

5.3 STEADY-STATE PLUG FLOW REACTOR

In a plug flow reactor the composition of the fluid varies from point to point along a flow path; consequently, the material balance for a reaction component must be made for a differential element of volume dV . Thus for reactant A, Eq. 4.1 becomes

$$\text{input} = \text{output} + \text{disappearance by reaction} + \text{accumulation} \quad (10)$$

Referring to Fig. 5.5, we see for volume dV that

$$\text{input of A, moles/time} = F_A$$

$$\text{output of A, moles/time} = F_A + dF_A$$

$$\begin{aligned} \text{disappearance of A by} \\ \text{reaction, moles/time} &= (-r_A)dV \end{aligned}$$

$$= \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})} \right) (\text{volume of element})$$

Introducing these three terms in Eq. 10, we obtain

$$F_A = (F_A + dF_A) + (-r_A)dV$$

Noting that

$$dF_A = d[F_{A0}(1 - X_A)] = -F_{A0}dX_A$$

We obtain on replacement

$$F_{A0}dX_A = (-r_A)dV \quad (16)$$

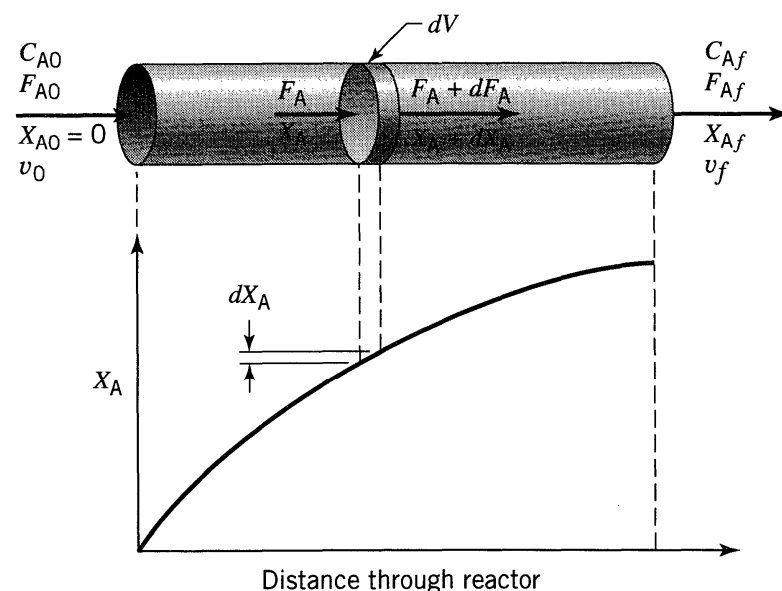


Figure 5.5 Notation for a plug flow reactor.

This, then, is the equation which accounts for A in the differential section of reactor of volume dV . For the reactor as a whole the expression must be integrated. Now F_{A0} , the feed rate, is constant, but r_A is certainly dependent on the concentration or conversion of materials. Grouping the terms accordingly, we obtain

$$\int_0^V \frac{dV}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

Thus

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} \quad \text{any } \varepsilon_A \quad (17)$$

$$\tau = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

Equation 17 allows the determination of reactor size for a given feed rate and required conversion. Compare Eqs. 11 and 17. The difference is that in plug flow r_A varies, whereas in mixed flow r_A is constant.

As a more general expression for plug flow reactors, if the feed on which conversion is based, subscript 0, enters the reactor partially converted, subscript i , and leaves at a conversion designated by subscript f , we have

$$\frac{V}{F_{A0}} = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}$$

or (18)

$$\tau = C_{A0} \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}$$

For the special case of *constant-density systems*

$$X_A = 1 - \frac{C_A}{C_{A0}} \quad \text{and} \quad dX_A = -\frac{dC_A}{C_{A0}}$$

in which case the performance equation can be expressed in terms of concentrations, or

