limiting reactant. It is added at a low flowrate to a CSTR that contains an excess of reactant B.

- In the top figure we depict the ideal-mixing case in which the rate of mixing is arbitrarily fast compared to the rate of either reaction. But this ideal mixing may be impossible to achieve if the reaction rates are reasonably large.

- So in the bottom figure, we model the formation of an A-rich zone near the feed entry point. This small CSTR exchanges mass with a larger reactor that contains the excess of reactant B.

- We can vary the recycle flowrate between the two CSTRs, Q_r, to vary the

degree of mixing. For large Q_r, we expect the two-reactor mixing model to approach the single, ideally mixed CSTR.

Conversion and yield

- As discussed in Chapter 4, the conversion and yield are the usual quantities of interest in competing parallel reactions of the type given in Reactions 57 and 58.

- We assume the density of this liquid-phase system is constant, and define the overall conversion of reactant A and yield of desired product C as follows:

$$x_A = \frac{Q_1 c_{Af} - (Q_1 + Q_2) c_A}{Q_1 c_{Af}} \qquad y_C = \frac{(Q_1 + Q_2) c_C}{Q_1 c_{Af} - (Q_1 + Q_2) c_A}$$

Compare conversions and yields and check the RTD

- Given the parameters and rate constants in Table 3, calculate x_A and y_C versus Q_r for the two-reactor mixing model shown in Figure 21, and compare the result to the single, well-mixed reactor.

- Then calculate the residence-time distribution $P(\theta)$ for tracer injected with the A feed stream for the two models. Discuss whether or not the residence-time distribution is a reliable indicator for problems with yield in the imperfectly mixed reactor.

Problem parameters

Parameter	Value	Units
k_1	1	min^{-1}
k_2	2	L/mol·min
n	2	
$\theta_1 = V_{R1}/Q_2$	1	min
$\theta_2 = V_{R2}/Q_2$	2	min
$\theta = V_R/Q_2$		
$= \theta_1 + \theta_2$	3	min
$\alpha = Q_1/Q_2$	0.1	
$\rho = Q_r/Q_2$	varies	

Table 3: Reactor and kinetic parameters for feed-mixing example.

Solution — single-reactor model

The steady-state mass balance for the single, well-mixed CSTR is

$$0 = Q_1 c_{Af} - (Q_1 + Q_2) c_A - (k_1 c_A c_B + k_2 c_A^n) V_R$$

$$0 = Q_2 c_{Bf} - (Q_1 + Q_2) c_B - k_1 c_A c_B V_R$$

Defining the following parameters

$$\alpha = \frac{Q_1}{Q_2} \qquad \theta = \frac{V_R}{Q_2} \qquad \rho = \frac{Q_r}{Q_2}$$

allows us to write these as

$$0 = \alpha c_{Af} - (1 + \alpha) c_A - (k_1 c_A c_B + k_2 c_A^n) \theta$$

$$0 = c_{Bf} - (1 + \alpha) c_B - k_1 c_A c_B \theta$$

Single-reactor model

We can solve numerically the two equations for the two unknowns c_A, c_B.

The concentration of C in the outflow is determined from the change in the concentration of B,

$$(Q_1 + Q_2)c_C = Q_2 c_{Bf} - (Q_1 + Q_2)c_B$$

Using this relationship and the defined parameters gives for conversion and yield,

$$x_A = \frac{\alpha c_{Af} - (1+\alpha)c_A}{\alpha c_{Af}} \qquad y_C = \frac{c_{Bf} - (1+\alpha)c_B}{\alpha c_{Af} - (1+\alpha)c_A}$$

Solution — two-reactor model

For the two-reactor system, we write mass balances for each reactor. Let $c_{A1}, c_{A2}, c_{B1}, c_{B2}$ be the unknown A and B concentrations in the two-reactors, respectively.

