CL223 CHEMICAL REACTION ENGINEERING-I

MODULE

V

Non-ideal flow (figures)

Lecture Notes:
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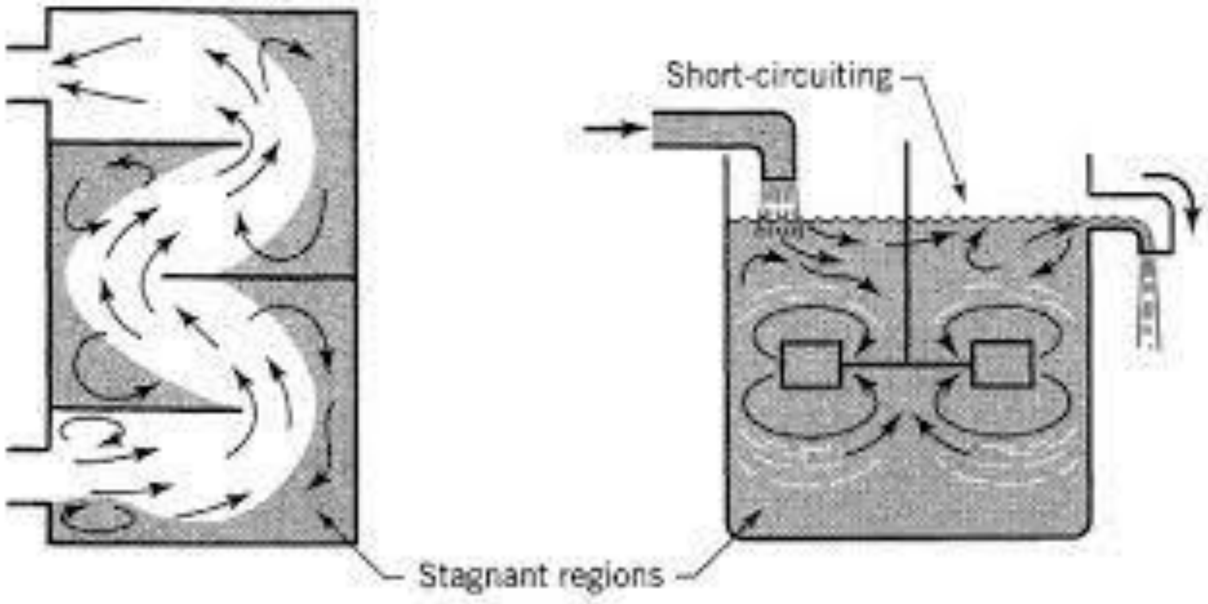
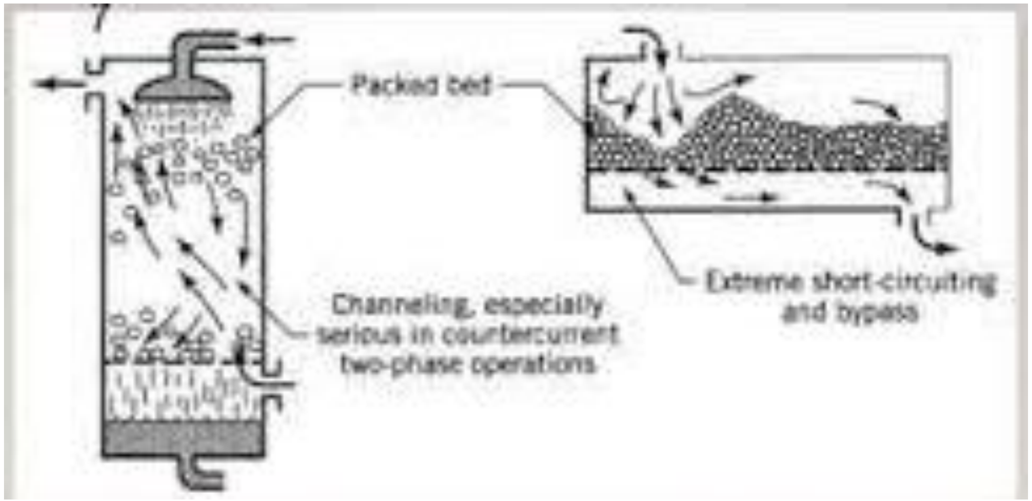
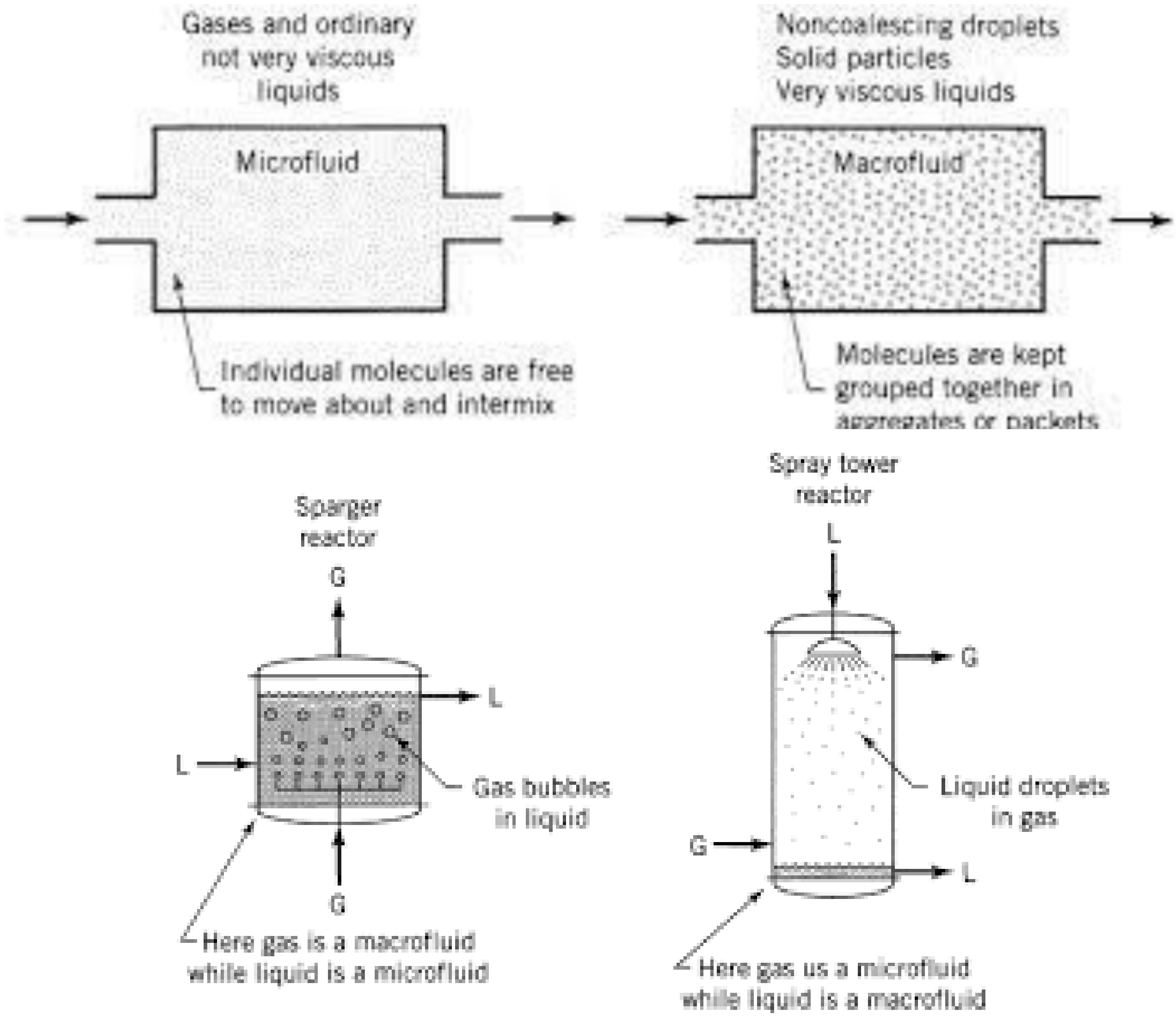
Residence time distribution





State of aggregation of the flowing stream



Early and late mixing

Mixing

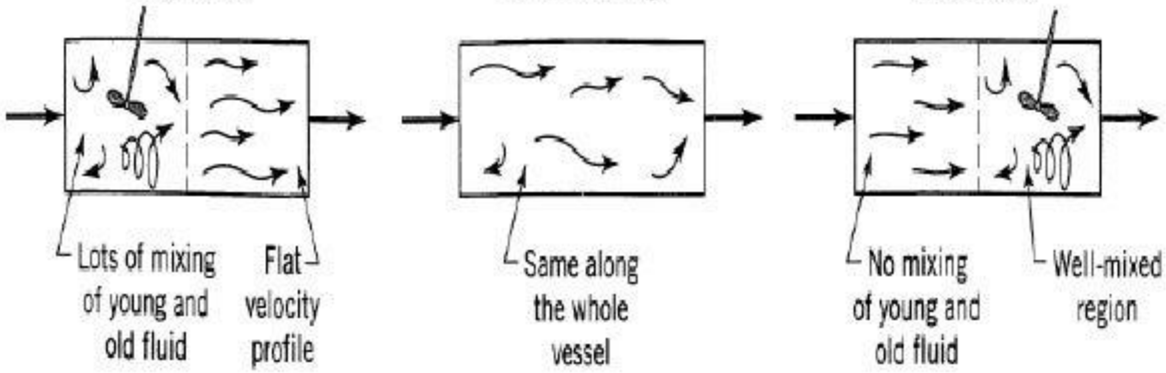
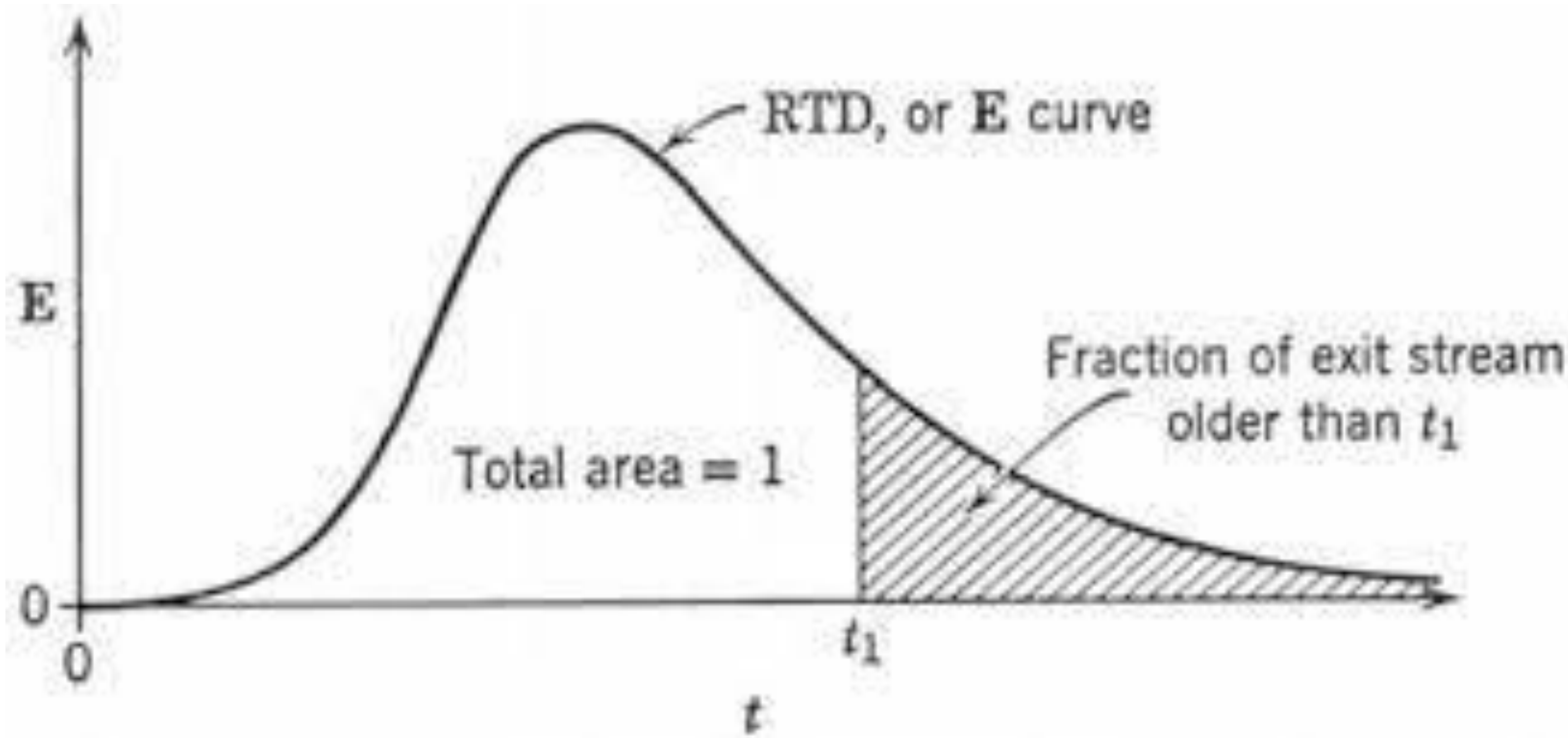


Figure 11.4 Examples of early and of late mixing of fluid.

Ref:
Chemical Reaction Engineering by Levenspiel
Chapter 11.