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\frac{1}{C_{A0}} \int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} \quad \varepsilon_A = 0 \quad (19)$$

$$\tau = \frac{V}{v_0} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A}$$

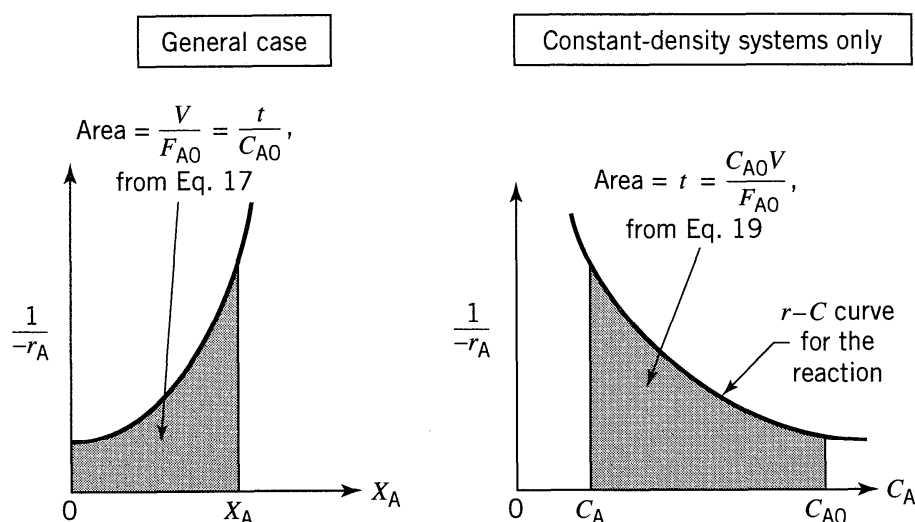


Figure 5.6 Graphical representation of the performance equations for plug flow reactors.

These performance equations, Eqs. 17 to 19, can be written either in terms of concentrations or conversions. For systems of changing density it is more convenient to use conversions; however, there is no particular preference for constant density systems. Whatever its form, the performance equations interrelate the *rate of reaction*, the *extent of reaction*, the *reactor volume*, and the *feed rate*, and if any one of these quantities is unknown it can be found from the other three.

Figure 5.6 displays these performance equations and shows that the space-time needed for any particular duty can always be found by numerical or graphical integration. However, for certain simple kinetic forms analytic integration is possible—and convenient. To do this, insert the kinetic expression for r_A in Eq. 17 and integrate. Some of the simpler integrated forms for plug flow are as follows:

Zero-order homogeneous reaction, any constant ε_A

$$k\tau = \frac{kC_{A0}V}{F_{A0}} = C_{A0}X_A \quad (20)$$

First-order irreversible reaction, $A \rightarrow$ products, any constant ε_A ,

$$k\tau = -(1 + \varepsilon_A) \ln(1 - X_A) - \varepsilon_A X_A \quad (21)$$

First-order reversible reaction, $A \rightleftharpoons rR$, $C_{R0}/C_{A0} = M$, kinetics approximated or fitted by $-r_A = k_1C_A - k_2C_R$ with an observed equilibrium conversion X_{Ae} , any constant ε_A ,

$$k_1\tau = \frac{M + rX_{Ae}}{M + r} \left[-(1 + \varepsilon_A X_{Ae}) \ln\left(1 - \frac{X_A}{X_{Ae}}\right) - \varepsilon_A X_A \right] \quad (22)$$

Second-order irreversible reaction, $A + B \rightarrow$ products with equimolar feed or $2A \rightarrow$ products, any constant ε_A ,

$$C_{A0}k\tau = 2\varepsilon_A(1 + \varepsilon_A)\ln(1 - X_A) + \varepsilon_A^2 X_A + (\varepsilon_A + 1)^2 \frac{X_A}{1 - X_A} \quad (23)$$

Where the density is constant, put $\varepsilon_A = 0$ to obtain the simplified performance equation.

By comparing the batch expressions of Chapter 3 with these plug flow expressions we find:

- (1) For systems of constant density (constant-volume batch and constant-density plug flow) the performance equations are identical, τ for plug flow is equivalent to t for the batch reactor, and the equations can be used interchangeably.
- (2) For systems of changing density there is no direct correspondence between the batch and the plug flow equations and the correct equation must be used for each particular situation. In this case the performance equations cannot be used interchangeably.

The following illustrative examples show how to use these expressions.

