

We can determine the number of tanks in series by calculating the dimensionless variance  $\sigma_{\Theta}^2$  from a tracer experiment.

$$\begin{aligned} \sigma_{\Theta}^2 &= \frac{\sigma^2}{\tau^2} = \int_0^{\infty} (\Theta - 1)^2 E(\Theta) d\Theta \\ &= \int_0^{\infty} \Theta^2 E(\Theta) d\Theta - 2 \int_0^{\infty} \Theta E(\Theta) d\Theta + \int_0^{\infty} E(\Theta) d\Theta \end{aligned} \quad (14-9)$$

$$\begin{aligned} \sigma_{\Theta}^2 &= \int_0^{\infty} \Theta^2 E(\Theta) d\Theta - 1 \\ &= \int_0^{\infty} \Theta^2 \frac{n(n\Theta)^{n-1}}{(n-1)!} e^{-n\Theta} d\Theta - 1 \end{aligned} \quad (14-10)$$

$$\begin{aligned} \sigma_{\Theta}^2 &= \frac{n^n}{(n-1)!} \int_0^{\infty} \Theta^{n+1} e^{-n\Theta} d\Theta - 1 \\ &= \frac{n^n}{(n-1)!} \left[ \frac{(n+1)!}{n^{n+2}} \right] - 1 \end{aligned}$$

$$\sigma_{\Theta}^2 = \frac{1}{n} \quad (14-11)$$

As the number of tanks increases the variance decreases

The number of tanks in series is

$$n = \frac{1}{\sigma_{\Theta}^2} = \frac{\tau^2}{\sigma^2} \quad (14-12)$$

This expression represents the number of tanks necessary to model the real reactor as  $n$  ideal tanks in series.

If the reaction is first-order, we can use Equation 4-11 to calculate the conversion,

$$X = 1 - \frac{1}{(1 + \tau_i k)^n} \quad (4-11)$$

where

$$\tau_i = \frac{V}{v_0 n}$$

It is acceptable (and usual) for the value of  $n$  calculated from Equation (14-12) to be a non-integer in Equation (4-11) to calculate the conversion. For reactions other than first-order, sequential mole balances on each reactor must be carried out.

### 14.2.2 The Dispersion Model

The dispersion model is also used to describe non-ideal tubular reactors. In this model, there is an axial dispersion of the material, which is

governed by an analogy to Fick's law of diffusion, superimposed on the flow. So, in addition to the bulk flow,  $UA_c$ , every component in the mixture is transported through any cross-section of the reactor at a rate equal to  $[-D_a A_c (dC/dz)]$  resulting from molecular and turbulent diffusion. At first sight, this simple model appears to have the possibility of accounting only for axial mixing effects. It can be shown however that this approach can compensate not only for problems caused by axial mixing, but also for those caused by radial mixing and other nonflat velocity profiles.<sup>3</sup> These fluctuations in concentration can result from different flow velocities and pathways and from molecular and turbulent diffusion.

To illustrate how dispersion affects concentration in a tubular reactor we consider the injection of a perfect tracer pulse. Figure 14-4 shows how dispersion causes the pulse to broaden as it moves down the reactor and becomes less concentrated.

The molar flow rate of tracer ( $F_T$ ) by both convection and dispersion is

$$F_T = -D_a A_c \frac{\partial C_T}{\partial z} + UA_c C_T$$

In this expression  $D_a$  is the effective dispersion coefficient ( $m^2/s$ ) and  $U$  is the superficial velocity. Correlations for the dispersion coefficients in both liquid and gas systems may be found in Levenspiel.<sup>4</sup>

A mole balance on the inert tracer  $T$  gives

$$-\frac{\partial F_T}{\partial z} = A_c \frac{\partial C_T}{\partial t}$$

Substituting for  $F_T$  and dividing by the cross-sectional area  $A_c$  we have

$$D_a \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial(U C_T)}{\partial z} = \frac{\partial C_T}{\partial t} \quad (14-13)$$

