

auxiliary relationships, such as the Fanning equation for the friction. Since the pressure drop is rather small for flow in empty pipes, which is the usual case for homogeneous reactors, the effect of pressure may sometimes be neglected. However, this is not invariably the case. Thermal cracking of hydrocarbons is accomplished by passing the fluid through pipes which may be several hundred feet long, and in such instances the pressure drop may be of the order of 100 psi at an absolute pressure of 500 psia.

### IDEAL STIRRED-TANK REACTORS (FLOW)

As we saw in Chap. 3, the relation between conversion and flow rate in a continuous-flow, stirred-tank reactor [Eq. (3-3)] is an algebraic one, in contrast to the integral relations for batch reactors [Eq. (3-10)] and plug-flow reactors [Eq. (3-13)]. If the volume (density) is constant, the simplified form, for the continuous-flow type analogous to Eqs. (4-2) and (4-5) for ideal batch and plug-flow reactors, is<sup>1</sup>

$$\frac{V}{Q} = \bar{\theta} = \frac{C_0 - C}{r} \quad (4-6)$$

Here  $C$  and  $r$  refer to conditions in the product stream (or in the reactor) and  $\bar{\theta}$  is the average residence time. It is equal to  $V/Q$  and also equal to the average of the distribution of residence times for an ideal stirred-tank reactor. This distribution function is developed in Chap. 6.

Since the temperature must be the same in all parts of this type of reactor, isothermal operation is always achieved as long as steady-state conditions prevail. However, the reactor temperature may be different from that of the feed stream, because of either the heat of reaction or the energy exchange with the surroundings. Hence the treatment in this chapter is restricted to cases where the feed and reactor temperatures are the same. The more general case will be considered in Chap. 5, along with nonisothermal behavior.

#### 4-5 Single-stirred-tank Reactors

The algebraic nature of Eq. (4-6) simplifies the analytical treatment for the case of multiple reactions to the solution of an assembly of algebraic equations. This is, in general, a simpler problem than treatment of an assembly of integral equations, applicable for plug-flow or batch reactors.

<sup>1</sup>The rate in this equation, as in Eqs. (3-10) and (3-13), is a positive quantity. That is, it is a rate of disappearance of reactant or production of product.

The following two examples illustrate the procedure for single and multiple reactions.

**Example 4-7** Eldridge and Piret<sup>1</sup> have investigated the hydrolysis of acetic anhydride in stirred-tank flow reactors of about 1,800 cm<sup>3</sup> volume at temperatures from 15 to 40°C. Their experimental results for several volumetric feed rates are shown in Table 4-10. Independent determination by these investigators from other experiments in

Table 4-10

Entering anhydride concentration, moles/cm <sup>3</sup>	Volumetric feed rate, cm <sup>3</sup> /min	% hydrolysis of anhydride	T, °C
$2.1 \times 10^{-4}$	378	25.8	15
$1.4 \times 10^{-4}$	582	33.1	25
$1.37 \times 10^{-4}$	395	40.8	25
$1.08 \times 10^{-4}$	555	15.3	10
$0.52 \times 10^{-4}$	490	16.4	10
$0.95 \times 10^{-4}$	575	55.0	40
$0.925 \times 10^{-4}$	540	55.7	40
$1.87 \times 10^{-4}$	500	58.3	40
$2.02 \times 10^{-4}$	88.5	88.2	40

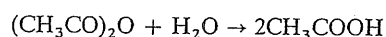
batch-operated reactors resulted in the following first-order equations for the rate of reaction, in g moles/(cm<sup>3</sup>)(min):

$$r = \begin{cases} 0.0567C & \text{at } 10^\circ\text{C} \\ 0.0806C & \text{at } 15^\circ\text{C} \\ 0.1580C & \text{at } 25^\circ\text{C} \\ 0.380C & \text{at } 40^\circ\text{C} \end{cases}$$

where  $C$  is the concentration of acetic anhydride, in gram moles per cubic centimeter.

For each run compute the percent of hydrolysis and compare it with the observed value in the table. In all cases the feed temperature is the same as the temperature of the reaction mixture. Since the concentrations are low, the density of the solution may be assumed constant.

**Solution** The hydrolysis reaction,



would be expected to be second order. In this case, since dilute aqueous solutions were employed, the water concentration is essentially constant, so that a first-order equation is satisfactory. Equation (4-6) is applicable because the reaction mixture is a constant-density liquid.

<sup>1</sup>J. W. Eldridge and E. L. Piret, *Chem. Eng. Progr.*, **46**, 290 (1950).

Substituting the rate equation  $r = kC$  into Eq. (4-6) and solving the resulting expression for the exit concentration  $C_1$ , we have

$$C_1 = \frac{C_0}{1 + k(V/Q)} = \frac{C_0}{1 + k\bar{\theta}}$$

The fraction of the anhydride hydrolyzed,  $y$ , is equal to  $(C_0 - C_1)/C_0$ , and so

$$y = 1 - \frac{C_1}{C_0} = 1 - \frac{1}{1 + k\bar{\theta}} \quad (\text{A})$$

Equation (A) can be employed to determine the percent hydrolyzed from  $\bar{\theta}$  and the reaction-rate constant. For the first set of data in the table, at 15°C,

$$k = 0.0806 \text{ min}^{-1} \quad \bar{\theta} = \frac{1,800}{378} \text{ min}$$

$$k\bar{\theta} = 0.0806 \frac{1,800}{378} = 0.384 \text{ (dimensionless)}$$

Substitution in Eq. (A) gives

$$y = 1 - \frac{1}{1 + 0.384} = 0.277 \quad \text{or } 27.7\%$$

This agrees reasonably well with the experimental value of 25.8%.

Table 4-11 shows the results of similar calculations for the other sets of data. The computed values are based on the concept of complete mixing and hence on the

Table 4-11

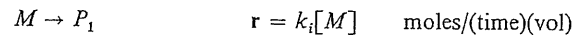
Volumetric feed rate, cm <sup>3</sup> /min	% hydrolysis	
	Experimental	Calculated from Eq. (A)
378	25.8	27.7
582	33.1	32.8
395	40.8	41.8
555	15.3	15.5
490	16.4	17.2
575	55.0	54.4
540	55.7	55.9
500	58.3	57.8
88.5	88.2	88.5

assumption of uniform composition and temperature throughout the mass. The agreement between the calculated results and the experimental ones is a measure of the validity of the complete mixing assumption. Tests with successively less stirring can be used to study the level of agitation required for complete mixing. MacDonald and Piret<sup>1</sup> have made such studies for a first-order reaction system.

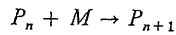
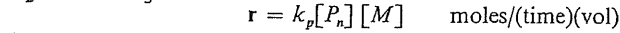
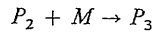
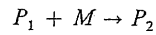
<sup>1</sup>R. W. MacDonald and E. L. Piret, *Chem. Eng. Progr.*, 47, 363 (1951).