EXAMPLE 5.4 PLUG FLOW REACTOR PERFORMANCE

A homogeneous gas reaction $A \rightarrow 3R$ has a reported rate at 215°C

$$-r_A = 10^{-2} C_A^{1/2}, \quad [\text{mol/liter} \cdot \text{sec}]$$

Find the space-time needed for 80% conversion of a 50% A–50% inert feed to a plug flow reactor operating at 215°C and 5 atm ($C_{A0} = 0.0625$ mol/liter).

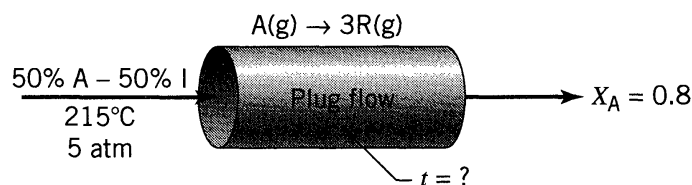


Figure E5.4a

SOLUTION

For this stoichiometry and with 50% inerts, two volumes of feed gas would give four volumes of completely converted product gas; thus

$$\varepsilon_A = \frac{4 - 2}{2} = 1$$

in which case the plug flow performance equation, Eq. 17, becomes

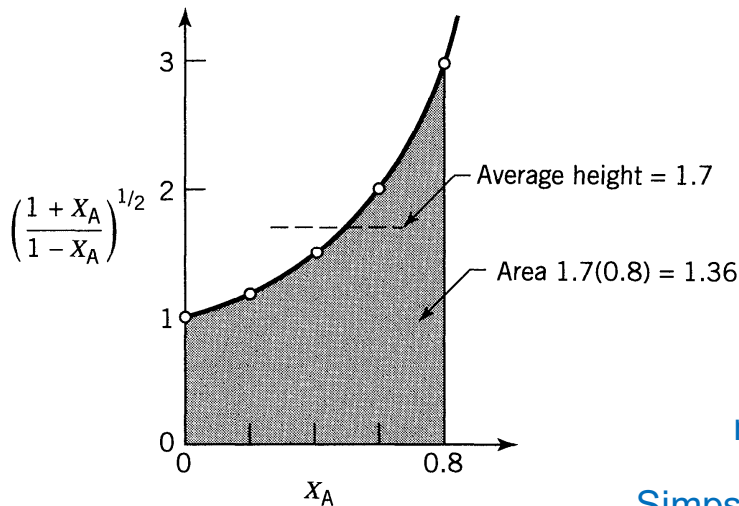
$$\tau = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{k C_{A0}^{1/2} \left(\frac{1 - X_A}{1 + \varepsilon_A X_A} \right)^{1/2}} = \frac{C_{A0}^{1/2}}{k} \int_0^{0.8} \left(\frac{1 + X_A}{1 - X_A} \right)^{1/2} dX_A \quad (i)$$

The integral can be evaluated in any one of three ways: graphically, numerically, or analytically. Let us illustrate these methods.

Table E5.4

X_A	$\frac{1 + X_A}{1 - X_A}$	$\left(\frac{1 + X_A}{1 - X_A}\right)^{1/2}$
0	1	1
0.2	$\frac{1.2}{0.8} = 1.5$	1.227
0.4	2.3	1.528
0.6	4	2
0.8	9	3

Graphical Integration. First evaluate the function to be integrated at selected values (see Table E5.4) and plot this function (see Fig. E5.4b).

**Figure E5.4b**

$$S = \frac{\Delta x}{3} (y_0 + 4y_1 + 2y_2 + \dots + 4y_{n-1} + y_n)$$

Simpson's rule

$$\Delta x = \frac{(b-a)}{n}$$

n = number of y - 1

Counting squares or estimating by eye we find

$$\text{Area} = \int_0^{0.8} \left(\frac{1 + X_A}{1 - X_A}\right)^{1/2} dX_A = (1.70)(0.8) = \underline{\underline{1.36}}$$

Numerical Integration. Using **Simpson's rule**, applicable to an even number of uniformly spaced intervals on the X_A axis, we find for the data of Table E5.4,

$$\begin{aligned} \int_0^{0.8} \left(\frac{1 + X_A}{1 - X_A}\right)^{1/2} dX_A &= (\text{average height})(\text{total width}) \\ &= \left[\frac{1(1) + 4(1.227) + 2(1.528) + 4(2) + 1(3)}{12} \right] (0.8) \\ &= \underline{\underline{1.331}} \end{aligned}$$