The dispersion model is a one-parameter model

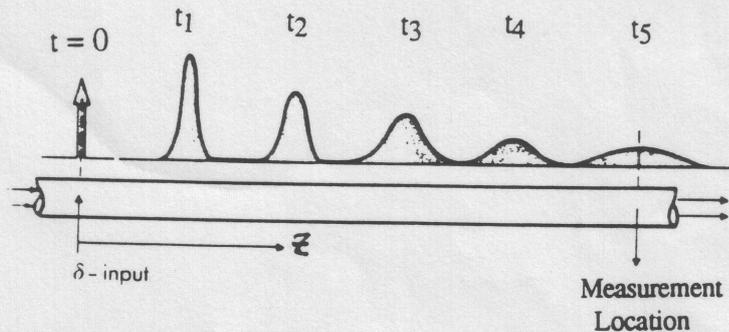


Figure 14-4 Dispersion in a tubular reactor [From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed., (1972). Reprinted by permission of John Wiley & Sons, Inc.]

<sup>3</sup> R. Aris, *Proc. R. Soc. (London)* A235, 67 (1956).

<sup>4</sup> O. Levenspiel, *Chemical Reaction Engineering* (New York: Wiley, 1962), pp. 290-293.

Before proceeding to solve this equation, we will first put the equation in dimensionless form to arrive at the dimensionless group(s) that characterize the process. Let

$$\Psi = \frac{C_T}{C_{T0}}, \quad \lambda = \frac{z}{L}, \quad \text{and} \quad \theta = \frac{tU}{L}$$

For a pulse input  $C_{T0}$  is defined as the mass of tracer injected,  $M$ , divided by the vessel volume,  $V$ .

Then

$$\frac{D_a}{UL} \frac{\partial^2 \Psi}{\partial \lambda^2} - \frac{\partial \Psi}{\partial \lambda} = \frac{\partial \Psi}{\partial \theta} \tag{14-14}$$

The quantity  $UL/D_e$  is a form of the Peclet number,  $Pe$ . The Peclet number can be regarded as the ratio of

$$\text{Peclet number} \quad Pe = \frac{\text{rate of transport by convection}}{\text{rate of transport by diffusion or dispersion}} = \frac{U\ell}{D_a}$$

in which  $\ell$  is the characteristic length term. There are two different types of Peclet numbers in common use. We can call  $Pe_r$  the reactor Peclet number; it uses the reactor length,  $L$ , for the characteristic length, so  $Pe_r \equiv UL/D_a$ . It is  $Pe_r$  that appears in Equation (14-14). The other type of Peclet number can be called the fluid Peclet number,  $Pe_f$ ; it uses the characteristic length that determines the fluid's mechanical behavior. In a packed bed this length is the particle diameter  $d_p$ , and  $Pe_f \equiv Ud_p/\epsilon D_a$ . (The term  $U$  is the empty tube or superficial velocity. For packed beds we often wish to use the average interstitial velocity and thus  $U/\epsilon$  is commonly used for the packed-bed velocity term.) In an empty tube the fluid behavior is determined by the tube diameter  $d_t$ , and  $Pe_f = Ud_t/D_a$ . The fluid Peclet number,  $Pe_f$ , is given in all correlations relating Peclet number to Reynolds number because both are directly related to the fluid mechanical behavior. It is, of course, very simple to convert  $Pe_f$  to  $Pe_r$ : multiply by the ratio  $L/d_p$  or  $L/d_t$ . The reciprocal of  $Pe_r$ ,  $[D_a/UL]$ , sometimes is called the vessel dispersion number. Writing Equation (14-14) in terms of the Peclet number yields

$$\frac{1}{Pe_r} \frac{\partial^2 \Psi}{\partial \lambda^2} - \frac{\partial \Psi}{\partial \lambda} = \frac{\partial \Psi}{\partial \theta} \tag{14-15}$$

**Boundary Conditions** There are two cases that we need to consider: boundary conditions for closed vessels and open vessels. In the case of closed-closed vessels we assume there is no dispersion or radial variation in concentration either upstream (closed) or downstream (closed) of the reaction section, hence this is a closed-closed vessel. In an open vessel, dispersion occurs both upstream (open) and downstream (open) of the reaction section;