**Example 4-8** An ideal continuous stirred-tank reactor is used for the homogeneous polymerization of monomer  $M$ . The volumetric flow rate is  $Q$ , the volume of the reactor is  $V$ , and the density of the reaction solution is invariant with composition. The concentration of monomer in the feed is  $[M]_0$ . The polymer product is produced by an initiation step and a consecutive series of propagation reactions. The reaction mechanism and rate equations may be described as follows, where  $P_1$  is the activated monomer and  $P_2, \dots, P_n$  are polymer molecules containing  $n$  monomer units:

INITIATION



PROPAGATION



All the propagation steps have the same second-order rate constant  $k_p$ .

If  $k_i, k_p, [M]_0, Q$ , and  $V$  are known, derive expressions for (a) the conversion of monomer, (b) the concentration of polymer  $P_n$  in the product stream, and (c) the weight fraction  $w_n$  of the polymer product (this is a form of the molecular weight distribution of the product).

*Solution* (a) Equation (4-6) is valid and may be applied to each polymer product and to the monomer. Solving Eq. (4-6) for the rate and applying it to the monomer, we obtain

$$r_m = \frac{M_0 - M}{V/Q} = \frac{M_0 - M}{\bar{\theta}} \quad (\text{A})$$

The monomer is consumed by the initiation step and all the propagation reactions, and so its rate of disappearance is

$$r_m = k_i[M] + k_p[M] \sum_{n=1}^{\infty} [P_n] \quad (\text{B})$$

Combining Eqs. (A) and (B) gives

$$\frac{M_0 - M}{\bar{\theta}} = k_i[M] + k_p[M] \sum_{n=1}^{\infty} [P_n] \quad (\text{C})$$

Writing Eq. (A) for  $P_1$ , noting that there is no  $P_1$  in the feed, and inserting the appropriate expressions for the rate, we obtain

$$r_1 = -k_i[M] + k_p[P_1][M] = \frac{0 - [P_1]}{\bar{\theta}} = -\frac{[P_1]}{\bar{\theta}}$$

This may be written

$$k_i[M] = \frac{[P_1]}{\bar{\theta}} + k_p[P_1][M] \quad (\text{D})$$

or

$$[P_1] = \frac{k_i[M]}{(1/\bar{\theta}) + k_p[M]} \quad (\text{E})$$

Similarly, for  $P_2$  and  $P_n$  the mass balances are

$$k_p[M][P_1] = \frac{[P_2]}{\bar{\theta}} + k_p[P_2][M] \quad (\text{F})$$

$$k_p[M][P_{n-1}] = \frac{[P_n]}{\bar{\theta}} + k_p[P_n][M] \quad (\text{G})$$

Solving for  $P_2$  from Eq. (F) and  $P_n$  from Eq. (G) gives

$$[P_2] = \frac{k_p[M][P_1]}{(1/\bar{\theta}) + k_p[M]} \quad (\text{H})$$

$$[P_n] = \frac{k_p[M][P_{n-1}]}{(1/\bar{\theta}) + k_p[M]} \quad (\text{I})$$

Inserting Eq. (E) in Eq. (H) to eliminate  $[P_1]$  and proceeding in a similar way for  $[P_2], [P_3], \dots, [P_{n-1}]$ , we can eliminate all intermediate concentrations to obtain

$$[P_n] = \frac{k_i([M])^n (k_p)^{n-1}}{\{k_p[M] + 1/\bar{\theta}\}^n} = \frac{k_i}{k_p} \frac{1}{\{1 + 1/\bar{\theta} k_p[M]\}^n} \quad (\text{J})$$

Summing up all the mass balances for the individual species written in the form of Eqs. (D), (F), and (G) gives a simple relationship between the concentration of unreacted monomer and the concentrations of all the polymer products,

$$k_i[M] = \frac{P_1}{\bar{\theta}} + \frac{P_2}{\bar{\theta}} + \dots = \frac{1}{\bar{\theta}} \sum_{n=1}^{\infty} P_n \quad (\text{K})$$

Combining this result with Eq. (C) provides a relationship between  $[M]$  and  $[M]_0$ ,

$$\frac{[M]_0 - [M]}{\bar{\theta}} = k_i[M] + k_i k_p [M]^2 \bar{\theta} \quad (\text{L})$$

Since the conversion of monomer is

$$x = \frac{[M]_0 - [M]}{[M]_0} \quad (\text{M})$$

Eq. (L) may be written

$$x = k_i \bar{\theta} (1 - x) \{1 + k_p \bar{\theta} [M]_0 (1 - x)\} \quad (\text{N})$$

This is the answer to the first part of the problem. Note that the conversion depends on the initial monomer concentration as well as on the rate constants and  $\bar{\theta}$ .

(b) If we know  $x$ , we can find  $[M]$  from Eq. (M) and then calculate  $[P_n]$  from Eq. (J) for any value of  $n$ .

(c) The weight fraction of  $P_n$  in the polymer product is the weight of polymer

$P_n$  divided by the weight of total polymer product. The latter is equal to the weight of monomer that has reacted. If  $W_0$  is the molecular weight of monomer, the weight fraction of  $P_n$  is

$$w_n = \frac{[P_n]nW_0}{([M]_0 - [M])W_0} = \frac{n[P_n]}{[M]_0 - [M]} \quad (\text{P})$$

Substituting Eq. (J) for  $[P_n]$  in Eq. (P) gives

$$w_n = \frac{k_i n}{k_p([M]_0 - [M])} \frac{1}{\{1 + 1/(\bar{\theta}k_p[M])\}^n} \quad (\text{Q})$$

As an illustration of these results Eqs. (N) and (Q) have been used to calculate the conversion and molecular weight distribution for the case

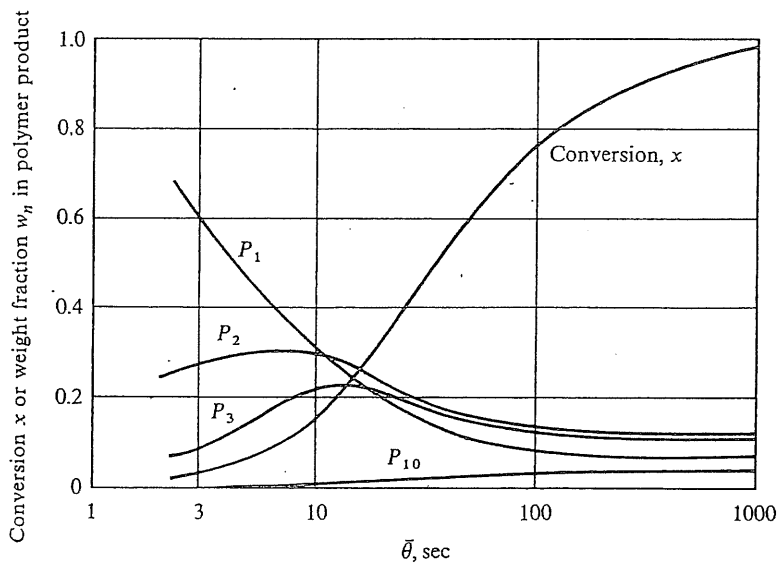
$$k_i = 10^{-2} \text{ sec}^{-1}$$

$$k_p = 10^2 \text{ cm}^3/(\text{g mole})(\text{sec})$$

$$[M]_0 = 1.0 \text{ g moles/liter}$$

Calculations were carried out for average residence times ( $\bar{\theta} = V/Q$ ) from 3 to 1,000 sec. Figure 4-12 shows the conversion and  $w_n$  for several products. In this range of  $\bar{\theta}$  the conversion increases from 3.7 to 97.3%. The weight fraction of  $P_1$  decreases continuously with residence time. This is expected, since  $w$  refers to the weight fraction of product (not of total effluent from the reactor), and at low  $\bar{\theta}$  the product will be nearly all  $P_1$ . At the other extreme,  $w_{10}$  is low but increases continuously, since higher

Fig. 4-12 Distribution of products in stirred-tank reactor for polymerization



products ( $m > 10$ ) are not formed in significant amounts. Curves are also shown for two products of intermediate molecular weight,  $P_2$  and  $P_3$ . These curves show maxima at intermediate  $\bar{\theta}$ .