The mass balances are

Reactor 1:

$$0 = Q_1 c_{Af} - (Q_1 + Q_r) c_{A1} + Q_r c_{A2} - (k_1 c_{A1} c_{B1} + k_2 c_{A1}^2) V_{R1}$$

$$0 = -(Q_1 + Q_r) c_{B1} + Q_r c_{B2} - k_1 c_{A1} c_{B1} V_{R1}$$

Reactor 2:

$$0 = (Q_1 + Q_r)c_{A1} - Q_r c_{A2} - (Q_1 + Q_2)c_{A2} - (k_1 c_{A2} c_{B2} + k_2 c_{A2}^2)V_{R2}$$

$$0 = Q_2 c_{Bf} + (Q_1 + Q_r)c_{B1} - Q_r c_{B2} - (Q_1 + Q_2)c_{B2} - (k_1 c_{A2} c_{B2})V_{R2}$$

We can summarize this case using the previously defined variables as four equations in four unknowns

$$0 = \alpha c_{Af} - (\alpha + \rho)c_{A1} + \rho c_{A2} - (k_1 c_{A1} c_{B1} + k_2 c_{A1}^2)\theta_1$$

$$0 = -(\alpha + \rho)c_{B1} + \rho c_{B2} - k_1 c_{A1} c_{B1}\theta_1$$

$$0 = (\alpha + \rho)c_{A1} - \rho c_{A2} - (1 + \alpha)c_{A2} - (k_1 c_{A2} c_{B2} + k_2 c_{A2}^2)\theta_2$$

$$0 = c_{Bf} + (\alpha + \rho)c_{B1} - \rho c_{B2} - (1 + \alpha)c_{B2} - (k_1 c_{A2} c_{B2}\theta_2$$

Conversion — OK

- The conversion is not adversely affected by the poor mixing. In fact, the conversion in the two-reactor system is higher than the single, well-mixed reactor.

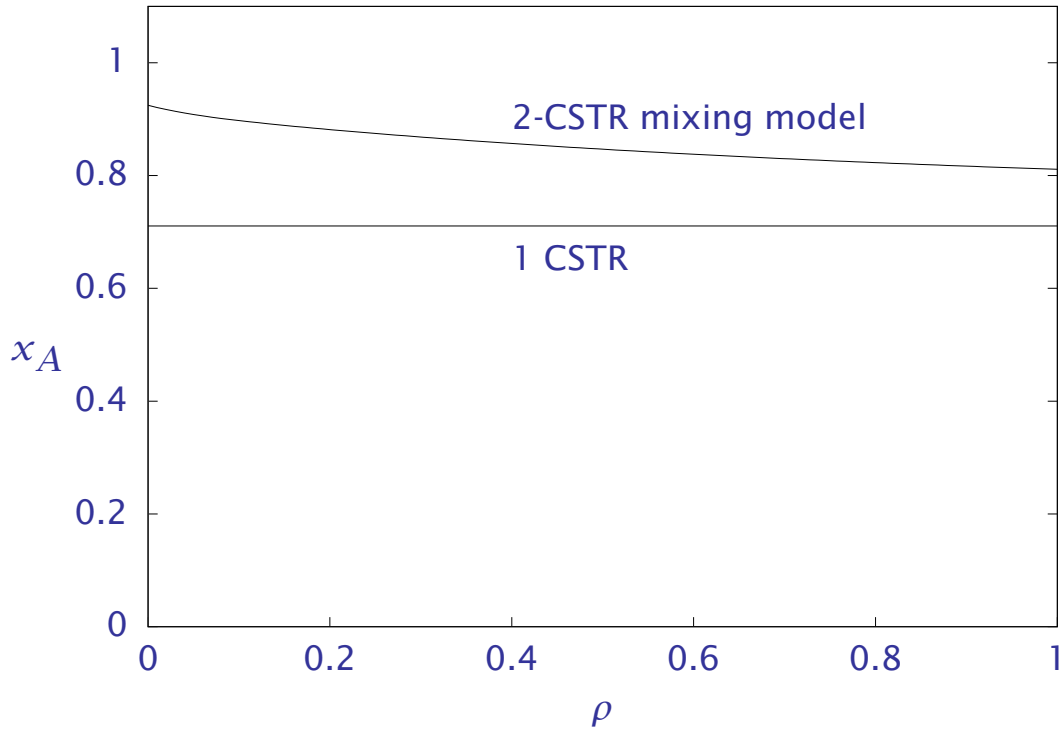


Figure 22: Conversion of reactant A for single, ideal CSTR, and as a function of internal flowrate, $\rho = Q_r/Q_2$, in a 2-CSTR mixing model.