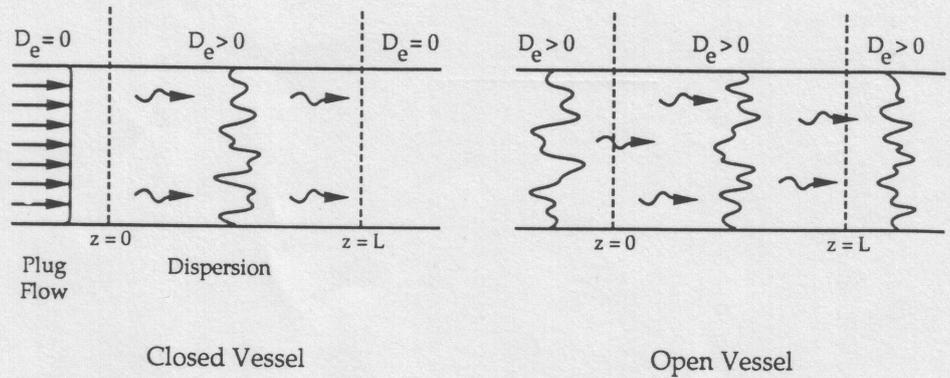


Figure 14-5

hence this is an open-open vessel. These two cases are shown in Figure 14-5 where fluctuations in concentration due to dispersion are superimposed on the plug flow velocity profile. A closed-open vessel boundary condition is one in which there is no dispersion in the entrance section but there is dispersion in the reaction and exit sections.

**Closed-Closed Vessel Boundary Condition** For a closed-closed vessel, we have plug flow (no dispersion) to the immediate left of the entrance line ( $z = 0^-$ ) (closed) and to the immediate right of  $z = L$  ( $z = L^+$ ) (closed). However between  $z = 0^+$  and  $z = L^-$  we have dispersion and reaction. The corresponding boundary condition is

$$F_T(0^-, t) = F_T(0^+, t)$$

Substituting for  $F_T$  yields

$$UA_c C_T(0^-, t) = -A_c D_a \left. \frac{\partial C_T}{\partial z} \right|_{z=0^+} + UA_c C_T(0^+, t)$$

Solving for the entering concentration  $C_T(0^-, t) = C_{T0}$

$$C_{T0} = \frac{-D_a}{U} \left. \frac{\partial C_T}{\partial z} \right|_{z=0^+} + C_T(0^+, t) \quad (14-16)$$

At the exit to the reaction section the concentration is continuous and there is no gradient in tracer concentration, i.e.,

Danckwerts  
boundary  
conditions

At  $z = L$ :

$$\begin{aligned} C_T(L^-) &= C_T(L^+) \\ \frac{\partial C_T}{\partial z} &= 0 \end{aligned} \quad (14-17)$$

These two boundary conditions, Eqns (14-16) and (14-17), were first stated by P. V. Danckwerts<sup>5</sup> and have become known as the famous Danck-

<sup>5</sup> P. V. Danckwerts, *Chem. Eng. Sci.*, 2, 1 (1953).

werts boundary conditions. Bischoff<sup>6</sup> has given a rigorous derivation of them, solving the differential equations governing the dispersion of component A in the entrance and exit sections and taking the limit as  $D_a$  in entrance and exit sections approaches zero. From the solutions he obtained boundary conditions on the reaction section identical with those Danckwerts proposed. The initial condition is

$$\text{At } t = 0, \quad z > 0, \quad C_T(0^+, 0) = 0 \quad (14-18)$$

The mass of tracer injected,  $M$  is

$$M = UA_c \int_0^\infty C_T(0^-, t) dt$$

In dimensionless form the Dankwerts boundary conditions are

$$\text{At } \lambda = 0: \quad -\frac{1}{\text{Pe}_r} \frac{\partial \Psi}{\partial \lambda} + \Psi = \frac{C_T(0^-, t)}{C_{T0}} = 1$$

$$\text{At } \lambda = 1: \quad \frac{\partial \Psi}{\partial \lambda} = 0 \quad (14-19)$$

Equation (14-15) has been solved numerically for a pulse injection and the resulting dimensionless effluent tracer concentration,  $\Psi$ , is shown as a function of the dimensionless time  $\theta$  in Figure 14-6 for various Peclet numbers. While analytical solutions for  $\Psi$  cannot be determined for this case, the following relations for the mean residence time and variance have been found.<sup>7</sup>