The curves in Fig. 4-12 are helpful in choosing a reactor size appropriate for producing a specified product distribution. For example, if the objective is to make the maximum amount of trimer ( $P_3$ ), the reactor volume should be such that  $\bar{\theta}$  is about 13 sec. This problem does not allow for destruction of active polymer  $P_n$  by termination reactions. This is often the case and leads to a more symmetrical distribution of molecular weights. Denbigh<sup>1</sup> has considered this and similar polymerization problems.

It was possible to solve this polymerization problem in closed form because we were dealing with algebraic equations, that is, with an ideal stirred-tank reactor. The same problem in a tubular-flow reactor would require the solution of a series of integral equations, which is possible only by numerical methods.

#### 4-6 Stirred-tank Reactors in Series

In some cases it may be desirable to use a series of stirred-tank reactors, with the exit stream from the first serving as the feed to the second, and so on. For constant density the exit concentration or conversion can be solved by consecutive application of Eq. (4-6) to each reactor. MacDonald and Piret<sup>1</sup> have derived solutions for a number of rate expressions and for systems of reversible, consecutive, and simultaneous reactions. Graphical procedures have also been developed. The kinds of calculations involved are illustrated for the simple case of a first-order reaction in Example 4-9.

- ④ **Example 4-9** Acetic anhydride is to be hydrolyzed in three stirred-tank reactors operated in series. Suppose that each has a volume of 1,800 cm<sup>3</sup>, that the temperature is constant and equal to 25°C, and that the feed rate to the first reactor is 582 cm<sup>3</sup>/min. Compute the percent of hydrolysis accomplished in the three reactors.

*Solution* From the results of Example 4-7, the fraction hydrolyzed in the stream leaving the first reactor is 0.328. If the anhydride concentration leaving the first reactor is designated as  $C_1$ , and that leaving the second is  $C_2$ , Eq. (4-6) applied to the second reactor is

$$C_2 = \frac{C_1}{1 + k\bar{\theta}_2}$$

or

$$\frac{C_1 - C_2}{C_1} = \text{fraction hydrolyzed in reactor 2} = 1 - \frac{1}{1 + k\bar{\theta}_2}$$

<sup>1</sup>K. G. Denbigh, *Trans. Faraday Soc.*, **43**, 648 (1947).

<sup>1</sup>R. W. MacDonald and E. L. Piret, *Chem. Eng. Progr.*, **47**, 363 (1951).

Since  $\bar{\theta}_2 = \bar{\theta}_1$ , the fraction hydrolyzed in the second reactor will be the same as in the first. Therefore the following equations may be written for the three reactors:

$$\frac{C_0 - C_1}{C_0} = 0.328 \quad \text{or } C_1 = (1 - 0.328)C_0 = 0.672C_0$$

$$\frac{C_1 - C_2}{C_1} = 0.328 \quad \text{or } C_2 = 0.672C_1 = (0.672)^2 C_0$$

$$\frac{C_2 - C_3}{C_2} = 0.328 \quad \text{or } C_3 = 0.672C_2 = (0.672)^3 C_0$$

The equation for  $C_3$  may be generalized to the form

$$C_n = (0.672)^n C_0 = \left( \frac{1}{1 + k\bar{\theta}_i} \right)^n C_0$$

or

$$1 - \frac{C_n}{C_0} = 1 - \frac{1}{(1 + k\bar{\theta}_i)^n} = \text{fraction hydrolyzed in } n \text{ reactors} \quad (\text{A})$$

where  $n$  is the number of reactors in series, and  $\bar{\theta}_i$  is the residence time in each stage. For  $n = 3$ , the fraction hydrolyzed is  $1 - 0.672^3 = 0.697$ , or 69.7%.

If the restriction of equal residence times in each reactor is removed, Eq. (A) of Example 4-9 becomes

$$x_n = 1 - \frac{1}{(1 + k\bar{\theta}_1) \dots (1 + k\bar{\theta}_i) \dots (1 + k\bar{\theta}_n)} \quad (4-6A)$$

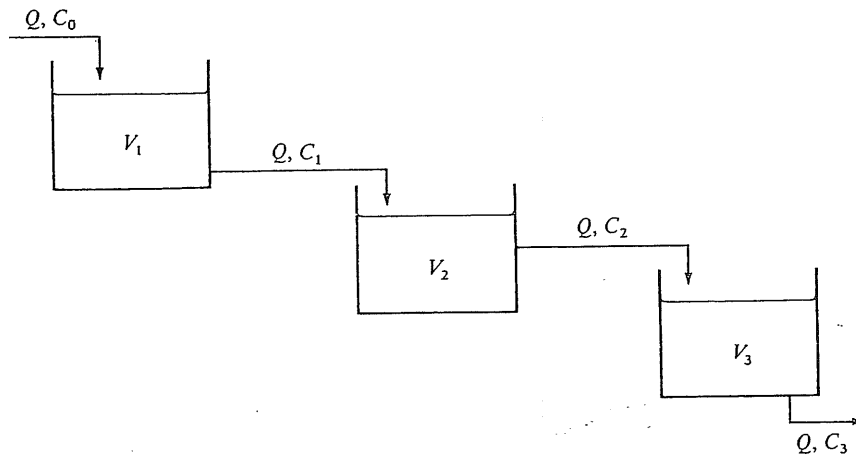
where  $x_n$  is the conversion in the effluent from the  $n$ th reactor and  $\bar{\theta}_i = V_i/Q$  is the mean residence time in the  $i$ th reactor.

Graphical methods can be used to obtain the conversion from a series of reactors and have the advantage of displaying the concentration in each reactor. Moreover, no additional complications are introduced when the rate equation is not first order. As an illustration of the procedure consider three stirred-tank reactors in series, each with a different volume, operating as shown in Fig. 4-13a. The density is constant, so that at steady state the volumetric flow rate to each reactor is the same. The flow rate and reactant concentration of the feed ( $Q$  and  $C_0$ ) are known, as are the volumes of each reactor. We construct a graph of the rate of reaction  $r$  vs reactant composition. The curved line in Fig. 4-13b shows how the rate varies with  $C$  according to the rate equation, which may be of any order.