E Curve


RTD, or E curve
E
Fraction of exit stream
older than t_1
Total area = 1
0
0
t_1
t

Different type of tracer input

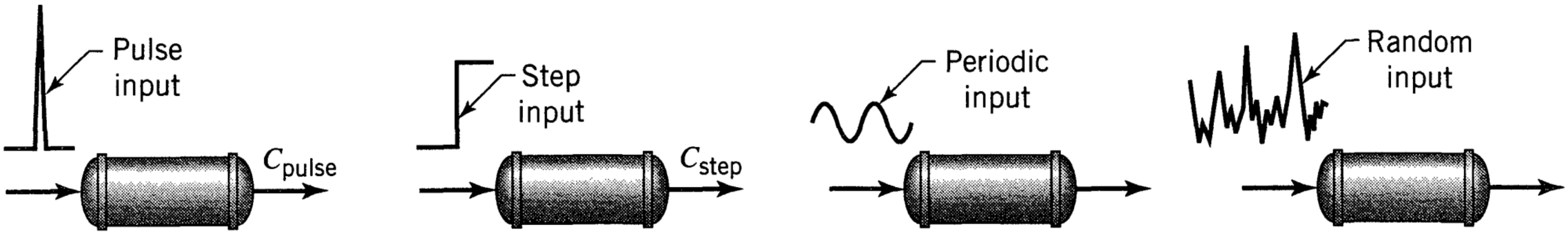


Figure 11.7 Various ways of studying the flow pattern in vessels.

Pulse experiment

$$\begin{pmatrix}\text{Area under the} \\ C_{\text{pulse}} \text{ curve}\end{pmatrix}: \quad A = \int_0^\infty C\,dt \cong \sum_i C_i \Delta t_i = \frac{M}{v} \qquad \left[\frac{\text{kg}\cdot\text{s}}{\text{m}^3}\right]$$

$$\begin{pmatrix}\text{Mean of the} \\ C_{\text{pulse}} \text{ curve}\end{pmatrix}: \quad \bar{t} = \frac{\int_0^\infty tC\,dt}{\int_0^\infty C\,dt} \cong \frac{\sum_i t_i C_i \Delta t_i}{\sum_i C_i \Delta t_i} = \frac{V}{v} \qquad [\text{s}]$$

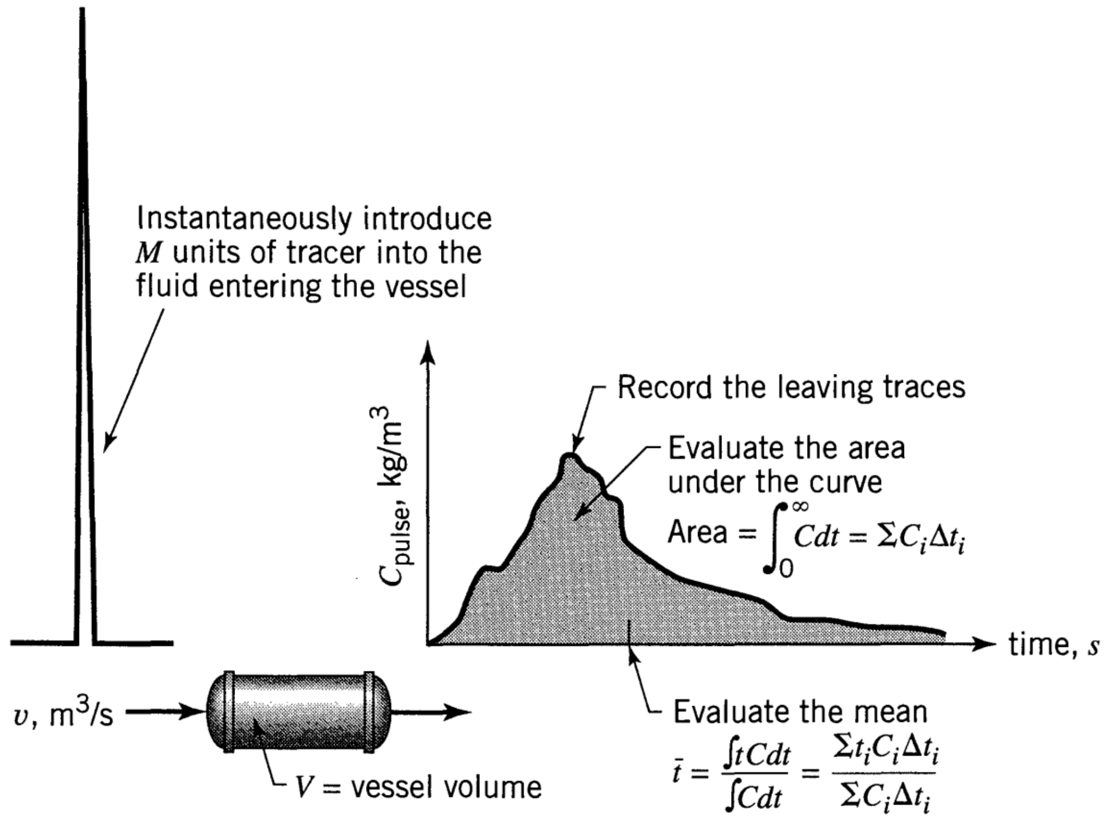


Figure 11.8 The useful information obtainable from the pulse trace experiment.

Step experiment

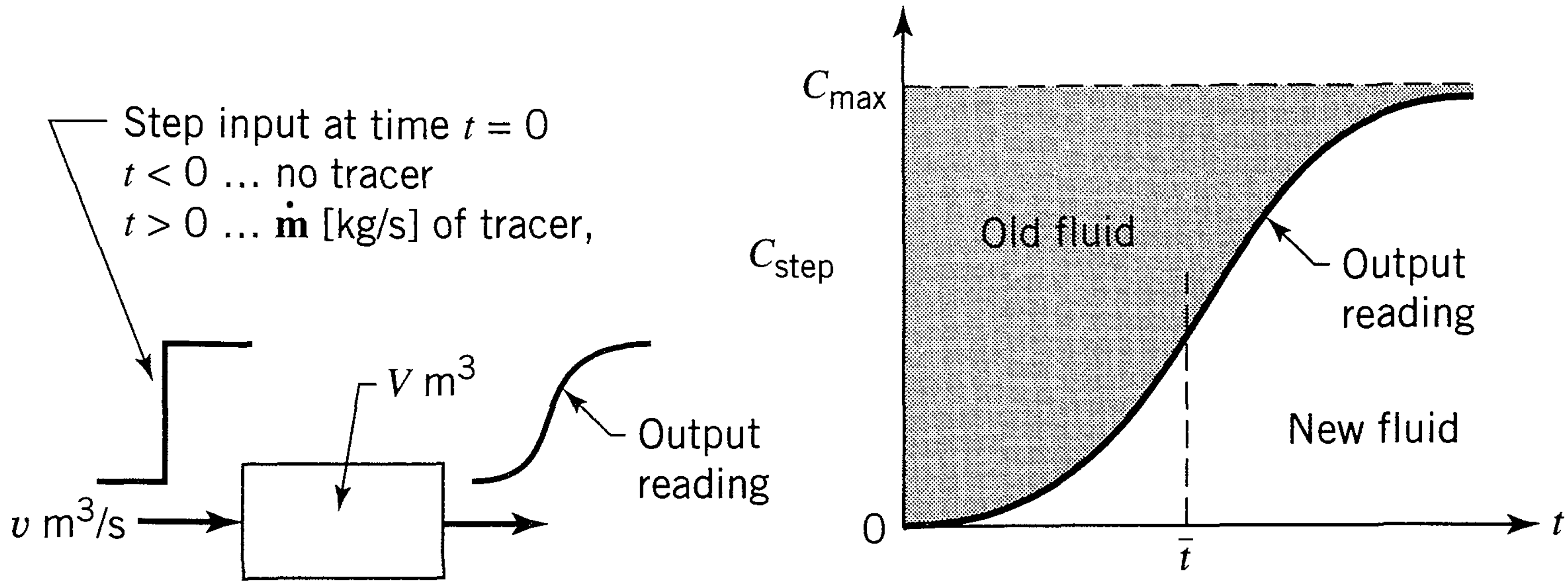


Figure 11.11 Information obtainable from a step tracer experiment.

F Curve

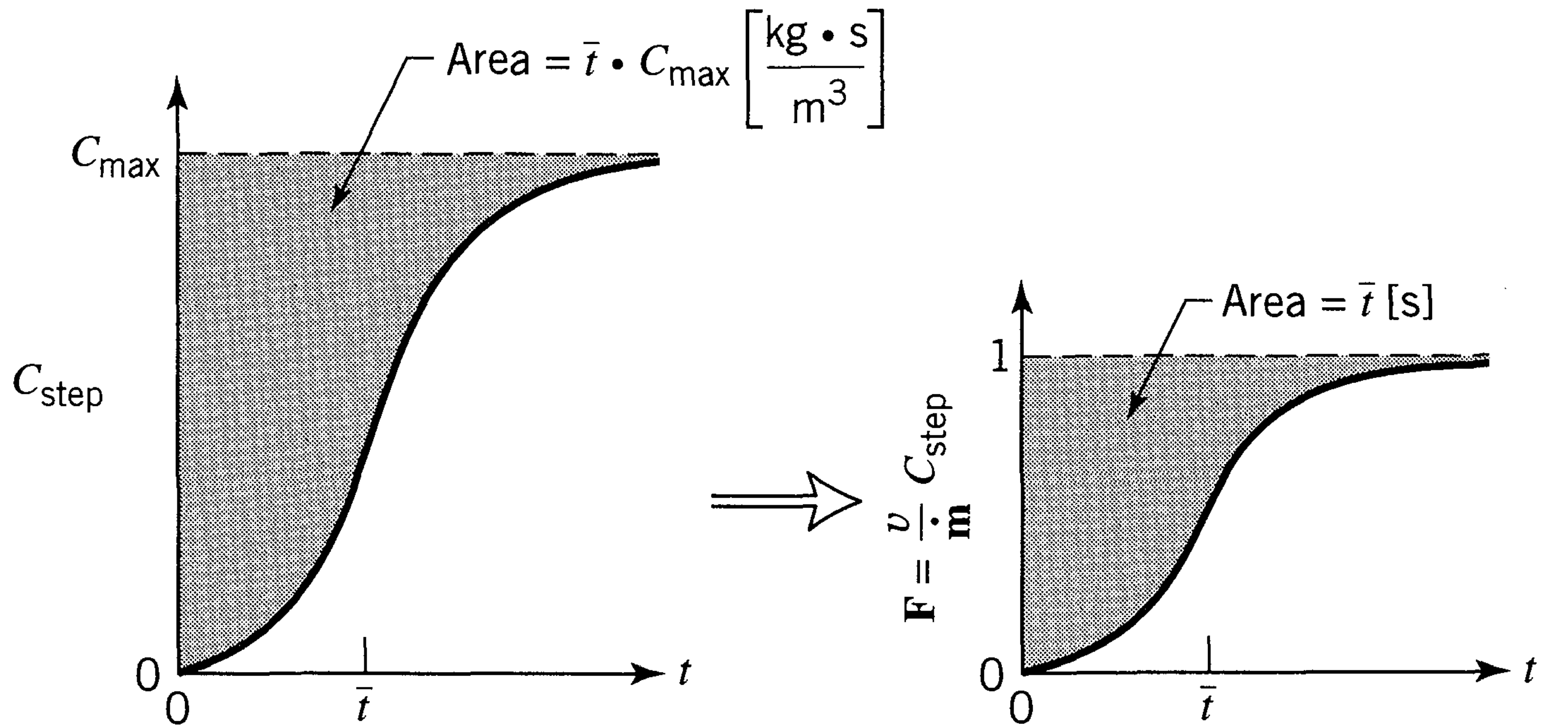


Figure 11.12 Transforming an experimental C_{step} curve to an **F** curve.

E vs F curve

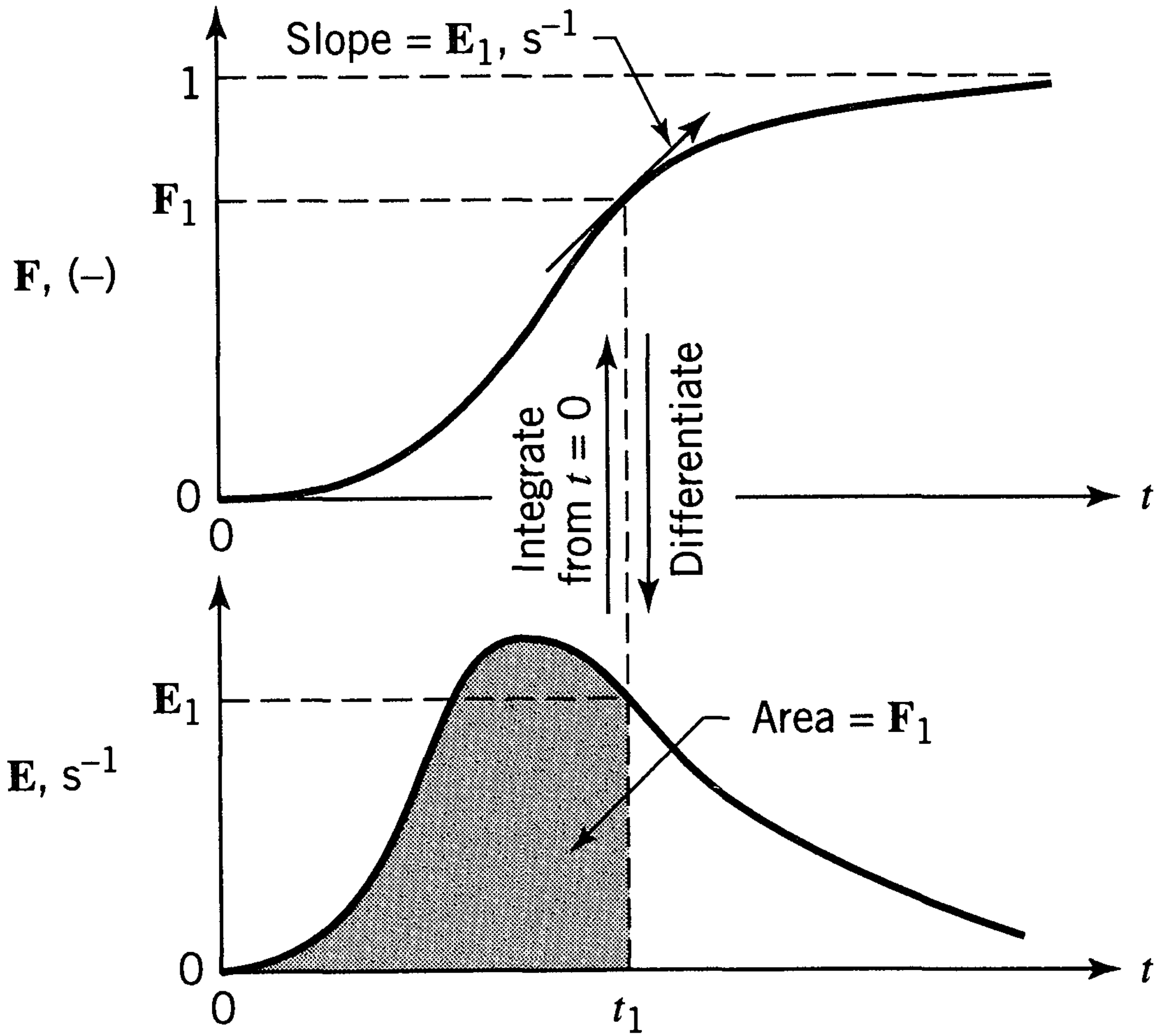


Figure 11.13 Relationship between the **E** and **F** curves.