$$t_m = \tau \quad (14-20)$$

and

$$\frac{\sigma^2}{t_m^2} = \frac{1}{\tau^2} \int_0^\infty (t - \tau)^2 E(t) dt$$

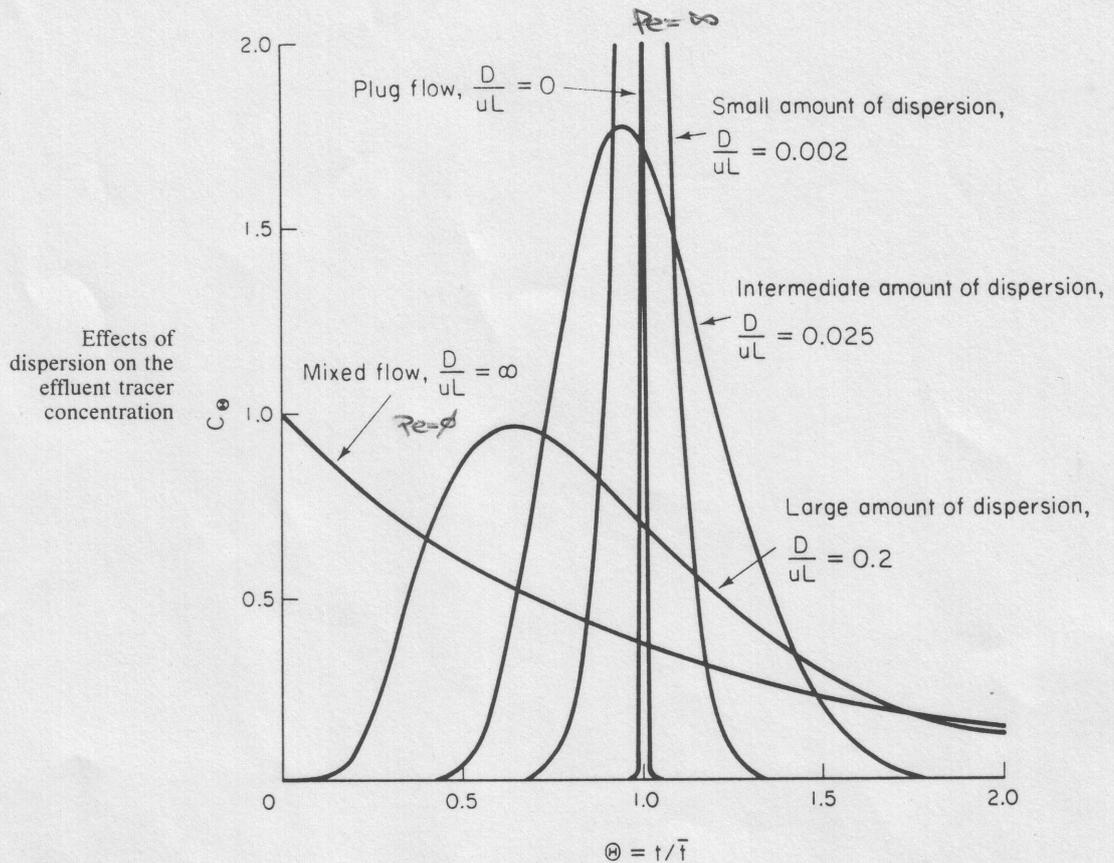
$$\frac{\sigma^2}{t_m^2} = \frac{2}{\text{Pe}_r} - \frac{2}{\text{Pe}_r^2} (1 - e^{-\text{Pe}_r}) \quad (14-21)$$

Correlations for the Peclet number as a function of the Reynolds and Schmidt numbers can be found in Levenspiel.<sup>8</sup>  $\text{Pe}_r$  can be found experimentally by determining  $t_m$  and  $\sigma^2$  from the RTD data and then solving Equation (14-21) for  $\text{Pe}_r$ .

<sup>6</sup> K. B. Bischoff, *Chem. Eng. Sci.*, 16, 131 (1961).

<sup>7</sup> See Bischoff, K. and O. Levenspiel, *Adv. Chem. Eng.* 4, p. 95, (New York: Academic Press (1963)).

<sup>8</sup> O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. (New York: Wiley 1972), pp. 282-284.



**Figure 14-6**  $C$  curves in closed vessels for various extents of back-mixing as predicted by the dispersion model. [From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed., (1972). Reprinted by permission of John Wiley & Sons, Inc.]

**Open-Open Vessel Boundary Conditions** When a tracer is injected into a packed bed at a location more than two or three particle diameters downstream from the entrance and measured some distance upstream from the exit, the open-open vessel boundary conditions apply. For an open-open system an analytical solution to Equation (14-15) can be obtained for a pulse tracer input.