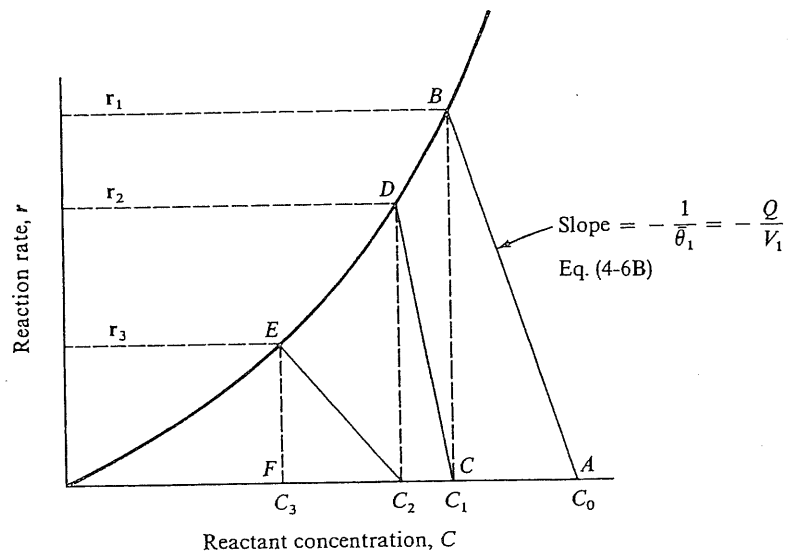
Equation (4-6) applied to the first stage is

$$\frac{V_1}{Q} = \bar{\theta}_1 = \frac{C_0 - C_1}{r_1}$$





(a)



(b)

Fig. 4-13 (a) Steady operation of three stirred-tank reactors in series.  
 (b) Graphical solution for stirred-tank reactors in series.

or

$$\frac{1}{\bar{\theta}_1} = \frac{r_1}{C_0 - C_1}$$

For a stirred-tank reactor,  $r_1$  and  $C_1$  will represent a point  $B$  on the rate line in Fig. 4-13b. If  $C_0$  is located on the abscissa of this figure (point  $A$ ), a straight line from that point to  $B$  will have a slope of  $r_1/(C_1 - C_0) = -r_1/(C_0 - C_1)$ . From the equation above, this slope is equal to  $-Q/V_1$ , which is known. Hence the conditions in the effluent stream from the first reactor can be found by constructing a straight line from point  $A$  with a slope of  $-Q/V_1$  and noting the point at which it intersects the rate curve.

The second stage is constructed by locating  $C_1$  on the abscissa (point  $C$ ) and then drawing a straight line from  $C$  with a slope of  $-Q/V_2$ . The intersection of this line with the reaction curve (point  $D$ ) establishes the effluent concentration  $C_2$  from the second reactor. Similar construction for the third reactor is shown in Fig. 4-13b.

#### 4-7 Comparison of Stirred-tank and Tubular-flow Reactors

The stirred-tank reactor has certain advantages because of the uniform temperature, pressure, and composition attained as a result of mixing. As mentioned, it is possible to operate such a reactor under isothermal conditions even when the heat of reaction is high—an impossibility in the long tubular type. When operation within a small temperature range is desired, for example, to minimize side reactions or avoid unfavorable rates, the opportunity for isothermal operation at the optimum temperature is a distinct advantage. Stirred-tank reactors, by virtue of their large volumes (and hence their large  $V/F$  values) provide a long residence time, which, combined with the isothermal nature of the reactor, permits operation at the optimum temperature for a long reaction time. For rate equations of certain types the selectivity in multiple reactions may be greater in tank reactors than in tubular-flow reactors for the same residence time. For other forms of the rate equations the reverse is true. Examples later in this section illustrate this point.

Efficient stirred-tank reactors are difficult to construct for gaseous systems because of the mixing problem. Fixed baffles and mechanical stirrers can be used, but these do not ensure complete mixing. Hence stirred-tank equipment is generally restricted to liquid systems.

For high-pressure reactions it is usually necessary, because of cost

considerations, to use small-diameter tubular reactors rather than tank types. Tank reactors that are to be operated at high pressures require a large wall thickness and complex sealing arrangements for the mixer shaft, factors which increase both initial and maintenance costs. Stirred-tank performance may be achieved in a recycle form of tubular-flow reactor, as illustrated in Fig. 1-3a. The diameter may be minimized for high-pressure operation by constructing the reactor in the form of a closed loop of tubing with entrance and exit connections and with a recycle pump in the loop.

The rate of heat transfer per unit mass of reaction mixture is generally lower in the conventional tank type than in a small-diameter tubular reactor, chiefly because of the lower ratio of surface area (available for heat transfer) to volume in the tank reactors and their lower heat-transfer coefficients. So, in instances where the heat of reaction is high it may be desirable to use a tubular reactor. For example, various thermal reactions of hydrocarbons require significant amounts of thermal energy at an elevated temperature level. This would be difficult to accomplish with a large-diameter reactor because of the limited external heat-transfer surface (per unit mass of reaction mixture) and the low coefficient of heat transfer from the oil in the tank to the tank wall. In the tubular reactors (pipe stills) used in industry the coefficient of heat transfer can be increased by forcing the oil through the tubes at a high speed. It is also apparent that severe difficulties would arise in attempting to provide for efficient stirring under reaction conditions (800 to 1200°F, 300 to 800 psia). The tubular-loop reactor operated at high circulation rates can give complete mixing in a small-diameter tube and high rates of heat transfer. By introducing small solid particles that are free to move, a type is obtained in which there is considerable mixing. Such fluidized-bed reactors also give improved heat-transfer coefficients between the fluid and the wall.

In general, then, stirred-tank reactors have been used mainly for liquid-phase reaction systems at low or medium pressures. Stirred-tank reactors can be used when the heat of reaction is high, but only if the temperature level obtained in their isothermal operation is satisfactory from other standpoints. If the reactions involved are endothermic and a high temperature is required, tubular reactors are usually indicated. However, a tank type may be employed for a highly exothermic reaction. For example, the production of hexamethylenetetramine by reacting ammonia and formaldehyde (in aqueous solution) is highly exothermic, but the rate of reaction is rapid and 100% conversion is possible over a range of temperature of at least 80 to 100°C. By adjusting the rate of feed and reactor volume, it is possible to add the feed at 20°C and remove enough heat to keep the reaction mixture below 100°C.

Denbigh and coworkers<sup>1</sup> have discussed the advantages and disadvantages of continuous-stirred-tank reactors, especially in comparison with batch-operated tank reactors. Stead, Page, and Denbigh<sup>2</sup> describe experimental techniques for evaluating rate equations from stirred-tank data. In stirred-tank equipment the reaction occurs at a rate determined by the composition of the exit stream from the reactor. Since the rate generally decreases with the extent of conversion, the tank reactor operates at the lowest point in the range between the high rate corresponding to the composition in the reactor feed and the low rate corresponding to the exit composition. In the tubular type maximum advantage is taken of the high rates corresponding to low conversions in the first part of the reactor. This means that the tank reactor must have a larger volume for a given feed rate (larger  $V/F$  value). Of course, this reasoning does not take into account the effects of side reactions or temperature variations; these may offset this disadvantage of the tank reactor, as illustrated in Example 5-3. Also, the total volume required in a tank-flow reactor can be reduced by using several small units in series.