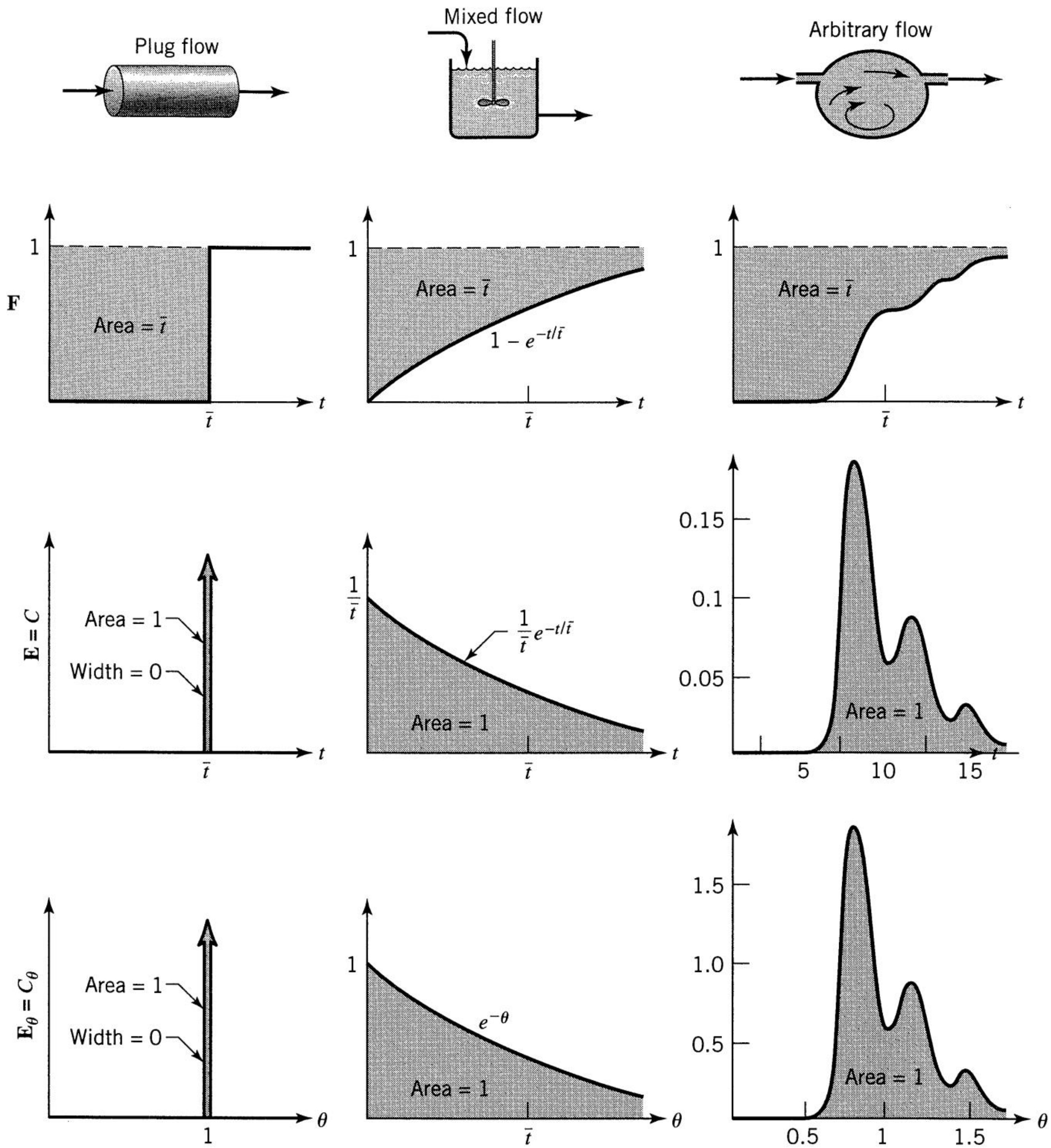


Figure 11.14 Properties of the **E** and **F** curves for various flows. Curves are drawn in terms of ordinary and dimensionless time units. Relationship between curves is given by Eqs. 7 and 8.

The concentration readings in Table E11.1 represent a continuous response to a pulse input into a closed vessel which is to be used as a chemical reactor. Calculate the mean residence time of fluid in the vessel $\bar{t}$, and tabulate and plot the exit age distribution **E**.

Table E11.1

Time t, min	Tracer Output Concentration, C_{pulse} gm/liter fluid
0	0
5	3
10	5
15	5
20	4
25	2
30	1
35	0

A large tank (860 liters) is used as a gas-liquid contactor. Gas bubbles up through the vessel and out the top, liquid flows in at one part and out the other at *5* liters/s. To get an idea of the flow pattern of liquid in this tank a pulse of tracer (M = 150 gm) is injected at the liquid inlet and measured at the outlet, as shown in Fig. E11.2a.

(a) Is this a properly done experiment?

(b) If so, find the liquid fraction in the vessel.

(c) Determine the E curve for the liquid.

(d) Qualitatively what do you think is happening in the vessel?

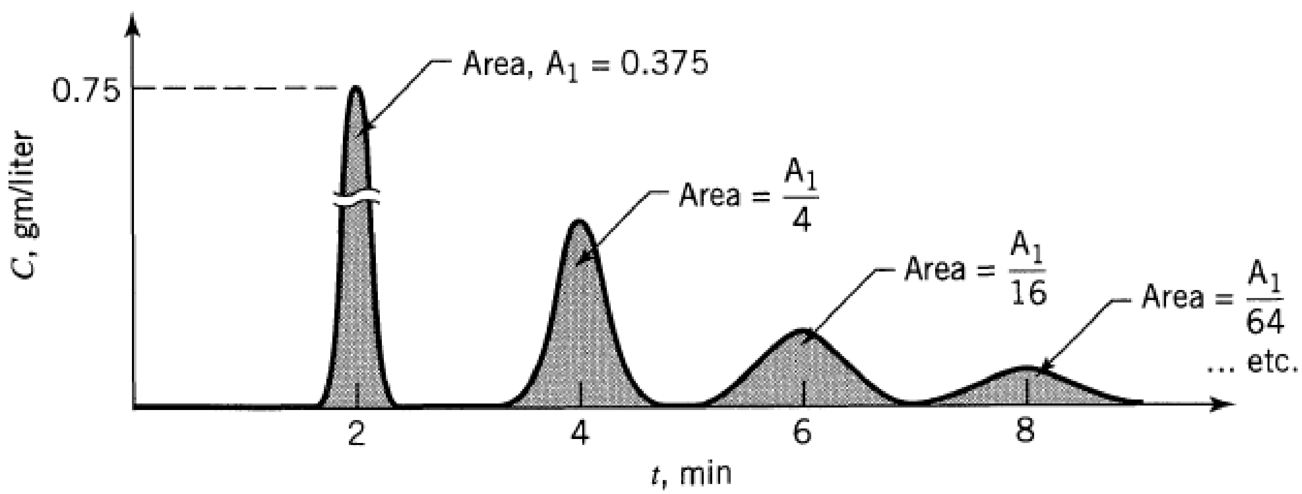


Figure E11.2*a*

The Convolution Integral

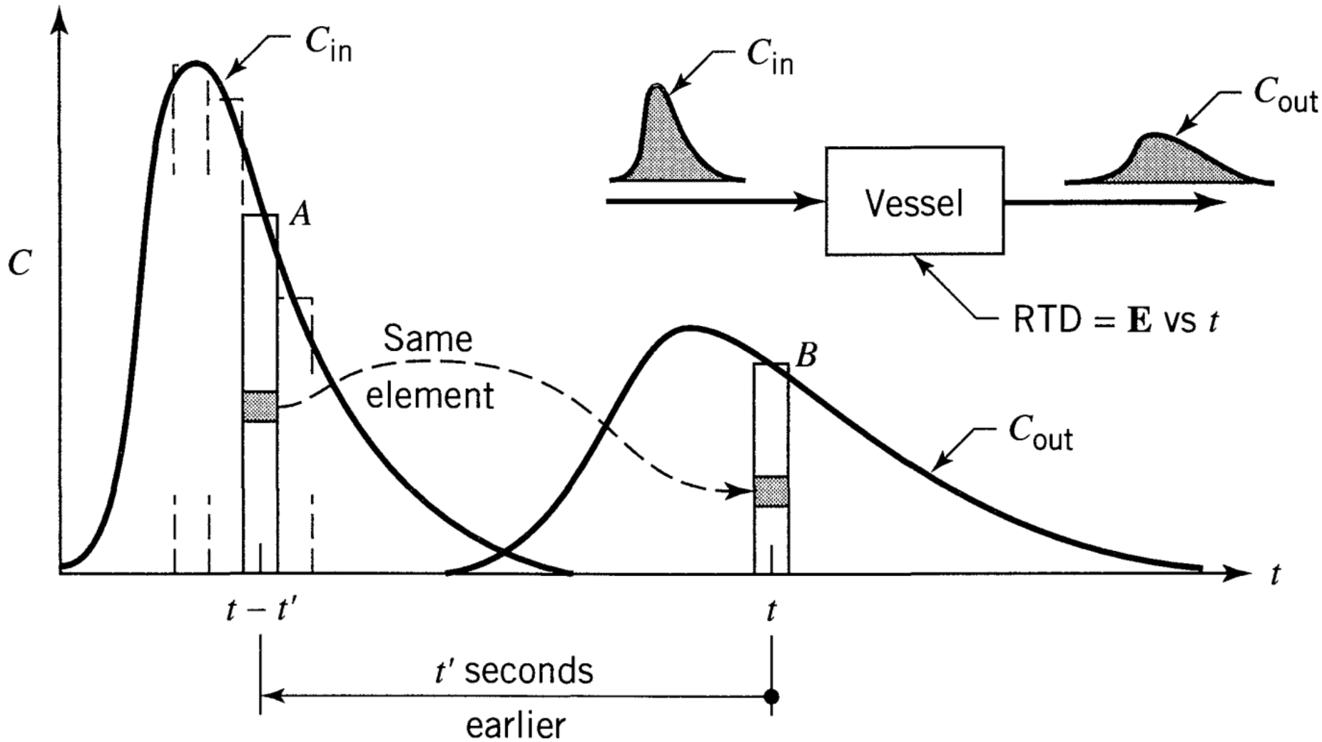


Figure 11.15 Sketch showing derivation of the convolution integral.

$$\begin{pmatrix}\text{tracer leaving}\\ \text{in rectangle } B\end{pmatrix} = \begin{pmatrix}\text{all the tracer entering } t' \text{ seconds earlier than } t,\\ \text{and staying for time } t' \text{ in the vessel}\end{pmatrix}$$

$$\begin{pmatrix}\text{tracer leaving}\\ \text{in rectangle } B\end{pmatrix} = \sum_{\substack{\text{all rectangles}\\ A \text{ which enter}\\ \text{earlier then}\\ \text{time } t}} \begin{pmatrix}\text{tracer in}\\ \text{rectangle}\\ A\end{pmatrix}\begin{pmatrix}\text{fraction of tracer in } A\\ \text{which stays for about}\\ t' \text{ seconds in the vessel}\end{pmatrix}$$

The Convolution Integral

$$C_{out}(t) = \int_0^t C_{in}(t - t')\mathbf{E}(t')dt'$$

$$C_{out}(t) = \int_0^t C_{in}(t')\mathbf{E}(t - t')dt'$$

$$C_{out} = \mathbf{E} * C_{in} \qquad \text{or} \qquad C_{out} = C_{in} * \mathbf{E}$$

Conversion in nonideal flow reactors

$$\begin{pmatrix}\text{mean concentration}\\ \text{of reactant}\\ \text{in exit stream}\end{pmatrix} = \sum_{\substack{\text{all elements}\\ \text{of exit stream}}} \begin{pmatrix}\text{concentration of}\\ \text{reactant remaining}\\ \text{in an element of}\\ \text{age between } t\\ \text{and } t+dt\end{pmatrix}\begin{pmatrix}\text{fraction of exit}\\ \text{stream which is}\\ \text{of age between } t\\ \text{and } t+dt\end{pmatrix}$$