For an open-open system the boundary conditions at the entrance are

$$F_T(0^-, t) = F_T(0^+, t)$$

then for the case when the dispersion coefficient is the same in the entrance and reaction sections

$$\left. \begin{aligned} -D_a \frac{\partial C_T}{\partial z} \Big|_{z=0^-} + UC_T(0^-, t) &= -D_a \frac{\partial C_T}{\partial z} \Big|_{z=0^+} + UC_T(0^+, t) \\ C_T(0^-, t) &= C_T(0^+, t) \end{aligned} \right\} (14-22)$$

At the exit  $C_T(L^-, t) = C_T(L^+, t)$  (14-23)

Open at the exit  $-D_a \left. \frac{\partial C_T}{\partial z} \right|_{z=L^-} + UC_T(L^-, t) = -D_a \left. \frac{\partial C_T}{\partial z} \right|_{z=L^+} + UC_T(L^+, t)$

There are a number of perturbations of these boundary conditions that can be applied. The dispersion coefficient can take on different values in each of the three regions: ( $z < 0$ ;  $0 \leq z \leq L$ , and  $z > 0$ ) and the tracer can also be injected at some point  $z_1$  rather than at the boundary,  $z = 0$ . These cases and others can be found in the supplementary reading given at the end of the chapter. We shall consider the case when there is no variation in the dispersion coefficient for all  $z$  and an impulse of tracer is injected at  $z = 0$  at  $t = 0$ .

Using the above boundary conditions we can solve Equation (14-15) to determine the effluent tracer concentration, i.e.,

$$\Psi(1, \theta) = \frac{C_T(L, t)}{C_{T0}} = \frac{1}{2\sqrt{\pi\theta^3/Pe_r}} \exp \left[ \frac{-(1 - \theta)^2}{4\theta/Pe_r} \right] \quad (14-24)$$

The corresponding mean residence time is

$$t_m = \left( 1 + \frac{2}{Pe_r} \right) \tau \quad (14-25)$$

where  $\tau$  is based on the volume between  $z = 0$  and  $z = L$  (i.e., reactor volume measured with a yardstick). We note that the mean residence time for an open system is greater than that for a closed system. The variance for an open system is

$$\frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2} \quad (14-26)$$

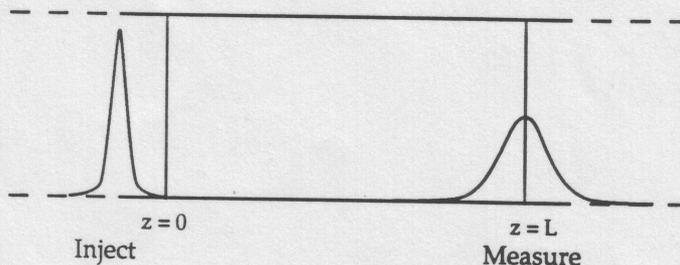
We now consider two cases for which we can use equations (14-25) and (14-26) to determine the system parameters:

*Case 1.* The space-time  $\tau$  is *known*. That is  $V$  and  $v_0$  are measured independently. Here we can determine the Peclet number by determining  $t_m$  and  $\sigma^2$  from the concentration-time data and then using Equation (14-26) to calculate  $Pe_r$ . We can also calculate  $t_m$  and then use Equation (14-25) as a check but, this is usually less accurate.

*Case 2.* The space-time  $\tau$  is *unknown*. This situation arises when there are dead or stagnant pockets that exist in the reactor along with the dispersion effects. To analyze this situation we first calculate  $t_m$  and  $\sigma^2$  from the data as in Case 1. Next we solve

Equation (14-26) for  $Pe_r$ . Finally we solve Equation (14-25) for  $\tau$  and hence  $V$ . The dead volume is the difference between the measured volume (i.e., with a yardstick) and the volume calculated from the RTD.

**Sloppy Tracer Inputs** It is not always possible to cleanly inject a tracer pulse as an input to a system owing to the fact that it takes a finite time to inject the tracer.



When the injection does not approach a perfect pulse input, the differences in the variances between the input and output tracer measurements are used to calculate the Peclet number; i.e.,

$$\Delta\sigma^2 = \sigma_{in}^2 - \sigma_{out}^2$$

where  $\sigma_{in}^2$  is the variance of the tracer measured at some point upstream (near the entrance) and  $\sigma_{out}^2$  is the variance measured at some point downstream (near the exit).