The relation between volumes required in stirred-tank and tubular-flow reactors can be illustrated by reference to a constant-density first-order reaction. Equation (4-6) is applicable for the stirred-tank reactor and gives

$$\frac{V}{Q} = \frac{C_0 - C}{r} = \frac{C_0 - C}{kC}$$

or

$$x = \frac{C_0 - C}{C_0} = \frac{k(V_s/Q)}{1 + k(V_s/Q)} \quad (4-7)$$

For the tubular-flow case Eq. (4-4) can be used:

$$\frac{V_p}{Q} = C_0 \int \frac{dx}{r} = C_0 \int_0^x \frac{dx}{kC_0(1-x)} = \frac{-1}{k} \ln(1-x)$$

or

$$x = 1 - e^{-k(V_p/Q)} \quad (4-8)$$

<sup>1</sup>K. G. Denbigh, *Trans. Faraday Soc.*, **40**, 352 (1944), **43**, 648 (1947); K. G. Denbigh, M. Hicks, and F. M. Page, *Trans. Faraday Soc.*, **44**, 479 (1948).

<sup>2</sup>B. Stead, F. M. Page, and K. G. Denbigh, *Disc. Faraday Soc.*, **2**, 263 (1947).

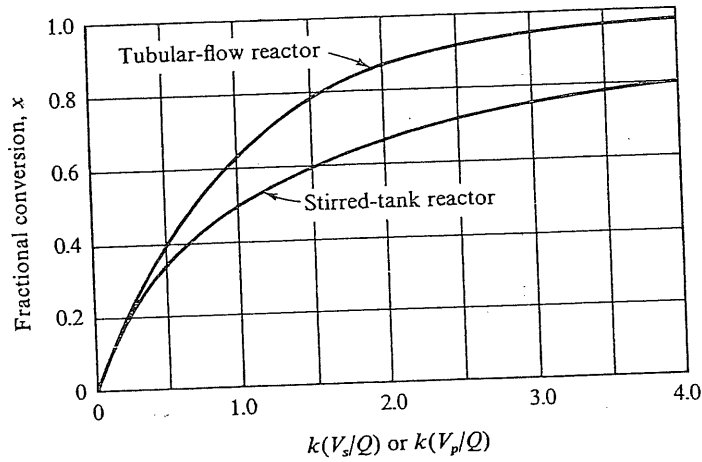
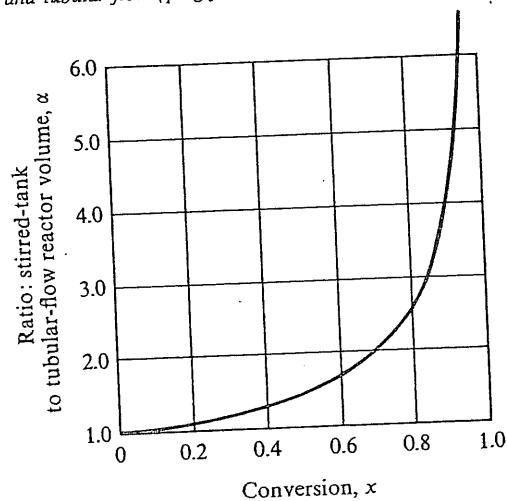


Fig. 4-14 Conversion in stirred-tank and tubular-flow (plug-flow) reactors

Equations (4-7) and (4-8) are plotted in Fig. 4-14 as conversion vs  $k(V/Q)$ . For equal flow rates  $k(V/Q)$  is proportional to the volume. It is clear that for any conversion the volume required is largest for the tank reactor and that the difference increases with residence time. We can obtain a direct measure of the ratio of volume  $V_s$  of the stirred-tank reactor to volume  $V_p$  of the tubular-flow (plug-flow) reactor at the same conversion by equating Eqs. (4-7) and (4-8).

Fig. 4-15 Ratio of volumes required for stirred-tank and tubular-flow (plug-flow) reactors



$$\frac{V_s/Q}{1 + k(V_s/Q)} = 1 - e^{-k(V_p/Q)}$$

If  $\alpha$  is the ratio of volumes,  $\alpha = V_s/V_p$ , then the previous equation can be written in terms of  $V_p$  and  $\alpha$ .

$$\frac{\alpha k(V_p/Q)}{1 + \alpha k(V_p/Q)} = 1 - e^{-k(V_p/Q)} \quad (4-9)$$

If we now replace  $k(V_p/Q)$  in Eq. (4-9) with the function of  $x$  from Eq. (4-8) and solve for  $\alpha$ , we have the ratio of volumes as a function of conversion,

$$\alpha = \frac{x}{(x-1) \ln(1-x)} \quad (4-10)$$

This result is plotted in Fig. 4-15 and shows that at low conversions there is little to be gained in using a tubular-flow reactor, but at conversions of 70% or larger more than twice as much volume is required for a stirred-tank unit.

Selectivity may also be different in stirred-tank and tubular-flow reactors. It has been shown<sup>1</sup> that, depending on the kinetics and nature of the multiple reactions, selectivity obtained in a stirred-tank reactor may be less, the same as, or greater than that for a tubular-flow reactor. Examples of reaction systems for each result are given in Table 4-12. The order of

Table 4-12 Effect of mixing on selectivity for various types of reaction systems

Reaction system	Reaction type	Overall selectivity*
1. $A \rightarrow B$ $B \rightarrow D$	Consecutive (first order)	$S_S < S_p$ (selectivity of $B$ with respect to $D$ )
2. $A + B \rightarrow R$ $A + R \rightarrow S$	Consecutive (second order)	$S_S < S_p$ (selectivity of $R$ with respect to $S$ )
3. $A \rightarrow B$ $A \rightarrow C$	Parallel (equal, first order)	$S_p = S_S$ (selectivity of $B$ with respect to $C$ )
4. $A + B \rightarrow C$ $A + B \rightarrow D$	Parallel (equal, second order)	$S_p = S_S$ (selectivity of $C$ with respect to $D$ )
5. $A + B \rightarrow C$ $2A \rightarrow D$	Parallel (unequal order with respect to $A$ )	$S_S > S_p$ (selectivity of $C$ with respect to $D$ )

\*Selectivity, as defined in Chap. 2, is the ratio of the yield of one product to that of another  
<sup>1</sup>T. E. Corrigan, G. A. Lessells, and M. J. Dean, *Ind. Eng. Chem.*, 60, 62 (1968).

the rate equation is assumed to follow the stoichiometry for each reaction. Since the stirred-tank reactor corresponds to complete mixing and the tubular-flow unit to no axial mixing, the table shows the effect of mixing upon selectivity. The following example illustrates the method of establishing the conclusions given in Table 4-12.

- **Example 4-10** Develop equations for the selectivity of product  $B$  with respect to  $D$  for reaction system 1 of Table 4-12 for stirred-tank and tubular-flow reactors. Assume isothermal conditions and constant density. In the feed  $[A] = [A]_0$  and  $[B] = [D] = 0$ .