Analytical Integration. From a table of integrals

$$\int_0^{0.8} \left(\frac{1 + X_A}{1 - X_A} \right)^{1/2} dX_A = \int_0^{0.8} \frac{1 + X_A}{\sqrt{1 - X_A^2}} dX_A$$

$$= \left(\arcsin X_A - \sqrt{1 - X_A^2} \right) \Big|_0^{0.8} = \underline{\underline{1.328}}$$

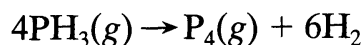
The method of integration recommended depends on the situation. In this problem probably the numerical method is the quickest and simplest and gives a good enough answer for most purposes.

So with the integral evaluated, Eq. (i) becomes

$$\tau = \frac{(0.0625 \text{ mol/liter})^{1/2}}{(10^{-2} \text{ mol}^{1/2}/\text{liter}^{1/2} \cdot \text{sec})} (1.33) = \underline{\underline{33.2 \text{ sec}}}$$

EXAMPLE 5.5 PLUG FLOW REACTOR VOLUME

The homogeneous gas decomposition of phosphine



proceeds at 649°C with the first-order rate

$$-r_{\text{PH}_3} = (10/\text{hr}) C_{\text{PH}_3}$$

What size of plug flow reactor operating at 649°C and 460 kPa can produce 80% conversion of a feed consisting of 40 mol of pure phosphine per hour?

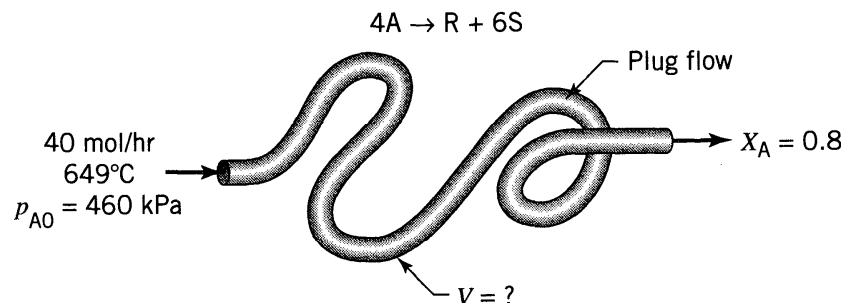


Figure E5.5

SOLUTION

Let $A = \text{PH}_3$, $R = \text{P}_4$, $S = \text{H}_2$. Then the reaction becomes



with

$$-r_A = (10/\text{hr}) C_A$$

The volume of plug flow reactor is given by Eq. 21

$$V = \frac{F_{A0}}{kC_{A0}} \left[(1 + \varepsilon_A) \ln \frac{1}{1 - X_A} - \varepsilon_A X_A \right]$$

Evaluating the individual terms in this expression gives

$$F_{A0} = 40 \text{ mol/hr}$$

$$k = 10/\text{hr}$$

$$C_{A0} = \frac{p_{A0}}{RT} = \frac{460\,000 \text{ Pa}}{(8.314 \text{ Pa} \cdot \text{m}^3/\text{mol} \cdot \text{K})(922 \text{ K})} = 60 \text{ mol/m}^3$$

$$\varepsilon_A = \frac{7 - 4}{4} = 0.75$$

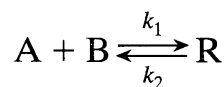
$$X_A = 0.8$$

hence the volume of reactor

$$\begin{aligned} V &= \frac{40 \text{ mol/hr}}{(10/\text{hr})(60 \text{ mol/m}^3)} \left[(1 + 0.75) \ln \frac{1}{0.2} - 0.75(0.8) \right] = 0.148 \text{ m}^3 \\ &= \underline{\underline{148 \text{ liters}}} \end{aligned}$$

EXAMPLE 5.6 TEST OF A KINETIC EQUATION IN A PLUG FLOW REACTOR

We suspect that the gas reaction between A, B, and R is an elementary reversible reaction



and we plan to test this with experiments in an isothermal plug flow reactor.

- (a) Develop the isothermal performance equation for these kinetics for a feed of A, B, R, and inerts.
- (b) Show how to test this equation for an equimolar feed of A and B.