For an open-open system, it has been shown<sup>9</sup> that the Peclet number can be calculated from the equation

$$\frac{\Delta\sigma^2}{t_m^2} = \frac{2}{Pe_r} \quad (14-27)$$

**Flow, Reaction, and Dispersion** Having discussed how to determine the dispersion coefficient we now return to the case where we have both dispersion and reaction in a tubular reactor. A mole balance is taken on a particular component of the mixture (say species A) over a short length  $\Delta z$  of a tubular reactor in an identical manner to that in Chapter 1 to arrive at

$$-\frac{1}{A_c} \frac{dF_A}{dz} + r_A = 0 \quad (14-28)$$

Combining Equation (14-28) and the equation for the molar flux  $F_A$  leads to

$$\frac{D_a}{U} \frac{d^2C_A}{dz^2} - \frac{dC_A}{dz} + \frac{r_A}{U} = 0 \quad (14-29)$$

This equation is a second-order, ordinary differential equation. It is nonlinear when  $r_A$  is other than zero- or first-order.

<sup>9</sup> Aris, R. *Chem. Eng. Sci.*, 9, 266 (1959).

When the reaction rate  $r_A$  is first-order, the equation is linear, i.e.,

$$\frac{D_a}{U} \frac{d^2 C_A}{dz^2} - \frac{dC_A}{dz} + \frac{kC_A}{U} = 0 \tag{14-30}$$

Flow, reaction, and dispersion

and amenable to analytical solution. However before obtaining a solution, we put our Equation (14-30) describing dispersion and reaction in dimensionless form by letting  $\psi = C_A/C_{A0}$  and  $\lambda = z/L$

$$\frac{1}{Pe_r} \frac{d^2 \Psi}{d\lambda^2} - \frac{d\Psi}{d\lambda} - Da\Psi = 0 \tag{14-31}$$

The quantity  $kL/U$  appearing in Equation (14-31) is called the *Damköhler number* for convection,  $Da$ , and physically represents the ratio

$$Da = \frac{\text{rate of consumption of A by reaction}}{\text{rate of transport of A by convection}} = \frac{kC_{A0}^{n-1}L}{U} = kC_{A0}^{n-1}\tau \tag{14-32}$$

[For a first-order reaction, such as we have in Equation (14-30),  $Da = kL/U$ .] We shall consider the case of a closed-closed system, in which case we use the Danckwerts boundary conditions

$$-\frac{1}{Pe_r} \frac{d\Psi}{d\lambda} + \Psi = 1 \quad \text{at } \lambda = 0 \tag{14-33}$$

and

$$\frac{d\Psi}{d\lambda} = 0 \quad \text{at } \lambda = 1 \tag{14-34}$$

At the end of the reactor, where  $\lambda = 1$ , the solution is

Conversion for a first-order reaction in a tubular or packed-bed reactor with dispersion

$$\begin{aligned} \psi_L &= \frac{C_{AL}}{C_{A0}} = 1 - X \\ &= \frac{4q \exp(Pe_r/2)}{(1+q)^2 \exp(Pe_r q/2) - (1-q)^2 \exp(-Pe_r q/2)} \end{aligned} \tag{14-35}$$

$$\text{where } q = \sqrt{1 + 4Da/Pe_r}$$

This solution was first obtained by Danckwerts<sup>10</sup> and has been published many places (e.g., Levenspiel<sup>11</sup>). Outside the limited case of a first-order reaction, a numerical solution of the equation is required, and because this is a split-boundary-value problem, an iterative technique is required. With a slight rearrangement of Equation (14-35) we obtain the conversion as a function of  $Da$  and  $Pe_r$ .

$$X = 1 - \frac{4q \exp(Pe_r/2)}{(1+q)^2 \exp(Pe_r q/2) - (1-q)^2 \exp(-Pe_r q/2)} \tag{14-36}$$

**Example 14-1 Conversion Using Dispersion and Tanks-in-Series Models**

The first-order reaction



<sup>10</sup> P. V. Danckwerts, *Chem. Eng. Sci.*, 2, 1 (1953).

<sup>11</sup> O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed., (New York: Wiley 1972).