Yield — Definitely not OK

- Notice, however, that at low values of Q_r, which corresponds to poor mixing at the feed location, the yield changes from *more than 90% to less than 15%*.
- Low yield is a qualitatively different problem than low conversion. If the conversion is low, we can design a separation system to remove the unreacted A and recycle it, or use it as feed in a second reactor.
- With low yield, however, the A has been irreversibly converted to an undesired product D. The raw material is lost and cannot be recovered.
- It is important to diagnose the low yield as a reactor mixing problem, and fix the problem at the reactor. A yield loss cannot be recovered by downstream processing.

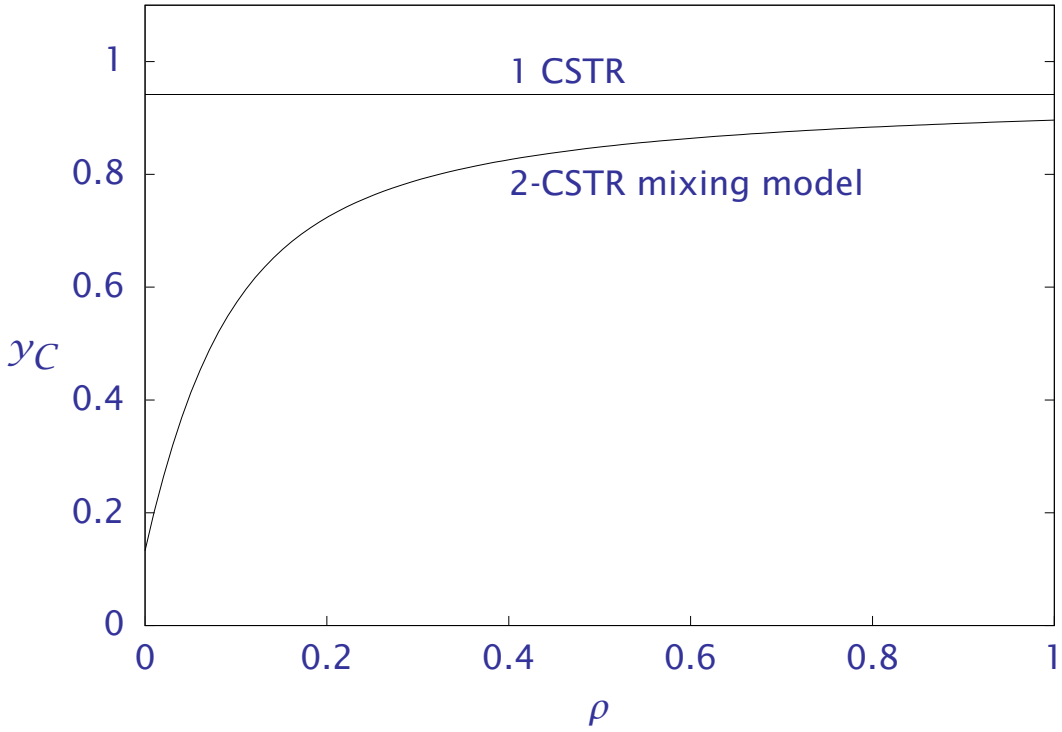


Figure 23: Yield of desired product C for single, ideal CSTR, and as a function of internal flowrate, $\rho = Q_r/Q_2$, in a 2-CSTR mixing model.

Solution — residence-time distribution

- Next we compute the outcome of injecting a unit step change in a tracer in the A feed stream.

- We solve the transient CSTR balances and calculate the tracer concentration at the outlet.

- Because the tracer does not take part in any reactions, this can be done analytically or numerically. The result is shown in Figure 24.