*Solution* The reaction sequence is



In Sec. 2-10 this system was analyzed for a constant-density batch reactor. Since the tubular-flow reactor will have the same performance (see Sec. 4-4), the results in Sec. 2-10 can be applied here if  $t$  is replaced with the residence time  $V/Q$ . Hence the overall selectivity for a tubular-flow reactor is given by the ratio of Eqs. (2-106) and (2-107). Since  $[A]/[A]_0 = 1 - x_p$ , this ratio is

$$S_p = \frac{x_B}{x_D} = \frac{[k_1/(k_1 - k_3)][(1 - x_t)^{k_3/k_1} - (1 - x_t)]}{[k_1/(k_1 - k_3)][1 - (1 - x_t)^{k_3/k_1}] - [k_3/(k_1 - k_3)]x_t} \quad (\text{A})$$

For the stirred-tank case Eq. (4-6) may be written for components  $A$ ,  $B$ , and  $D$  as follows:

$$\bar{\theta} = \frac{V}{Q} = \frac{[A]_0 - [A]}{k_1[A]} \quad \text{or} \quad [A] = \frac{[A]_0}{1 + k_1\bar{\theta}} \quad (\text{B})$$

$$\bar{\theta} = \frac{V}{Q} = \frac{0 - [B]}{k_3[B] - k_1[A]} \quad \text{or} \quad [B] = \frac{k_1\bar{\theta}[A]}{1 + k_3\bar{\theta}} \quad (\text{C})$$

$$\bar{\theta} = \frac{V}{Q} = \frac{0 - [D]}{-k_3[B]} \quad \text{or} \quad [D] = k_3\bar{\theta}[B] \quad (\text{D})$$

From Eqs. (B) and (C),

$$\frac{[B]}{[A]_0} = x_B = \frac{k_1\bar{\theta}}{(1 + k_1\bar{\theta})(1 + k_3\bar{\theta})} \quad (\text{E})$$

Using this result in Eq. (D) gives

$$\frac{[D]}{[A]_0} = x_D = \frac{k_1\bar{\theta}k_3\bar{\theta}}{(1 + k_1\bar{\theta})(1 + k_3\bar{\theta})} \quad (\text{F})$$

Then the selectivity  $S_s$  in the stirred-tank reactor will be

$$S_s = \frac{x_B}{x_D} = \frac{1}{k_3\bar{\theta}} \quad (\text{G})$$

This result may be expressed in terms of the total conversion of  $A$  by noting, from Eq. (B), that

$$k_1 \bar{\theta} = \frac{[A]_0}{[A]} - 1 = \frac{x_t}{1 - x_t}$$

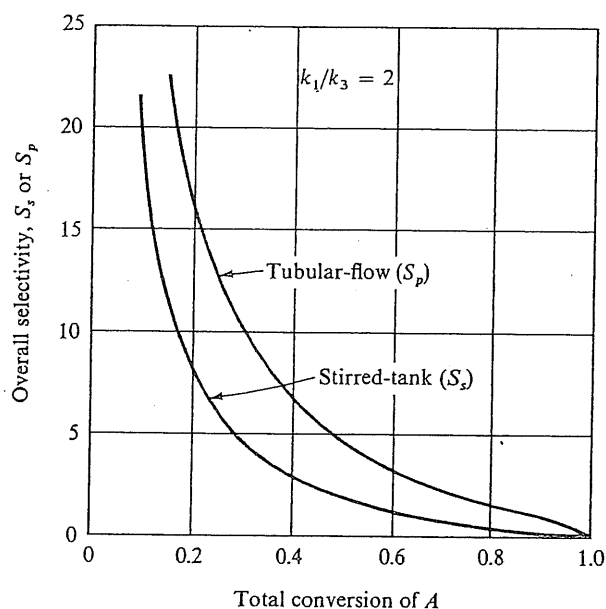
Using this result in Eq. (G) to eliminate  $\bar{\theta}$  gives

$$S_s = \frac{k_1}{k_3} \frac{1 - x_t}{x_t} \quad (\text{H})$$

Equations (A) and (H) can be employed to calculate  $S_p$  and  $S_s$  for any conversion. The results are shown in Fig. 4-16 for  $k_1/k_3 = 2$ . The *relative* position of the two curves would be the same for other values of  $k_1/k_3$ . Note that the selectivity of  $B$  with respect to  $D$  is greater in the tubular-flow reactor for all conversions, although the difference approaches zero as the conversion approaches zero.

Table 4-12 compares selectivities for *single* reactors. For some reaction systems a combination of stirred-tank and tubular-flow units may give higher selectivities than a single reactor of the same total volume. The combinations of number and arrangement of reactors and reaction systems are huge. However, the approach to selectivity evaluation is always the same and follows the methods described in Example 4-10. A simple illus-

Fig. 4-16 Selectivity for consecutive reactions in stirred-tank and tubular-flow reactors





tration of the conversion obtained in a combination of reactors is given in the following example.

**Example 4-11** A dilute aqueous solution of acetic anhydride is to be hydrolyzed continuously at 25°C. At this temperature the rate equation is

$$r = 0.158C, \text{ g mole}/(\text{cm}^3)(\text{min})$$

where  $C$  is the concentration of anhydride, in gram moles per cubic centimeter. The feed rate to be treated is 500 cm<sup>3</sup>/min of solution, with an anhydride concentration of  $1.5 \times 10^{-4}$  g mole/cm<sup>3</sup>.

There are two 2.5-liter and one 5-liter reaction vessels available, with excellent agitation devices.

(a) Would the conversion be greater if the one 5-liter vessel were used as a steady-flow tank reactor or if the two 2.5-liter vessels were used as reactors in series? In the latter case all the feed would be sent to the first reactor and the product from that would be the feed to the second reactor.

(b) Would a higher conversion be obtained if the two 2.5-liter vessels were operated in parallel; that is, if 250 cm<sup>3</sup>/min of feed were fed to each reactor and then the effluent streams from each reactor joined to form the final product?

(c) Compare the conversions calculated in parts (a) and (b) with that obtainable in a tubular-flow reactor of 5-liter volume.

(d) Would the conversion be increased if a tank-flow reactor of 2.5 liters were followed with a 2.5-liter tubular-flow reactor?

Assume that the density of the solutions is constant and that operation is steady state.

*Solution* Since this is a first-order constant-density reaction, Eqs. (4-7) and (4-8) give the conversions for single-stirred-tank and ideal tubular-flow reactors in terms of residence time  $V/Q$ . For multiple-stirred-tank reactors Eq. (A) of Example (4-9) is applicable.

(a) For a single 5-liter vessel,  $\bar{\theta} = 5,000/500 = 10$  min. From Eq. (4-7),

$$x = \frac{0.158(10)}{1 + 0.158(10)} = 0.612$$

For two 2.5-liter reactors in series,

$$\bar{\theta}_1 = \bar{\theta}_2 = \frac{2,500}{500} = 5 \text{ min}$$

Substituting in Eq. (A) of Example 4-9 gives

$$x = 1 - \frac{1}{(1 + k\bar{\theta})^2} = 1 - \frac{1}{[1 + 0.158(5)]^2} = 0.688$$

(b) For a 2.5-liter reactor with a feed rate of 250 cm<sup>3</sup>/min,  $\bar{\theta} = 10$  min. Hence the conversion will be the same as for the 5-liter reactor with  $Q = 500$  cm<sup>3</sup>/min, that is, 0.612.