In symbols this becomes

$$\left(\frac{\overline{C}_A}{C_{A0}}\right)_{\text{at exit}} = \int_0^\infty \left(\frac{C_A}{C_{A0}}\right)_{\substack{\text{for an element or little}\\ \text{batch of fluid of age } t}} \cdot \mathbf{E}\, dt$$

or in terms of conversions

$$\overline{X}_A = \int_0^\infty (X_A)_{\text{element}} \cdot \mathbf{E}\, dt \qquad \textbf{(13)}$$

or in a form suitable for numerical integration

$$\frac{\overline{C}_A}{C_{A0}} = \sum_{\substack{\text{all age}\\ \text{intervals}}} \left(\frac{C_A}{C_{A0}}\right)_{\text{element}} \cdot \mathbf{E}\, \Delta t$$

From Chapter 3 on batch reactors we have

- for first-order reactions $$\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = e^{-kt}$$
- for second-order reactions $$\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = \frac{1}{1 + kC_{A0}t}$$
- for an nth-order reaction $$\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = [1 + (n-1)C_{A0}^{n-1}kt]^{1/1-n}$$

Dispersion model (small deviation from PFR)

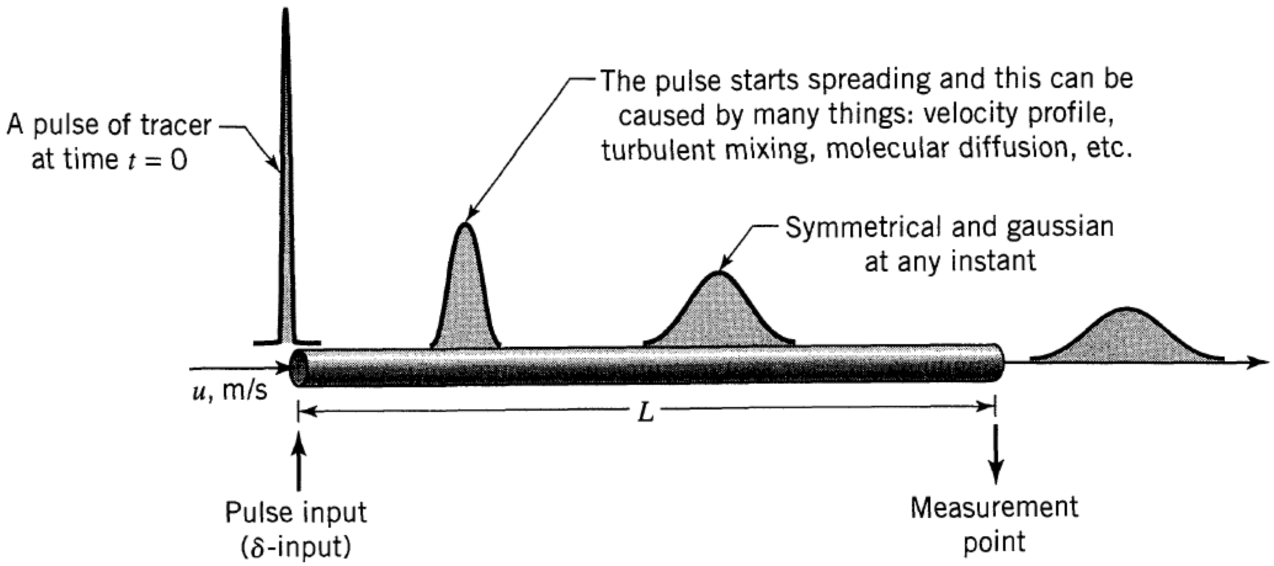


Figure 13.1 The spreading of tracer according to the dispersion model.

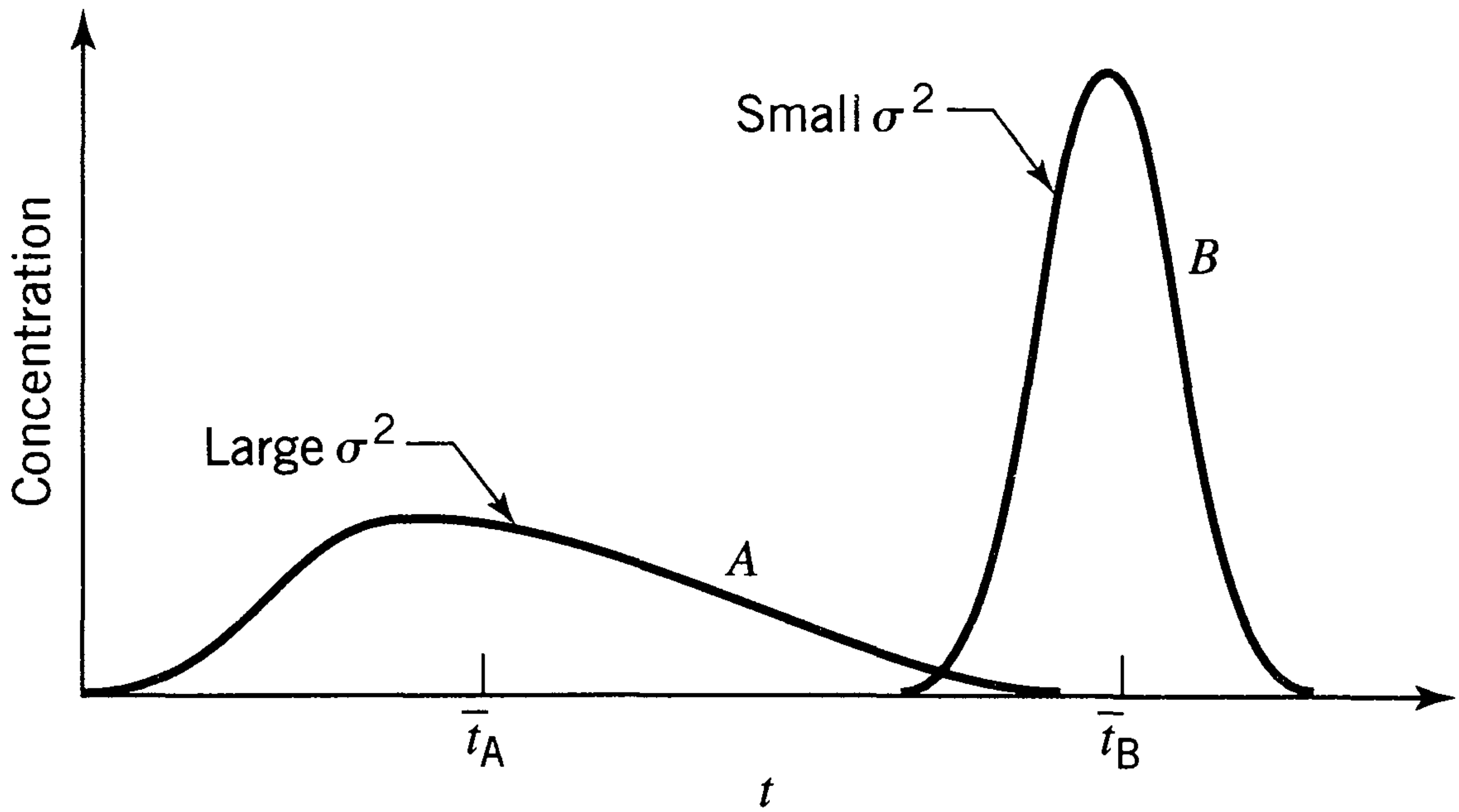
Diffusion-like process superimposed on plug flow. This is known as dispersion or longitudinal dispersion to distinguish it from molecular diffusion. The dispersion coefficient D (m2/s) represents this spreading process. Thus, large D means rapid spreading of the tracer curve, small D means slow spreading and D = 0 means no spreading, hence plug flow

$\bar{t}$ = mean time of passage, or when the curve passes by the exit

σ^2 = variance, or a measure of the spread of the curve

$$\bar{t} = \frac{\int_0^\infty t\, C\, dt}{\int_0^\infty C\, dt} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i}$$

$$\sigma^2 = \frac{\int_0^\infty (t-\bar{t})^2\, C\, dt}{\int_0^\infty C\, dt} = \frac{\int_0^\infty t^2 C\, dt}{\int_0^\infty C\, dt} - \bar{t}^2$$


Small σ^2
B
Concentration
Large σ^2
A
$\bar{t}_A$
$\bar{t}_B$
t

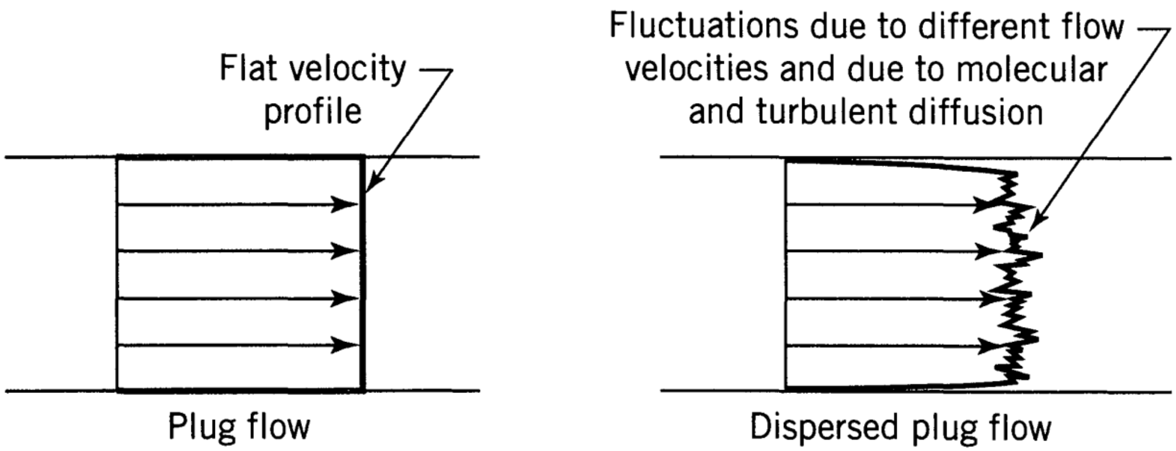


Figure 13.3 Representation of the dispersion (dispersed plug flow) model.

For molecular diffusion in the x-direction the governing differential equation is given by Fick's law:

$$\frac{\partial C}{\partial t} = \mathscr{D}\frac{\partial^2 C}{\partial x^2}$$

$$\frac{\partial C}{\partial t} = \mathbf{D}\frac{\partial^2 C}{\partial x^2}$$

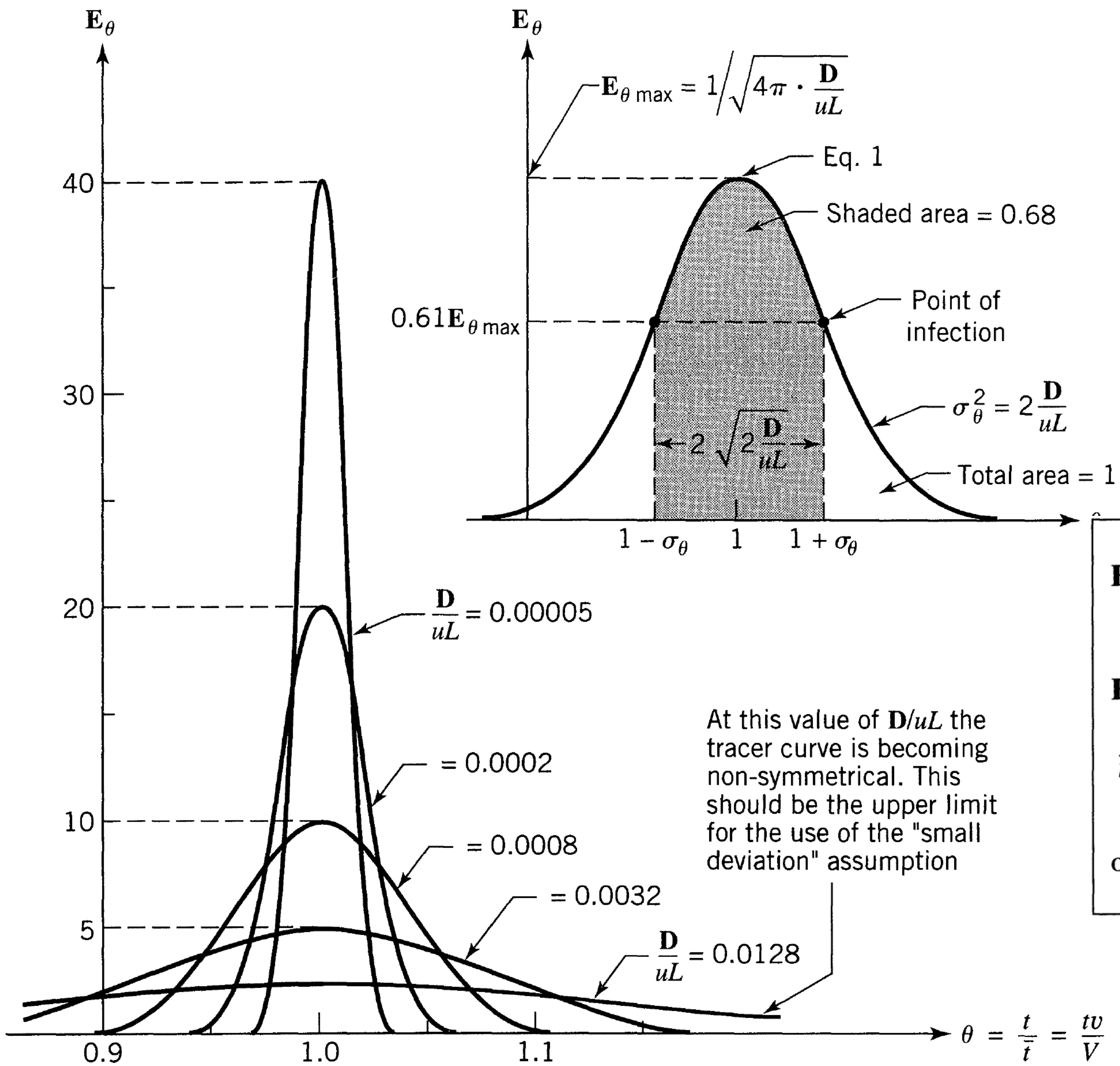
$$\frac{\partial C}{\partial \theta} = \left(\frac{\mathbf{D}}{uL}\right)\frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z}$$

In dimensionless form where $z = (ut + x)/L$ and $\theta = t/\bar{t} = tu/L$, the basic differential equation representing this dispersion model becomes

$\frac{\mathbf{D}}{uL} \rightarrow 0$ negligible dispersion, hence plug flow

$\frac{\mathbf{D}}{uL} \rightarrow \infty$ large dispersion, hence mixed flow

Dispersion model for small extents of Dispersion,(D/uL<0.01)



$$\mathbf{E}_\theta = \bar{t}\cdot\mathbf{E} = \frac{1}{\sqrt{4\pi(\mathbf{D}/uL)}}\exp\left[-\frac{(1-\theta)^2}{4(\mathbf{D}/uL)}\right]$$

$$\mathbf{E} = \sqrt{\frac{u^3}{4\pi\mathbf{D}L}}\exp\left[-\frac{(L-ut)^2}{4\mathbf{D}L/u}\right]$$

$$\bar{t}_\mathbf{E} = \frac{V}{v} = \frac{L}{u} \quad \text{or} \quad \bar{\theta}_\mathbf{E} = 1$$

mean of **E** curve

$$\sigma_\theta^2 = \frac{\sigma_t^2}{\bar{t}^2} = 2\left(\frac{\mathbf{D}}{uL}\right) \quad \text{or} \quad \sigma^2 = 2\left(\frac{\mathbf{D}L}{u^3}\right)$$

Figure 13.4 Relationship between $\mathbf{D}/uL$ and the dimensionless $\mathbf{E}_\theta$ curve for small extents of dispersion, Eq. 7.