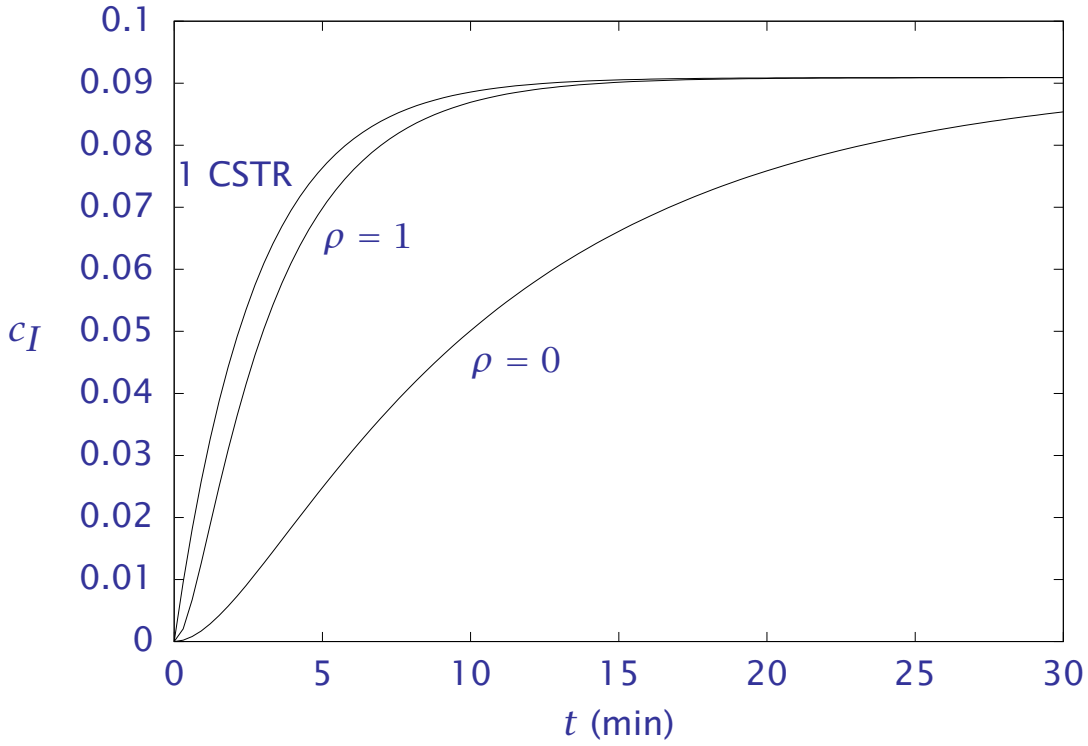


Figure 24: Step response for single, ideal CSTR, and 2-CSTR mixing model with $\rho = 0, 1$.

RTD diagnoses the problem well

- We see the familiar single-CSTR step response.
- For the two-reactor mixing model, when $\rho = 0$, which corresponds to the poorest mixing and lowest yield, the step test does reliably indicate the poor mixing.

  At the end of this chapter and also in Chapter 9 we show how to use this step response to determine the best value of ρ to model the mixing.
- When ρ is reasonably large, $Q_r = Q_2$, and the single CSTR and two-reactor cases have similar yields and step responses.
- Notice in all three step responses, the tracer concentration reaches only $c_{Is} = 0.091 = \alpha/(1+\alpha)$ because we inject tracer in only one of the two feed streams.

Example summary

- This example is one of the classic sets of reactions in which mixing has a significant impact on the reactor performance and the product yield.

- It deserves careful study because it builds intuition and leads us to ask good questions when confronted with more complex cases.

- For example, Villa et al. [17] discuss similar issues that arise in more complex polymerization reaction engineering problems.

Example 8.4: Maximizing yield in dispersed plug flow

Consider the following two liquid-phase reactions in which B is the desired product

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}, \qquad r_1 = k_1 c_A \tag{59}$$

$$2\mathrm{B} \xrightarrow{k_2} \mathrm{C}, \qquad r_2 = k_2 c_B^2 \tag{60}$$

The second reaction can represent the first step in a polymerization process of species B, which is undesirable in this case.