(c) For a single tubular-flow reactor, from Eq. (4-8),

$$x = 1 - e^{-0.158(5,000/500)} = 1 - 0.206 = 0.794$$

(d) In the first reactor  $\bar{\theta}_1 = 2,500/500 = 5$  min. Hence the conversion in the product stream from the first reactor will be

$$x_1 = \frac{k\bar{\theta}_1}{1 + k\bar{\theta}_1} = \frac{0.158(5)}{1 + 0.158(5)} = 0.442$$

When the feed stream to a tubular-flow reactor is  $x_1$  rather than zero, integration of Eq. (4-5) gives

$$\theta = C_0 \int_{x_1}^{x_2} \frac{dx}{r} = C_0 \int_{x_1}^{x_2} \frac{dx}{kC_0(1-x)} = -\frac{1}{k} [\ln(1-x_2) - \ln(1-x_1)]$$

or

$$x_2 = 1 - (1 - x_1)e^{-k\theta}$$

The residence time in the second tubular-flow reactor is also 5 min. With a feed of conversion  $x_1 = 0.442$ , the final conversion would be

$$x_2 = 1 - (1 - 0.442)e^{-0.158(5)} = 1 - 0.254 = 0.746$$

The various results, arranged in order of increasing conversion, are shown in Table 4-13.

Table 4-13

Type	Conversion, %
Single-stirred tank (5 liters)	61.2
Two stirred tanks in parallel (each 2.5 liters)	61.2
Two stirred tanks in series (each 2.5 liters)	68.8
Stirred tank followed by tubular- flow reactor (each 2.5 liters)	74.6
Single tubular-flow reactor (5 liters)	79.4

In the previous example increasing the number of stirred-tank reactors from one to two (with the same total residence time) caused an increase in conversion from 61.2% to 68.8%. Further increase in number of tank reactors in series would lead to a maximum conversion of 79.4%, the value for a tubular-flow reactor with the same residence time. Thus an infinite number of stirred-tank reactors in series is equivalent to a tubular-flow reactor, provided the total residence time is the same. This may be

demonstrated by comparing Eq. (4-8) with Eq. (A) of Example 4-9, which is applicable for equal residence time in each stirred tank. For a total residence time of  $\bar{\theta}_t$ , Eq. (A) becomes

$$x = 1 - \frac{1}{(1 + k\bar{\theta}_t/n)^n} \quad (4-11)$$

It is known that

$$\lim_{n \rightarrow \infty} \left(1 + \frac{\alpha}{n}\right)^n = e^\alpha$$

If we use this result with  $\alpha = k\bar{\theta}_t$ , Eq. (4-11) becomes

$$x = 1 - e^{-k\bar{\theta}_t}$$

which is the same as Eq. (4-8).

#### 4-8 Non-steady-flow (Semibatch) Reactors

The semibatch reactor was defined in Chap. 3 (Fig. 3-1c) as a tank type operated on a non-steady-flow basis. Semibatch behavior occurs when a tank-flow reactor is started up, when its operating conditions are changed from one steady state to another, or when it is shut down. Purging processes in which an inert material is added to the reactor can also be classified as semibatch operation.

In addition to applications arising from short-period deviations from steady state, the semibatch reactor often is used for its own particular characteristics. For example, it is sometimes advantageous to add all of one reactant initially and then add the other reactant continuously. When the heat of reaction is large, the energy evolution can be controlled by regulating the rate of addition of one of the reactants. In this way the poor heat-transfer characteristic of tank reactors can be partially eliminated. This form of operation also allows for a degree of control of concentration of the reaction mixture, and hence rate of reaction, that is not possible in batch or continuous-flow reactors. Another example is the case in which the reactants are all added initially to the vessel but one of the products is removed continuously, as in the removal of water by boiling in esterification reactions. The advantage here is an increase in rate, owing to the removal of one of the products of a reversible reaction and to increased concentrations of reactants.

The mass-balance equations for semibatch operation may include all four of the terms in the general balance, Eq. (3-1). The feed and withdrawal streams from the reactor cause changes in the composition and volume of

the reaction mixture, in addition to the changes due to the reaction itself. Many operating alternatives exist. Frequently numerical solution is required because of the complicated form of the mass balance. After a discussion of general equations, this class of design problem will be illustrated with two specific examples. Here again ideal reactor performance (complete mixing) is assumed.

In general the conversion of reactant is not a very useful term for semibatch operation because when reactant is present initially in the reactor and is added and deleted in feed and exit streams, there may be ambiguity about the total amount upon which to define  $x$ . Instead we shall formulate Eq. (3-1) in terms of the mass fraction  $w$  of reactant. If  $F_0$  is the total mass feed rate and  $F_1$  is the withdrawal rate, the mass balance for the reactant is

$$F_0 w_0 - F_1 w_1 - rV = M \frac{d(VC_1)}{dt} \quad (4-12)$$

where  $C_1$  is the molal concentration of reactant in the reactor and  $M$  is the molecular weight of reactant. Alternately, the term on the right side for the accumulation could be expressed as  $d(m, w_1)/dt$  where  $m$ , is the total mass in the reactor.

If the feed-stream conditions and the initial state in the reactor are known, Eq. (4-12) can always be integrated, although numerical procedures may be required. An important case in which analytical integration is possible is when the feed and exit flow rates, feed composition, and density are all constant and the reaction is first order. Piret and Mason<sup>1</sup> have analyzed single and cascades (reactors in series) of stirred-tank reactors operating under these restrictions. The results are a reasonable representation of the behavior for many systems under startup and shutdown periods. With constant density, the concentration accounts fully for changes in amount of reactant. Also, constant density along with constant flow rates means that the reactor volume  $V$  will remain constant. Under these restrictions Eq. (4-12) may be written

$$QC_0 - QC_1 - rV = V \frac{dC_1}{dt}$$

or

$$C_0 - C_1 - r\bar{\theta} = \bar{\theta} \frac{dC_1}{dt} \quad (4-13)$$

If the rate is first order and the temperature is constant, Eq. (4-13)

<sup>1</sup>D. R. Mason and E. L. Piret, *Ind. Eng. Chem.*, 42, 817 (1950); *Ind. Eng. Chem.*, 43, 1210 (1951).

is a linear differential equation which can be integrated analytically. In terms of  $\bar{\theta}$ , it may be written

$$\frac{dC_1}{dt} + \left( \frac{1}{\bar{\theta}} + k \right) C_1 = \frac{C_0}{\bar{\theta}} \quad (4-14)$$

where  $k$  is the first-order rate constant.