Dispersion model for small extents of Dispersion,(D/uL<0.01)

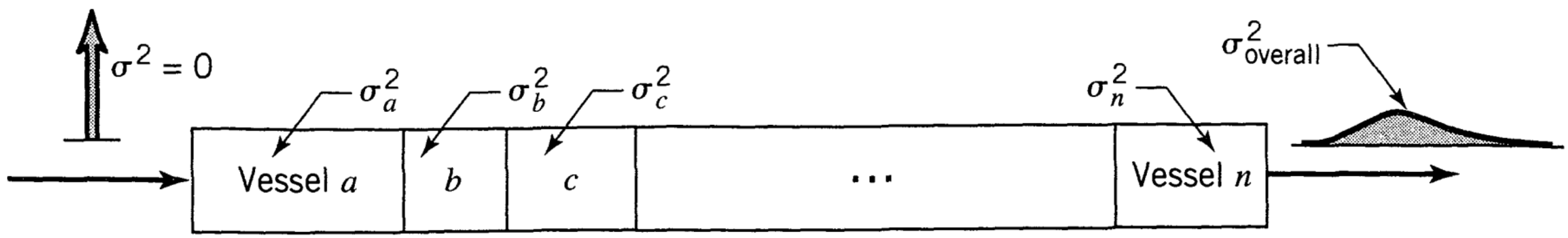


Figure 13.5 Illustration of additivity of means and of variances of the **E** curves of vessels $a, b, \ldots, n$.

For a *series of vessels* the $\bar{t}$ and σ^2 of the individual vessels are additive, thus, referring to Fig. 13.5 we have

$$\bar{t}_{\text{overall}} = \bar{t}_a + \bar{t}_b + \cdots = \frac{V_a}{v} + \frac{V_b}{v} + \cdots = \left(\frac{L}{u}\right)_a + \left(\frac{L}{u}\right)_b + \cdots \qquad \textbf{(9)}$$

and

$$\sigma^2_{\text{overall}} = \sigma^2_a + \sigma^2_b + \cdots = 2\left(\frac{\mathbf{D}L}{u^3}\right)_a + 2\left(\frac{\mathbf{D}L}{u^3}\right)_b + \cdots \qquad \textbf{(10)}$$

Dispersion model for small extents of Dispersion,(D/uL<0.01)

- The additivity of times is expected, but the additivity of variance is not generally expected. This is a useful property since it allows us to subtract for the distortion of the measured curve caused by input lines, long measuring leads, etc.
- This additivity property of variances also allows us to treat any one-shot tracer input, no matter what its shape, and to extract from it the variance of the E curve of the vessel.

$$\Delta\sigma^2 = \sigma^2_{out} - \sigma^2_{in} \quad \textbf{(11)}$$

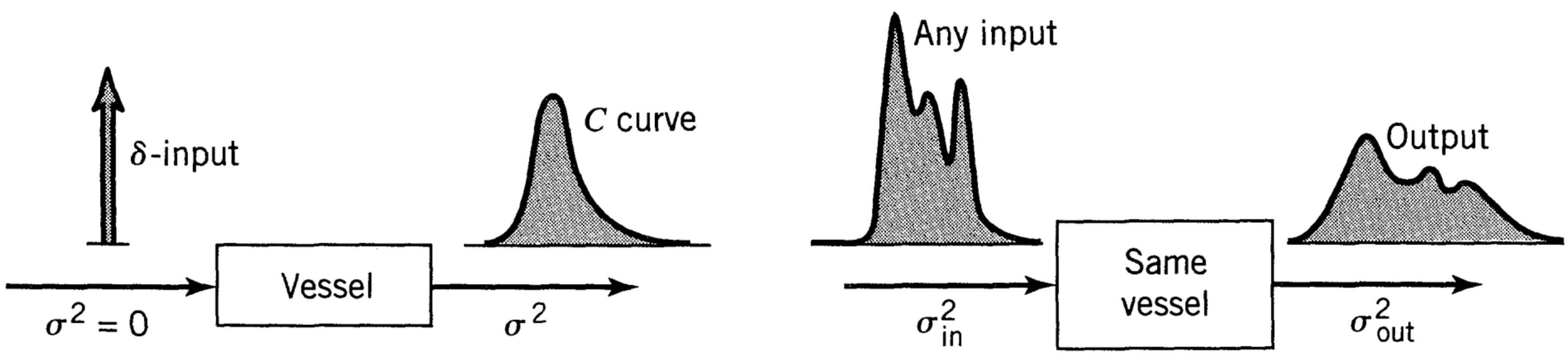


Figure 13.6 Increase in variance is the same in both cases, or $\sigma^2 = \sigma^2_{out} - \sigma^2_{in} = \Delta\sigma^2$.

Dispersion model for small extents of Dispersion,(D/uL<0.01)

Aris (1959) has shown, for small extents of dispersion, that

$$\frac{\sigma^2_{\text{out}} - \sigma^2_{\text{in}}}{(\bar{t}_{\text{out}} - \bar{t}_{\text{in}})^2} = \frac{\Delta\sigma^2}{(\Delta\bar{t})^2} = \Delta\sigma^2_\theta = 2\left(\frac{\mathbf{D}}{uL}\right)$$

Thus, no matter what the shape of the input curve, the *D/uL* value for the vessel can be found.

Dispersion model for large deviation from PFR flow,(D/uL>0.01)

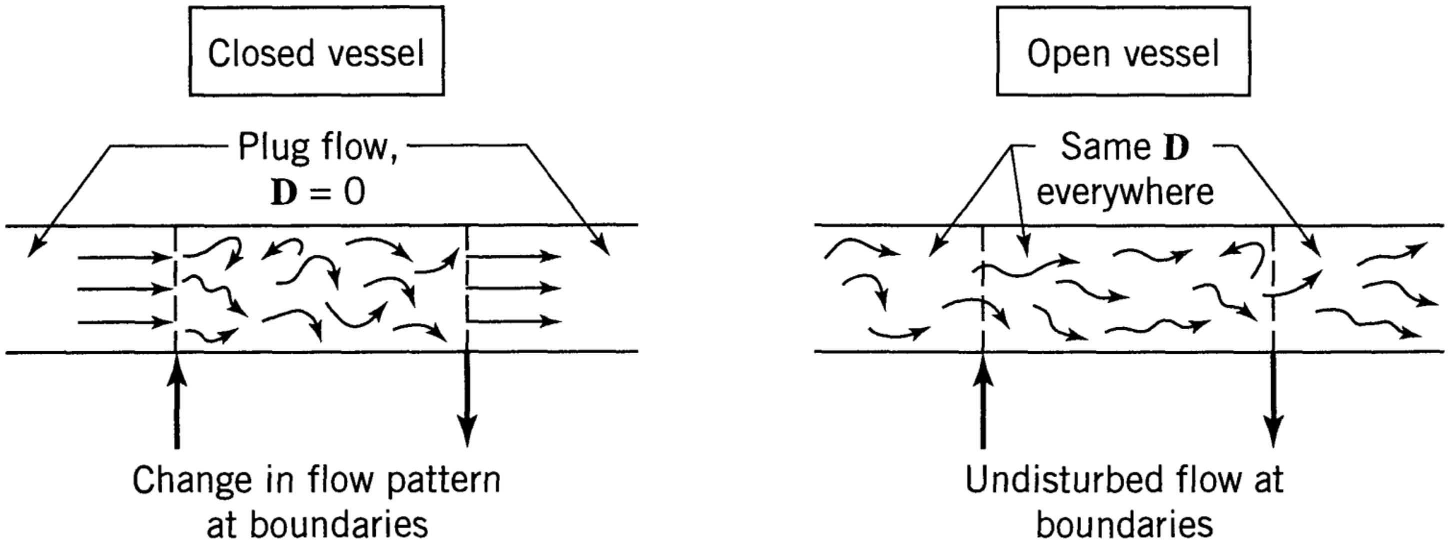


Figure 13.7 Various boundary conditions used with the dispersion model.

Dispersion model for large deviation from PFR flow,(D/uL>0.01)

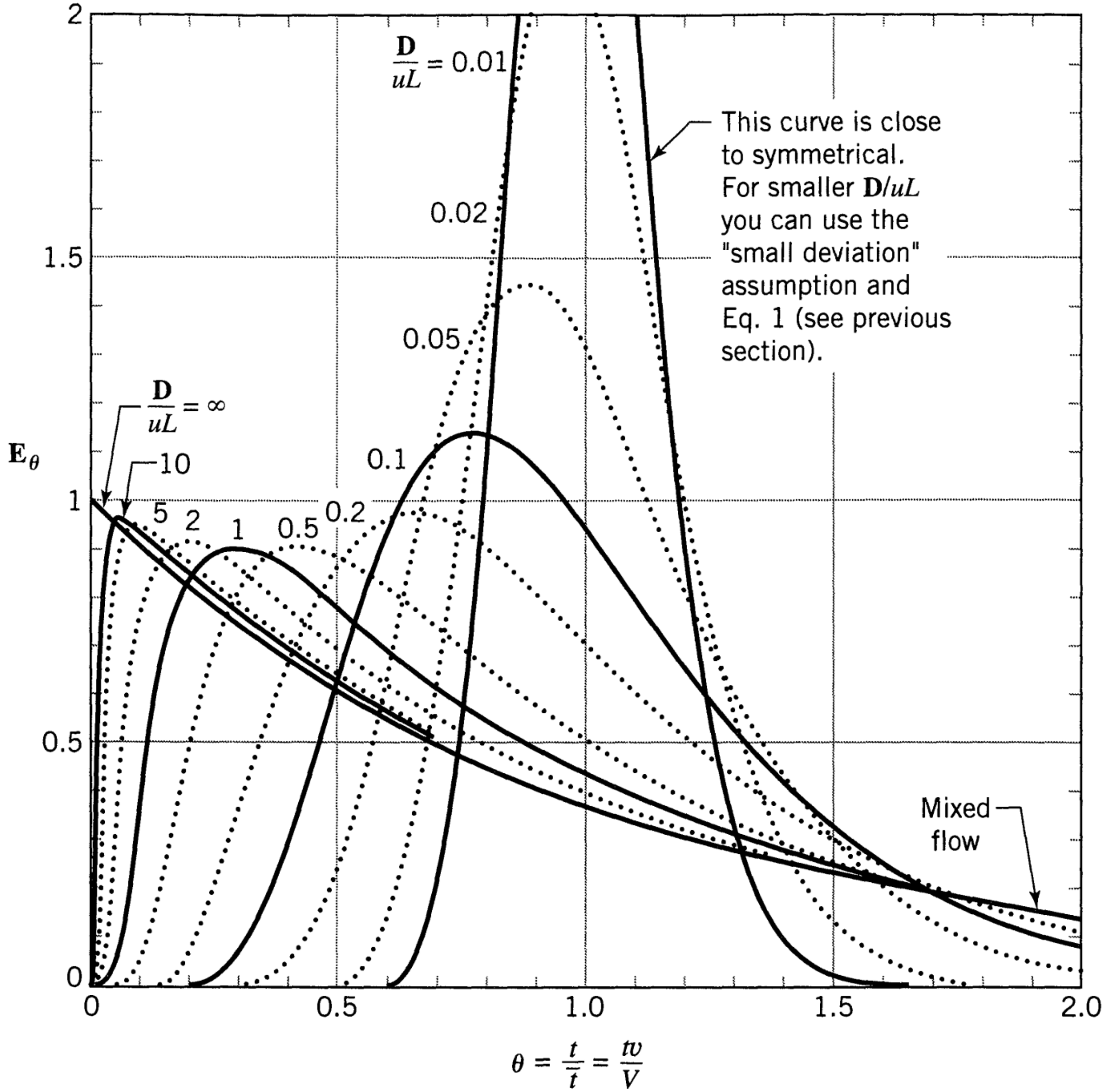


Figure 13.8 Tracer response curves for closed vessels and large deviations from plug flow.