SOLUTION

(a) Feed of A, B, R, and inerts. For this elementary reaction the rate is

$$-r_A = k_1 C_A C_B - k_2 C_R = k_1 \frac{N_A}{V} \frac{N_B}{V} - k_2 \frac{N_R}{V}$$

At constant pressure, basing expansion and conversion on substance A,

$$-r_A = k_1 \frac{N_{A0} - N_{A0} X_A}{V_0 (1 + \varepsilon_A X_A)} \frac{N_{B0} - N_{A0} X_A}{V_0 (1 + \varepsilon_A X_A)} - k_2 \frac{N_{R0} + N_{A0} X_A}{V_0 (1 + \varepsilon_A X_A)}$$

Letting $M = C_{B0}/C_{A0}$, $M' = C_{R0}/C_{A0}$, we obtain

$$-r_A = k_1 C_{A0}^2 \frac{(1 - X_A)(M - X_A)}{(1 + \varepsilon_A X_A)^2} - k_2 C_{A0} \frac{M' + X_A}{1 + \varepsilon_A X_A}$$

Hence, the design equation for plug flow, Eq. 17, becomes

$$\tau = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} = \int_0^{X_{Af}} \frac{(1 + \varepsilon_A X_A)^2 dX_A}{k_1 C_{A0} (1 - X_A)(M - X_A) - k_2 (M' + X_A)(1 + \varepsilon_A X_A)}$$

In this expression ε_A accounts for the stoichiometry and for inerts present in the feed.

(b) Equimolar feed of A and B. For $C_{A0} = C_{B0}$, $C_{R0} = 0$, and no inerts, we have $M = 1$, $M' = 0$, $\varepsilon_A = -0.5$; hence the expression for part a reduces to

$$\tau = \int_0^{X_{Af}} \frac{(1 - 0.5X_A)^2 dX_A}{k_1 C_{A0} (1 - X_A)^2 - k_2 X_A (1 - 0.5X_A)} \quad \text{call this} \quad \int_0^{X_{Af}} f(X_A) dX_A \quad \text{(i)}$$

Having V , v_0 , and X_A data from a series of experiments, separately evaluate the left side and the right side of Eq. (i). For the right side, at various X_A

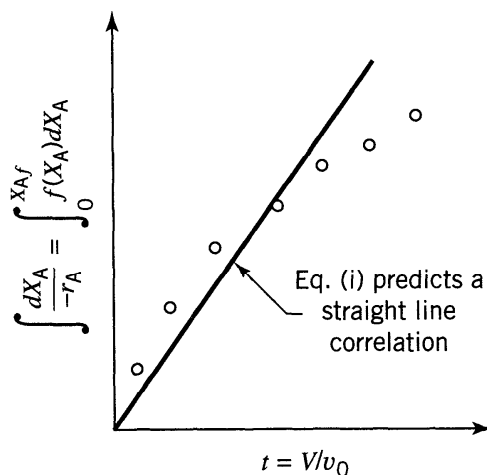


Figure E5.6

evaluate $f(X_A)$, then integrate graphically to give $\int f(X_A)dX_A$ and then make the plot of Fig. E5.6. If the data fall on a reasonably straight line, then the suggested kinetic scheme can be said to be satisfactory in that it fits the data.

Holding Time and Space Time for Flow Reactors

We should be clearly aware of the distinction between these two measures of time, \bar{t} and τ . They are defined as follows:

$$\tau = \left(\begin{array}{l} \text{time needed to} \\ \text{treat one reactor} \\ \text{volume of feed} \end{array} \right) = \frac{V}{v_0} = \frac{C_{A0}V}{F_{A0}}, \quad [\text{hr}] \quad (6) \text{ or } (8)$$

$$\bar{t} = \left(\begin{array}{l} \text{mean residence time} \\ \text{of flowing material} \\ \text{in the reactor} \end{array} \right) = C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)(1 + \epsilon_A X_A)}, \quad [\text{hr}] \quad (24)$$

For constant density systems (all liquids and constant density gases)

$$\tau = \bar{t} = \frac{V}{v}$$

For changing density systems $\bar{t} \neq \tau$ and $\bar{t} \neq V/v_0$ in which case it becomes difficult to find how these terms are related.

As a simple illustration of the difference between \bar{t} and τ , consider two cases of the steady-flow popcorn popper of Problem 4.7 which takes in 1 liter/min of raw corn and produces 28 liters/min of product popcorn.