Because the second reaction is second order in B, it is desirable to keep the *average* B concentration in the reactor low, to avoid yield losses, but achieve high B concentration near the reactor exit to maximize the production rate. Intuitively the CSTR is a bad choice, because it maintains the same B concentration everywhere in the reactor. A PFR should offer higher yield. The B concentration

is low near the tube entrance, and increases to its maximum value at the tube exit if we choose the right length or residence time. If we make the tube too long, however, the B is largely converted to C and the yield is again low. In this case, yield is adversely affected by mixing.

Calculate the steady-state conversion of A and yield of B versus PFR length for the kinetic and reactor parameters in Table 4. What is an appropriate reactor length to maximize yield of B? Study the effect of dispersion. Approximately how large can the dispersion number be before the advantages of the PFR over the CSTR are lost?

Parameter	Value	Units
k_1	1	min^{-1}
k_2	1	L/mol·min
c_{Af}	1	mol/L
c_{Bf}	0	
v	1	m/min
l	0.5	m
D_l	varies	m^2/min

Table 4: Parameters for the dispersed PFR example.

Solution

The steady-state mass balances for components A and B are

$$v\frac{dc_A}{dz} - D_l\frac{d^2c_A}{dz^2} = R_A \tag{61}$$

$$v\frac{dc_B}{dz} - D_l\frac{d^2c_B}{dz^2} = R_B \tag{62}$$

in which

$$R_A = -k_1c_A, \qquad R_B = k_1c_A - 2k_2c_B^2$$

and we have assumed the dispersion numbers of both species are the same, $D_{Al} = D_{Bl} = D_l$. Because the fluid is a liquid, we assume the velocity is constant.

We use Danckwerts boundary conditions for both species

$$vc_{jf} = vc_j(0) - D_l \frac{dc_A}{dz}(0), \qquad z = 0 \tag{63}$$

$$\frac{dc_j}{dz} = 0, \qquad z = l \tag{64}$$

$j = (A, B)$. Given the concentrations, and because the flowrate is constant, the conversion and yield are

$$x_A = \frac{c_{Af} - c_A}{c_{Af}} \qquad y_B = \frac{c_B}{c_{Af} - c_A}$$

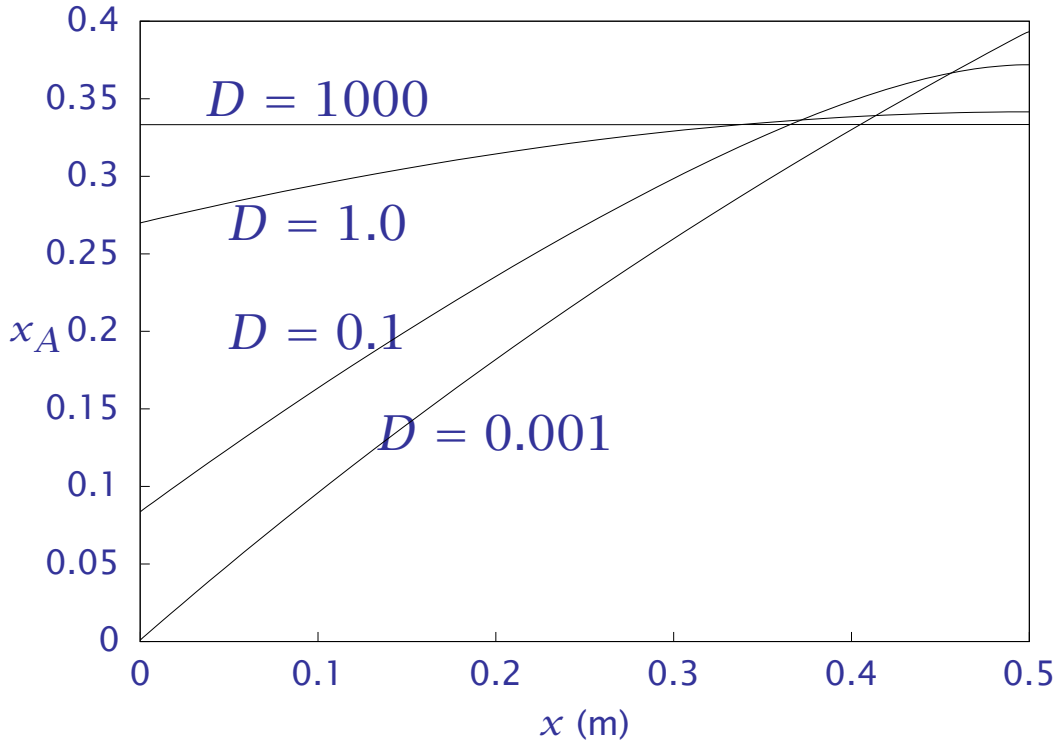


Figure 25: Conversion of reactant A versus reactor length for different dispersion numbers.