Dispersion model for large deviation from PFR flow,(D/uL>0.01)

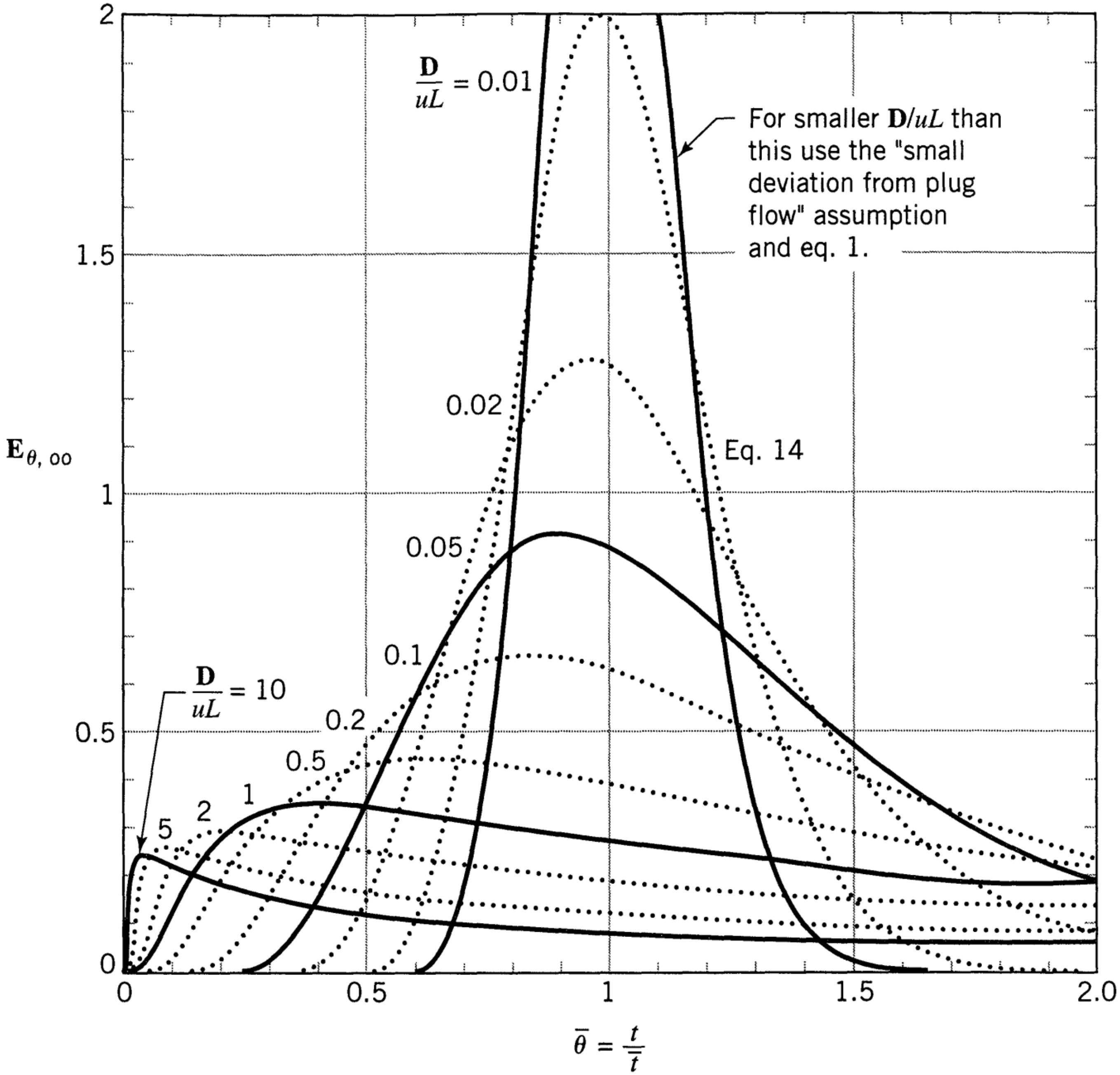


Figure 13.10 Tracer response curves for "open" vessels having large deviations from plug flow.

Dispersion model for small deviation from PFR flow,(D/uL<0.01)

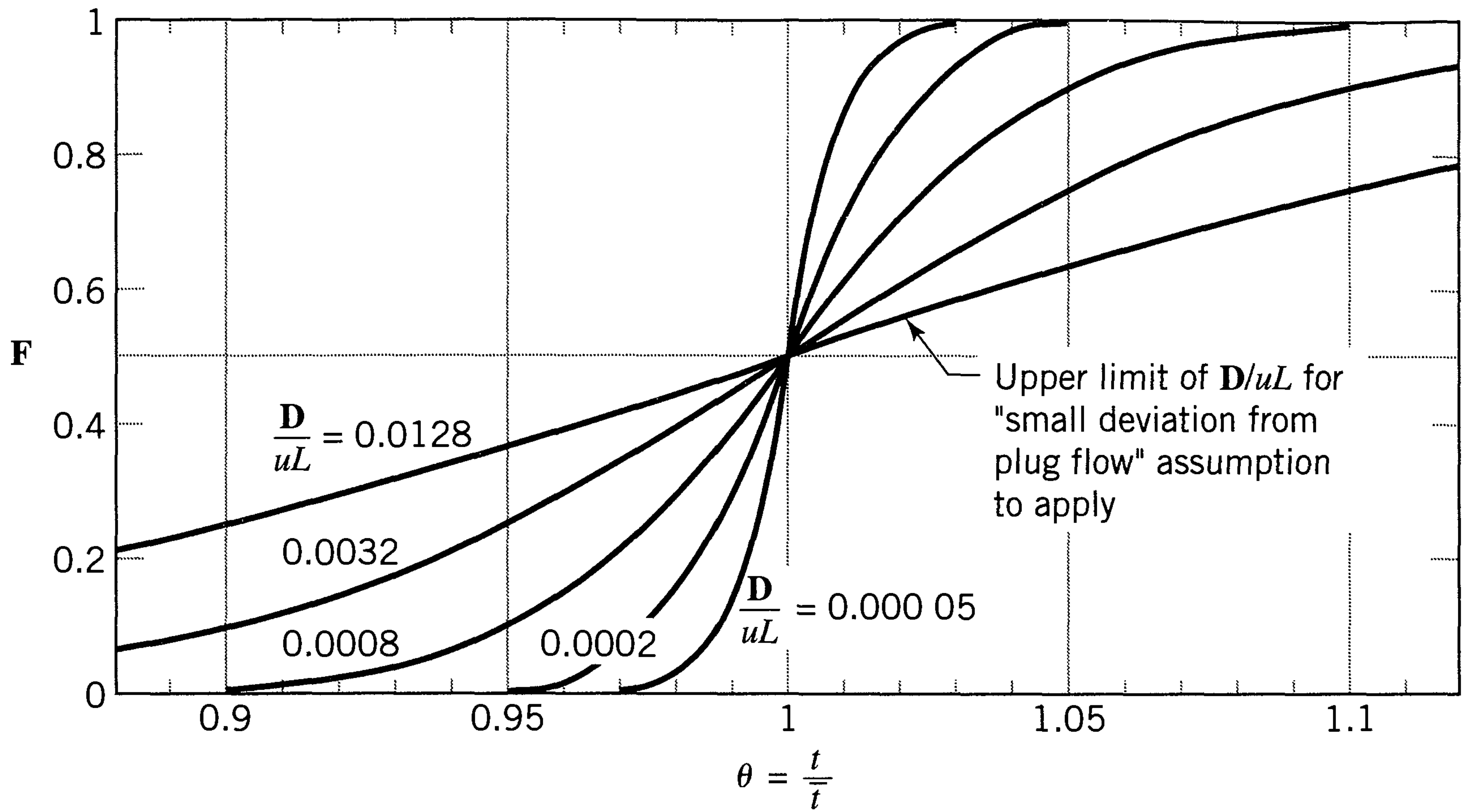


Figure 13.11 Step response curves for small deviations from plug flow.

Dispersion model for small deviation from PFR flow,(D/uL<0.01)

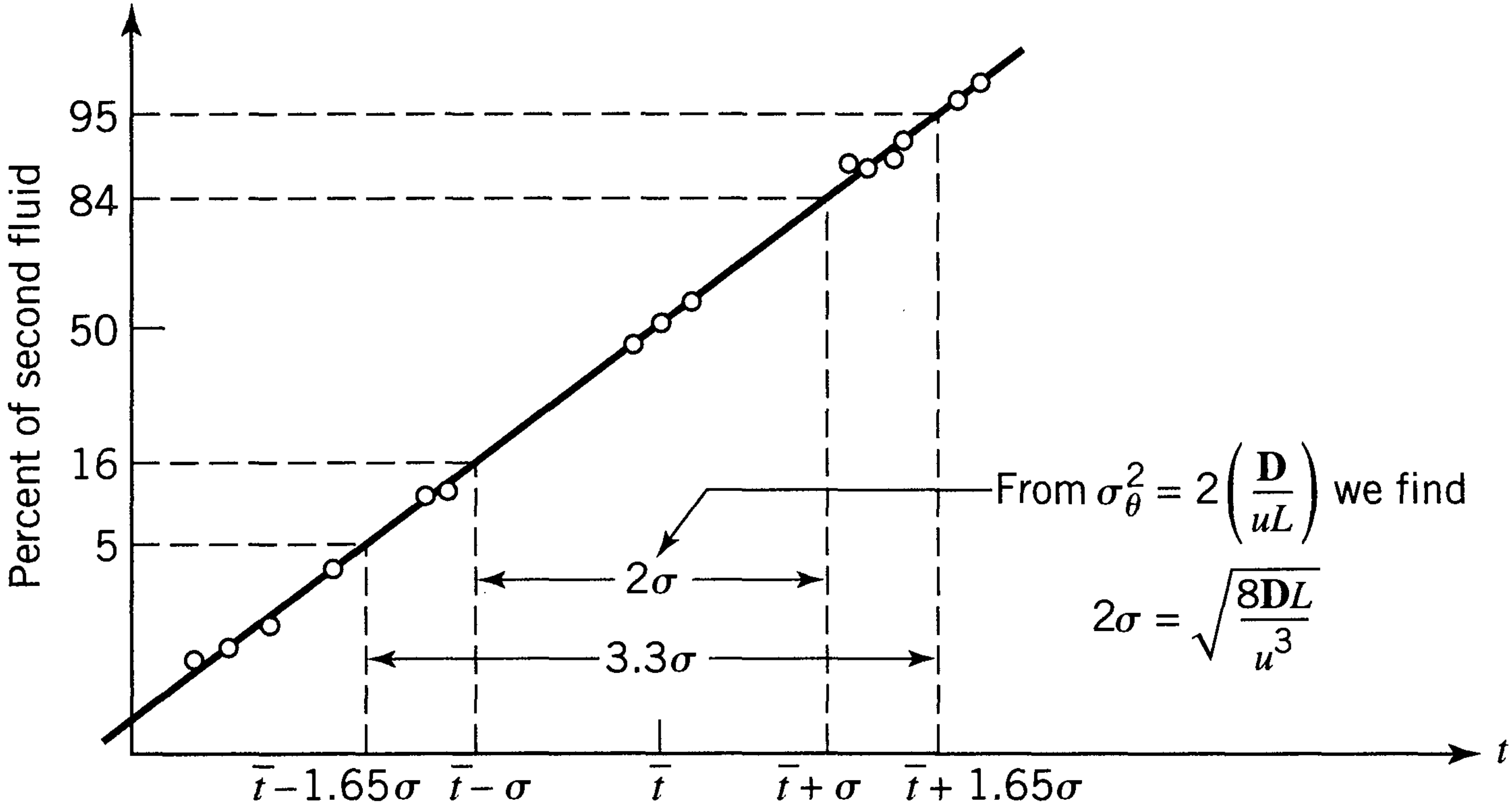


Figure 13.12 Probability plot of a step response signal. From this we find **D**/uL directly.