Consider three cases, called X, Y, and Z, which are shown in Fig. 5.7. In the first case (case X) all the popping occurs at the back end of the reactor. In the

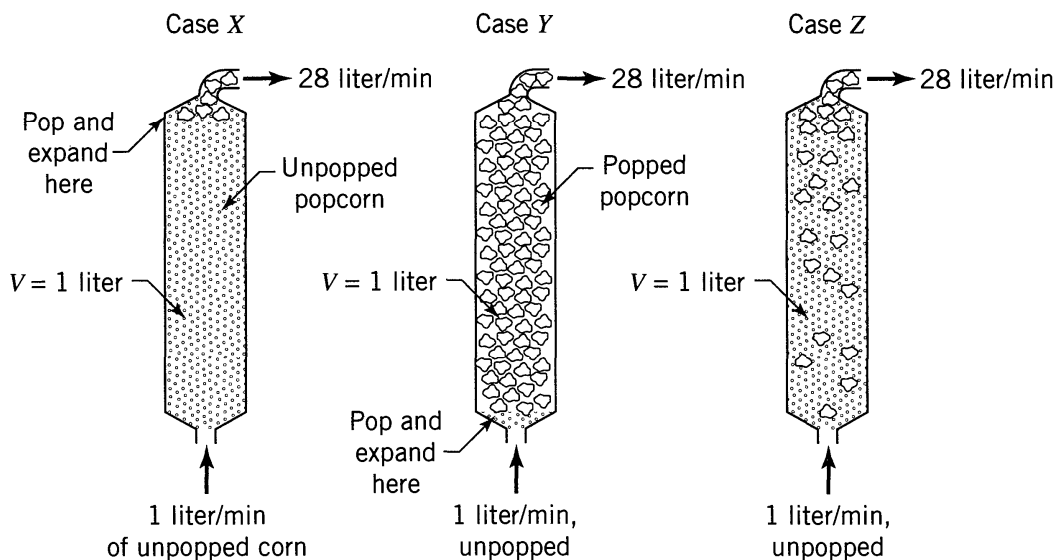


Figure 5.7 For the same τ value the \bar{t} values differ in these three cases.

second case (case Y) all the popping occurs at the front end of the reactor. In the third case (case Z) the popping occurs somewhere between entrance and exit. In all three cases

$$\tau_X = \tau_Y = \tau_Z = \frac{V}{v_0} = \frac{1 \text{ liter}}{1 \text{ liter/min}} = 1 \text{ min}$$

irrespective of where the popping occurs. However, we see that the residence time in the three cases is very different, or

$$\bar{t}_X = \frac{1 \text{ liter}}{1 \text{ liter/min}} = 1 \text{ min}$$

$$\bar{t}_Y = \frac{1 \text{ liter}}{28 \text{ liter/min}} \cong 2 \text{ sec}$$

\bar{t}_Z is somewhere between 2 and 60 s, depending on the kinetics

Note that the value of \bar{t} depends on what happens in the reactor, while the value of τ is independent of what happens in the reactor.

This example shows that \bar{t} and τ are not, in general, identical. Now which is the natural performance measure for reactors? For batch systems Chapter 3 shows that it is the time of reaction; however, holding time does not appear anywhere in the performance equations for flow systems developed in this chapter, Eqs. 13 to 19, while it is seen that space-time or V/F_{A0} does naturally appear. Hence, τ or V/F_{A0} is the proper performance measure for flow systems.

The above simple example shows that in the special case of constant fluid density the space-time is equivalent to the holding time; hence, these terms can be used interchangeably. This special case includes practically all liquid phase reactions. However, for fluids of changing density, e.g., nonisothermal gas reactions or gas reactions with changing number of moles, a distinction should be made between τ and \bar{t} and the correct measure should be used in each situation.

Summary of Performance Equations

Tables 5.1 and 5.2 present the integrated performance equations for single ideal reactors.

REFERENCES

- Corcoran, W. H., and Lacey, W. N., *Introduction to Chemical Engineering Problems*, McGraw Hill, New York, 1970, p. 103.
Pease, R. N., *J. Am. Chem. Soc.*, **51**, 3470 (1929).