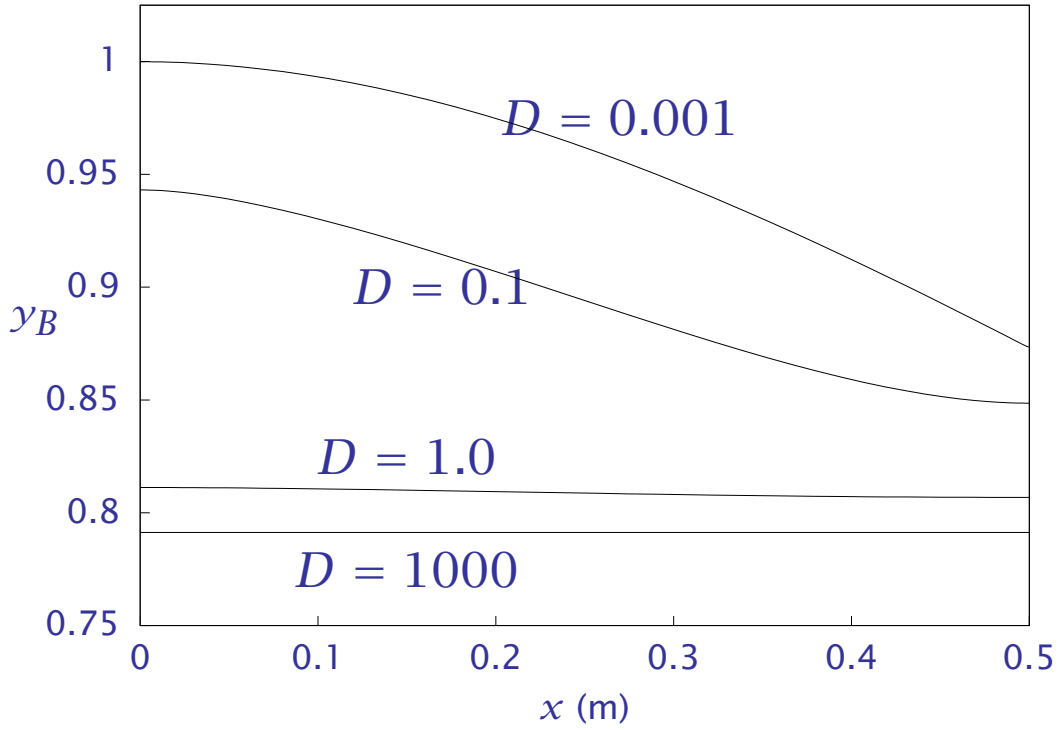


Figure 26: Yield of desired product B versus reactor length for different dispersion numbers.

Figures 25 and 26 show the conversion of A and yield of B versus tube length for a tube designed to maximize the yield of B. A tube length of about 0.5 m

is appropriate. As the length increases above this value, the conversion of A increases, but the yield of B drops rapidly, defeating the main purpose of using a PFR. For the kinetic parameters chosen, the CSTR yield can be improved by about 8% with a PFR. As shown in Figure 25, the high-dispersion PFR is essentially a CSTR, and achieves $y_B = 0.79$. The PFR with $D = 0.001$ achieves $y_B = 0.87$. We see that the dispersion number must be kept less than about 0.1 to maintain this advantage in yield. □

Summary

- In this chapter we generalized the two flow assumptions of the idealized reactor models: the perfect mixing assumption of the batch reactor and CSTR, and the plug-flow assumption of the PFR.

- We defined the residence-time distribution (RTD) of a reactor, and showed how to measure the RTD with simple tracer experiments such as the step test, pulse test and (idealized) impulse test.