Dispersion model for large deviation from PFR flow,(D/uL>0.01)

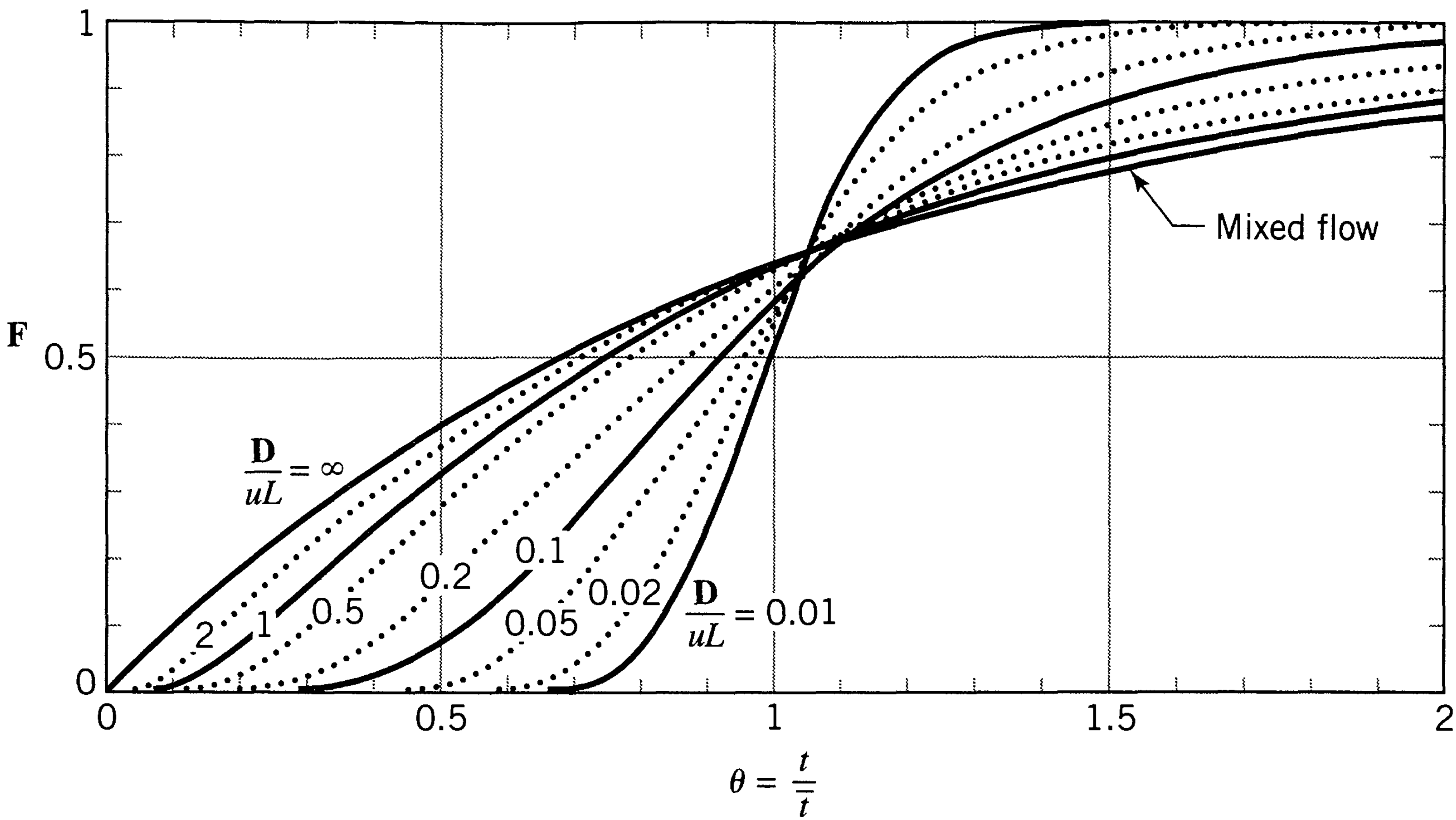


Figure 13.13 Step response curves for large deviations from plug flow in closed vessels.

CHEMICAL REACTION AND DISPERSION

Our discussion has led to the measure of dispersion by a dimensionless group $\mathbf{D}/uL$. Let us now see how this affects conversion in reactors.

Consider a steady-flow chemical reactor of length L through which fluid is flowing at a constant velocity u, and in which material is mixing axially with a dispersion coefficient $\mathbf{D}$. Let an nth-order reaction be occurring.

$$A \rightarrow \text{products}, \qquad -r_A = kC_A^n$$

By referring to an elementary section of reactor as shown in Fig. 13.18, the basic material balance for any reaction component

$$\text{input} = \text{output} + \text{disappearance by reaction} + \text{accumulation} \qquad \textbf{(4.1)}$$

becomes for component A, at steady state,

$$(\text{out–in})_{\text{bulk flow}} + (\text{out–in})_{\text{axial dispersion}} + \begin{matrix}\text{disappearance}\\ \text{by reaction}\end{matrix} + \text{accumulation} = 0 \qquad \textbf{(17)}$$

The individual terms (in moles A/time) are as follows:

CHEMICAL REACTION AND DISPERSION

$$\text{entering by bulk flow} = \left(\frac{\text{moles A}}{\text{volume}}\right)\left(\begin{matrix}\text{flow}\\ \text{velocity}\end{matrix}\right)\left(\begin{matrix}\text{cross-sectional}\\ \text{area}\end{matrix}\right)$$

$$= C_{A,l}uS, \quad [\text{mol/s}]$$

$$\text{leaving by bulk flow} = C_{A,l+\Delta l}uS$$

$$\text{entering by axial dispersion} = \frac{dN_A}{dt} = -\left(\mathbf{D}S\frac{dC_A}{dl}\right)_{l+\Delta l}$$

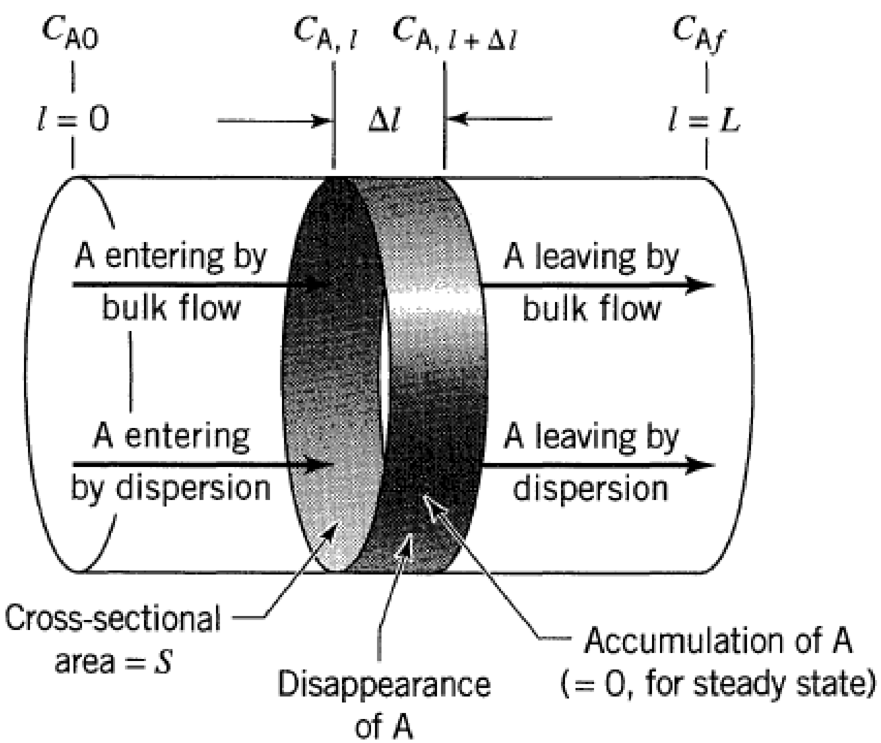


Figure 13.18 Variables for a closed vessel in which reaction and dispersion are occurring.

$$\text{leaving by axial dispersion} = \frac{dN_A}{dt} = -\left(\mathbf{D}S\frac{dC_A}{dl}\right)_{l+\Delta l}$$

$$\text{disappearance by reaction} = (-r_A)\,V = (-r_A)S\,\Delta l, \quad [\text{mol/s}]$$

Note that the difference between this material balance and that for the ideal plug flow reactors of Chapter 5 is the inclusion of the two dispersion terms, because material enters and leaves the differential section not only by bulk flow but by dispersion as well. Entering all these terms into Eq. 17 and dividing by $S\,\Delta l$ gives

$$u\,\frac{(C_{A,l+\Delta l} - C_{A,l})}{\Delta l} - \mathbf{D}\,\frac{\left[\left(\frac{dC_A}{dl}\right)_{l+\Delta l} - \left(\frac{dC_A}{dl}\right)_{l}\right]}{\Delta l} + (-r_A) = 0$$

Now the basic limiting process of calculus states that for any quantity Q which is a smooth continuous function of l

$$\lim_{l_2\to l_1}\frac{Q_2 - Q_1}{l_2 - l_1} = \lim_{\Delta l\to 0}\frac{\Delta Q}{\Delta l} = \frac{dQ}{dl}$$

So taking limits as $\Delta l \to 0$ we obtain

$$u\frac{dC_A}{dl} - \mathbf{D}\frac{d^2C_A}{dl^2} + kC_A^n = 0 \qquad \textbf{(18a)}$$

In dimensionless form where $z = l/L$ and $\tau = \bar{t} = L/u = V/v$, this expression becomes

$$\frac{\mathbf{D}}{uL}\frac{d^2C_A}{dz^2} - \frac{dC_A}{dz} - k\tau C_A^n = 0 \qquad \textbf{(18b)}$$

or in terms of fractional conversion

$$\frac{\mathbf{D}}{uL}\frac{d^2X_A}{dz^2} - \frac{dX_A}{dz} + k\tau C_{A0}^{n-1}(1 - X_A)^n = 0 \qquad \textbf{(18c)}$$

This expression shows that the fractional conversion of reactant A in its passage through the reactor is governed by three dimensionless groups: a reaction rate group $k\tau C_{A0}^{n-1}$, the dispersion group $\mathbf{D}/uL$, and the reaction order n.

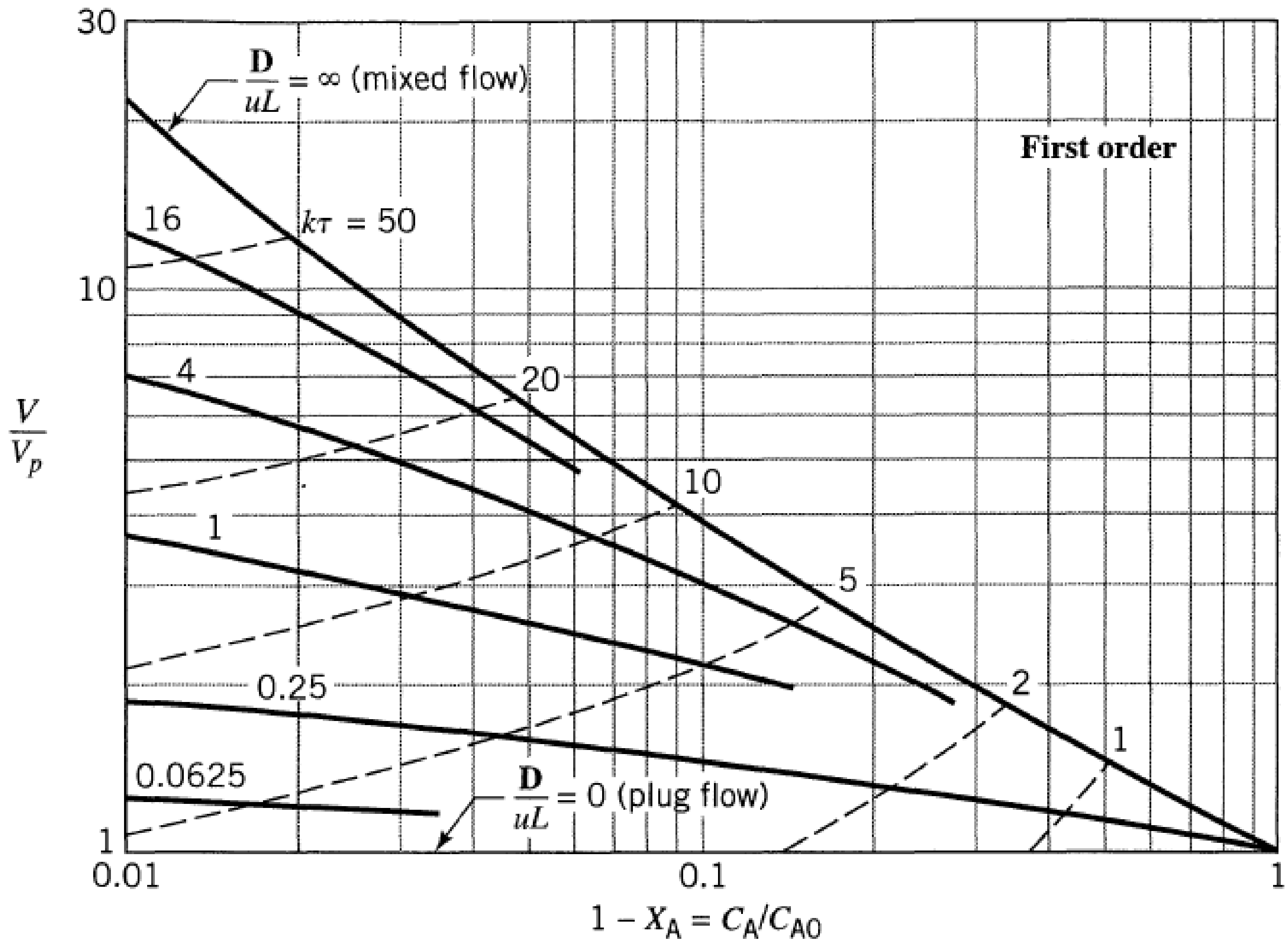


Figure 13.19 Comparison of real and plug flow reactors for the first-order A → products, assuming negligible expansion; from Levenspiel and Bischoff (1959, 1961).

THE TANKS-IN-SERIES MODEL

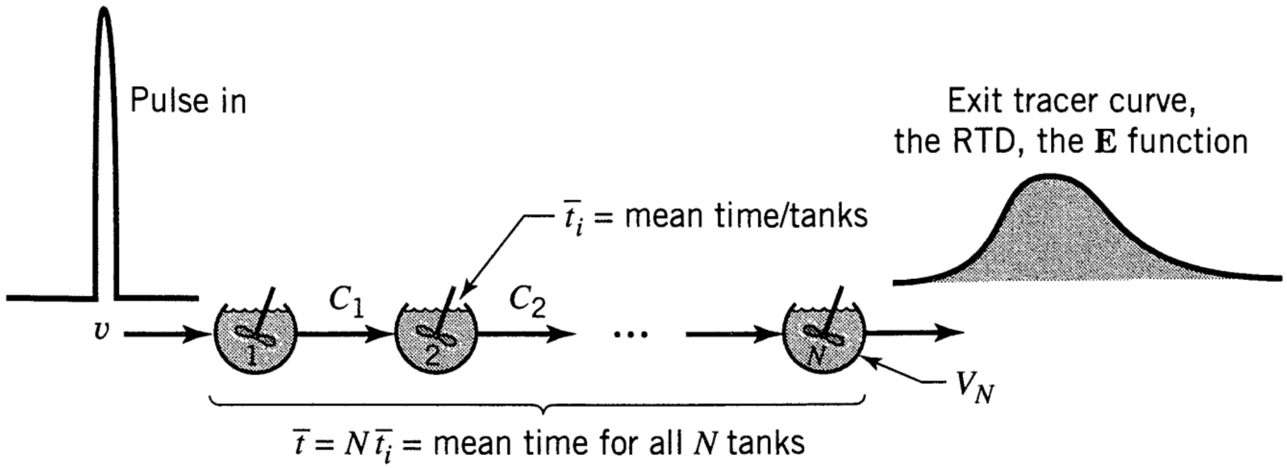


Figure 14.1 The tanks-in-series model.

$$\begin{pmatrix}\text{rate of disappearance}\\ \text{of tracer}\end{pmatrix} = \begin{pmatrix}\text{input}\\ \text{rate}\end{pmatrix} - \begin{pmatrix}\text{output}\\ \text{rate}\end{pmatrix}$$

$$V_1 \frac{dC_1}{dt} = 0 - vC_1 \qquad \left[\frac{\text{mol tracer}}{\text{s}}\right]$$

$$\int_{C_0}^{C_1} \frac{dC_1}{C_1} = -\frac{1}{\bar{t}_1}\int_0^t dt$$

$$\frac{C_1}{C_0} = e^{-t/\bar{t}_1} \qquad \bar{t}_1 \mathbf{E}_1 = e^{-t/\bar{t}_1} \quad [-] \qquad N = 1$$

THE TANKS-IN-SERIES MODEL

$$V_2 \frac{dC_2}{dt} = \upsilon \cdot \underbrace{\frac{C_0}{\bar{t}_1} e^{-t/\bar{t}_1}}_{C_1} - \upsilon C_2 \qquad \left[\frac{\text{mol tracer}}{\text{s}}\right]$$

$$\bar{t}_2 \, \mathbf{E}_2 = \frac{t}{\bar{t}_2} e^{-t/\bar{t}_2} \qquad [-] \qquad N = 2$$

$$\bar{t}\,\mathbf{E} = \left(\frac{t}{\bar{t}}\right)^{N-1} \frac{N^N}{(N-1)!} e^{-tN/\bar{t}} \qquad \cdots \bar{t} = N\bar{t}_i \cdots \sigma^2 = \frac{\bar{t}^2}{N}$$

$$\bar{t}_i\,\mathbf{E} = \left(\frac{t}{\bar{t}_i}\right)^{N-1} \frac{1}{(N-1)!} e^{-t/\bar{t}_i} \qquad \cdots \bar{t}_i = \frac{\bar{t}}{N} \cdots \sigma^2 = N\bar{t}_i^2$$

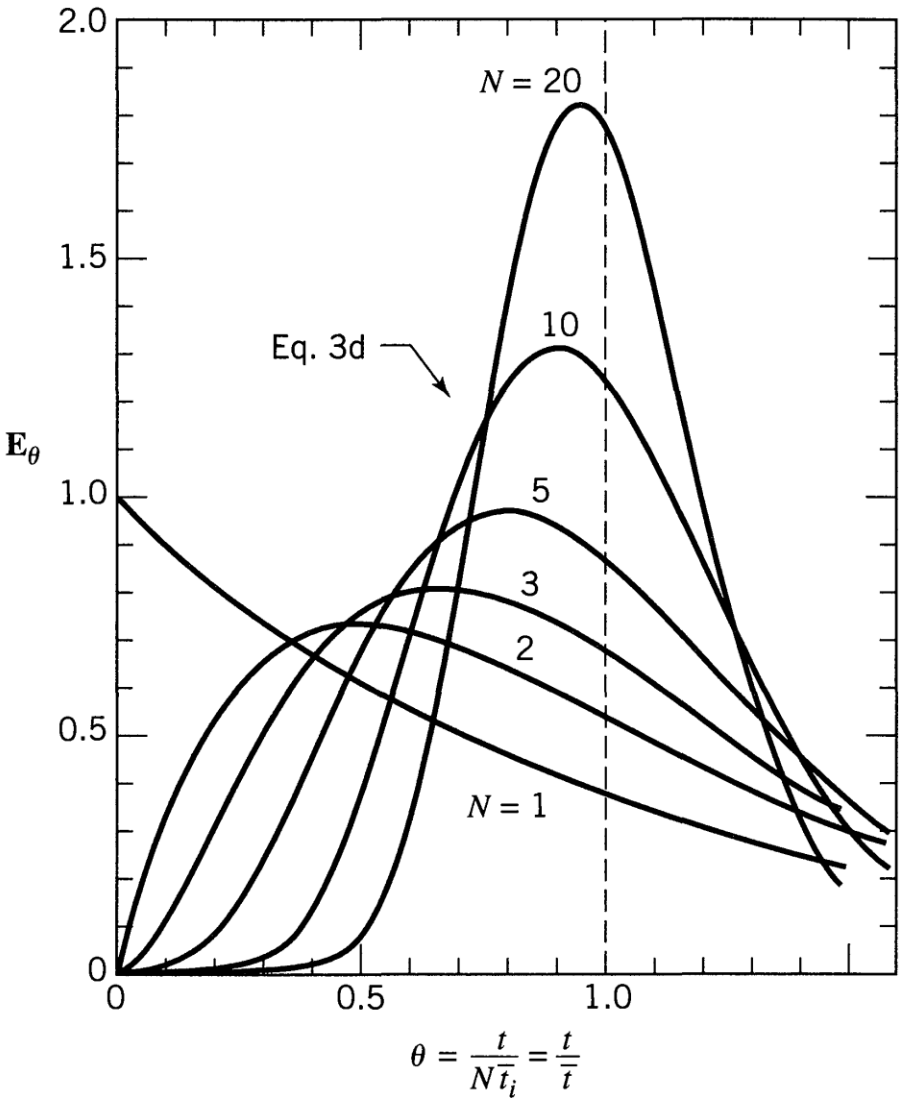
$$\mathbf{E}_{\theta i} = \bar{t}_i\,\mathbf{E} = \frac{\theta_i^{N-1}}{(N-1)!} e^{-\theta_i} \qquad \cdots \sigma_{\theta i}^2 = N$$

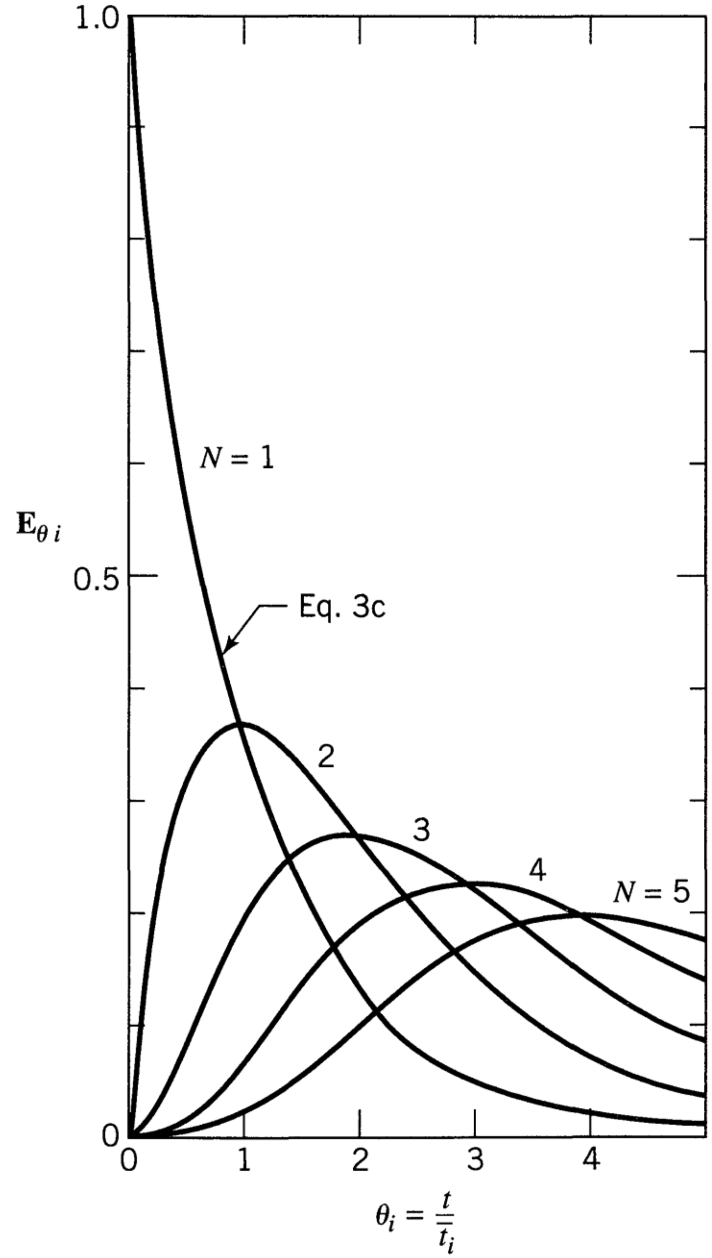
$$\mathbf{E}_\theta = (N\bar{t}_i)\,\mathbf{E} = N\frac{(N\theta)^{N-1}}{(N-1)!} e^{-N\theta} \cdots \sigma_\theta^2 = \frac{1}{N}$$

$\theta_i = \frac{t}{\bar{t}_i}$ = dimensionless time based on the mean residence time per tank $\bar{t}_i$

$\theta = \frac{t}{\bar{t}}$ = dimensionless time based on the mean residence time in all N tanks, $\bar{t}$.

THE TANKS-IN-SERIES MODEL





$$\mathbf{E}_\theta = (N\bar{t}_i)\,\mathbf{E} = N\frac{(N\theta)^{N-1}}{(N-1)!}e^{-N\theta} \cdots \sigma_\theta^2 = \frac{1}{N}$$

$$\mathbf{E}_{\theta i} = \bar{t}_i\,\mathbf{E} = \frac{\theta_i^{N-1}}{(N-1)!}e^{-\theta_i} \cdots \sigma_{\theta i}^2 = N$$

THE TANKS-IN-SERIES MODEL

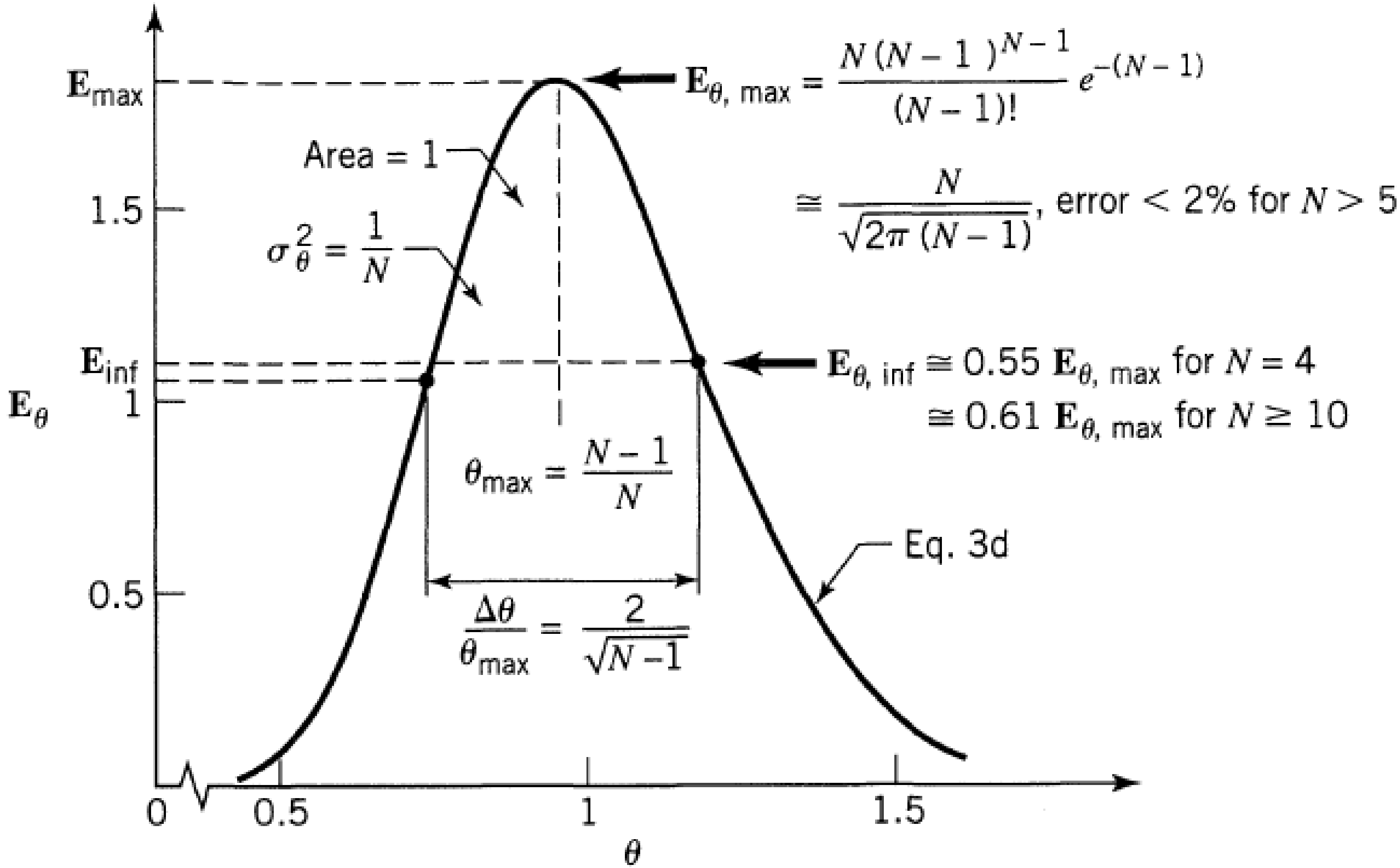


Figure 14.3 Properties of the RTD curve for the tanks-in-series model.

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