- The RTD gives a rough measure of the flow pattern in the reactor, but it does not determine completely the reactor performance. Indeed, reactors with different flow patterns, and therefore different performances, may have identical RTDs.

RTD for ideal reactors

- We showed the CSTR has an exponential RTD. The derivation of the RTD of the CSTR also illustrated the following general principle: given an event with constant probability of occurrence, the time until the next occurrence of the event is distributed as a decreasing exponential function. This principle was used, for example, to choose the time of the next reaction in the stochastic simulations of Chapter 4.

- The residence-time distribution of the PFR was shown to be arbitrarily sharp because all molecules spend identical times in the PFR. We introduced the delta function to describe this arbitrarily narrow RTD.

- We added a dispersion term to the PFR equations to model the spread of the RTD observed in actual tubular reactors. Introducing the dispersion term's

second derivative necessitates new boundary conditions different from the PFR's. These are called Danckwerts boundary conditions.

- We computed the full, transient behavior of the dispersed plug-flow model, and displayed the evolution of the concentration profile after a step change in the feed concentration.

Reactor mixing limits

- We then examined the limits of reactor mixing consistent with a given RTD. The two limits are segregated flow and maximum mixedness.

- We showed how a physical process such as mass transfer between a continuous phase and a particle phase can approach segregated flow for large particles (small mass-transfer rates) and can approach maximum mixedness for small particles (high mass-transfer rates).

- We also showed that the mixing limits bound the possible reactor behavior for the case of a single, convex reaction-rate expression.

- For more general reaction networks, however, the mixing limits do not bound the reactor performance. For the general reaction network, recent research

on the attainable region has started to shed light on the possible reactor performance.

Some examples

- Next we discussed two contrasting cases in which mixing plays a critical role. In the mixing of two liquid reactants, we showed that formation of a poorly mixed zone can lead to significant yield losses.

- By contrast, for the kinetics of the second example, good mixing leads to yield losses; in this example the reactor should be designed to approach segregated flow.

- Finally, the recent progress in the area of computational fluid dynamics (CFD) gives us reason to believe that direct solution of the equations of motion for the fluid will be a tractable approach for designing reactors and evaluating their performance [1].

- It seems reasonable to expect the classical RTD methods and simple flow models to complement the computationally intensive CFD methods. CFD methods may be used to validate simpler mixing models. These validated, simple mixing models may continue to play important roles in reactor analysis, design and optimization.

Notation

c_e	effluent concentration in RTD measurement
c_f	feed concentration
c_j	concentration of species j
c_m	concentration in a maximally mixed flow model
c_s	concentration in a segregated flow model
c_∞	concentration boundary condition in maximum mixedness model
D	dimensionless dispersion number, $D = D_l \tau / l^2$
D_A	molecular diffusivity
D_{jl}	dispersion coefficient for species j
D_l	dispersion coefficient
$\mathrm{erf}(x)$	error function, Equation 30
$H(x)$	Heaviside or unit step function, Equation 17
k_{mj}	mass-transfer coefficient

l	tubular reactor length
n	number of CSTRs in a mixing model
$p(\theta)$	probability that a molecule spends time θ to $\theta + d\theta$ in reactor, RTD
$P(\theta)$	probability that a molecule spends time zero to θ in the reactor, integrated form of the RTD
Pe	Péclet number, Pe $= vl/D_A$
Q	volumetric flowrate
Q_f	feed volumetric flowrate
r	particle radius in mixing model
r	reaction rate of (single) reaction
R_j	production rate of species j
v	fluid axial velocity
V_R	reactor volume
x_j	molar conversion of component j
y_j	yield of species j
z	reactor length variable
$\gamma(n,x)$	incomplete gamma function of order n and argument x

$\Gamma(n)$	gamma function of n
$\delta(x)$	delta or impulse function, Equations 7 and 18
θ	residence time of tracer molecule in reactor
$\overline{\theta}$	mean residence time, $\overline{\theta} = \int_0^\theta \theta' p(\theta') d\theta'$
λ	time-to-go before molecule exits reactor
τ	V_R / Q_f

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