**Example 4-12** Acetic anhydride is hydrolyzed at 40°C in a semibatch system operated by initially charging the stirred-tank reactor with 10 liters of an aqueous solution containing  $0.50 \times 10^{-4}$  g mole anhydride/cm<sup>3</sup>. The vessel is heated to 40°C, and at that time a feed solution containing  $3.0 \times 10^{-4}$  g mole anhydride/cm<sup>3</sup> is added at the rate of 2 liters/min. Product is withdrawn at the same rate. The density may be assumed constant, and the rate is

$$r = kC \quad \text{g moles/(cm}^3\text{)(min)}$$

$$k = 0.380 \text{ min}^{-1}$$

Determine the concentration of the solution leaving the reactor as a function of time.

*Solution* Equation (4-14) is applicable, and in this case  $C_0/\bar{\theta}$  is a constant. Thus

$$\bar{\theta} = \frac{V}{Q} = \frac{10,000}{2,000} = 5 \text{ min}$$

$$\frac{C_0}{\bar{\theta}} = \frac{3.00 \times 10^{-4}}{5} = 6 \times 10^{-5} \text{ g mole/(cm}^3\text{)(min)}$$

$$\frac{1}{\bar{\theta}} + k = \frac{1}{5} + 0.380 = 0.580 \text{ min}^{-1}$$

The integrated solution of Eq. (4-14) is

$$C_1 = \frac{C_0}{\bar{\theta}} \frac{1}{(1/\bar{\theta}) + k} + I e^{-(1/\bar{\theta} + k)t}$$

The constant of integration  $I$  may be obtained by noting that at  $t = 0$  and  $C_1 = 0.50 \times 10^{-4}$

$$\begin{aligned} I &= 0.50 \times 10^{-4} - \frac{C_0}{\bar{\theta}} \frac{1}{(1/\bar{\theta}) + k} \\ &= 0.50 \times 10^{-4} - \frac{6 \times 10^{-5}}{0.580} = -5.34 \times 10^{-5} \end{aligned}$$

Then the final expression for the product concentration is

$$\begin{aligned} C_1 &= \frac{6 \times 10^{-5}}{0.580} - 5.34 \times 10^{-5} e^{-0.58t} \\ &= 10.3 \times 10^{-5} - 5.34 \times 10^{-5} e^{-0.58t} \end{aligned}$$

Table 4-14 shows values of  $C_1$  for increasing time, measured from the instant of addition of the feed stream. These results indicate that after 5 min the reactor is operating at very nearly steady-state conditions. Hence, the concentration at this time could also be obtained directly from Eq. (4-6) for steady-state operation.

Table 4-14

$t$ , min	$C_1$ , g moles/cm <sup>3</sup>
0	$5.00 \times 10^{-5}$
1	$7.35 \times 10^{-5}$
2	$8.67 \times 10^{-5}$
3	$9.40 \times 10^{-5}$
5	$10.0 \times 10^{-5}$
$\infty$	$10.3 \times 10^{-5}$

Figure 4-17 shows a special type of semibatch reactor system in which there is a continuous feed, no withdrawal of product, and a mass  $(m_A)_i$  of component  $A$  initially in the reactor. The application of Eq. (4-12) will be considered for a reactor of this type when the rate equation is not first order and when the volume of the reaction mixture varies. Since there is no exit stream, Eq. (4-12) takes the form

$$F_0(w_A)_0 - rV = M_A \frac{d(V[A]_1)}{dt} \quad (4-15)$$

The rate  $r$  could be expressed in terms of the concentrations of the reactants and this equation integrated numerically for any rate function. However, in this case conversion has meaning, and concentration can be expressed in terms of this variable. Define  $x$  at any time  $t$  as the ratio of the amount of reactant  $A$  converted to the total amount of  $A$  added up to that time. Then the concentration of  $A$  in the reactor will be related to  $x$  by

$$[A]_1 = \frac{[(m_A)_i + F_0(w_A)_0 t](1 - x)}{M_A V} \quad (4-16)$$

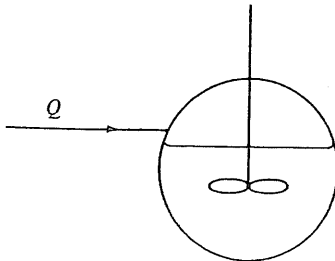


Fig. 4-17 Semibatch reactor with a feed, but no product, stream

and

$$d(V[A]_i) = \frac{1}{M_A} \{ -[(m_A)_i + F_0(w_A)_0 t] dx + (1 - x)F_0(w_A)_0 dt \}$$

Substituting this expression into Eq. (4-15) and simplifying leads to the result

$$F_0(w_A)_0 x dt + [(m_A)_i + F_0(w_A)_0 t] dx = rV dt \quad (4-17)$$

This is the mass balance from which the conversion may be computed at any time.

Note that if reactant  $A$  were not present in both the initial charge and the feed stream, one of the two terms on the left side of the equation would disappear. If there were no reactant  $A$  in the feed, the batch-reactor equation would be obtained. If there were no  $A$  in the initial charge to the reactor, the expression would become

$$F_0(w_A)_0 (x dt + t dx) = Vr dt \quad (4-18)$$

In general, the volume will vary with changes in both the mass and the density of the reaction mixture. However, for most systems, density changes will be small. With this restriction,

$$V = V_0 + \frac{F_0}{\rho} t \quad (4-19)$$

The rate of reaction is the other quantity that must be expressed in terms of  $x$  and  $t$  before the mass balance can be integrated. This may be accomplished by substituting expressions for the concentration, such as Eq. (4-16), into the normal form,  $r = f([A], [B], \dots)$ , of the rate equation.

The general procedure for designing the reactor is as follows:

1. The mass balance is first written in difference form,

$$[(m_A)_i + F_0(w_A)_0 t] \Delta x = [rV - F_0(w_A)_0 x] \Delta t \quad (4-20)$$

and the value of  $\Delta x$  is computed for a chosen time increment  $\Delta t$ . The average values of  $rV$  and  $x$  for the first  $\Delta t$  can be taken equal to the known values at  $t = 0$  as a first estimate.

2. The reactor volume at time  $\Delta t$  is computed from Eq. (4-19).
3. With the conversion computed in step 1 and the reactor volume  $V$  from step 2, the concentrations at the end of the first time increment are determined from equations such as Eq. (4-16).
4. The rate at the end of the first increment is evaluated from the concentrations established in step 2.
5. A second estimate of the average value of  $rV$  is determined from the

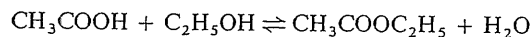
known values at the beginning and end of the increment.

6. Equation (4-20) is employed to calculate a second estimate of  $\Delta x$ .
7. This procedure is continued until the average values of  $rV$  do not change. Generally the second estimate is sufficient.
8. Subsequent time increments are chosen, and steps 1 to 7 are repeated.

This procedure follows the same pattern as that for stepwise solutions of design equations for simple batch and flow reactors. In each case all the quantities in the differential mass balance are functions of two variables, conversion and reactor volume for the flow case and conversion and time for the batch case.

**Example 4-13** The esterification of acetic acid and ethyl alcohol is to be carried out in a semibatch stirred-tank reactor at a constant temperature of 100°C. The alcohol is added initially as 400 lb of pure  $C_2H_5OH$ . An aqueous solution of acetic acid is then added at a rate of 3.92 lb/min for 120 min. The solution contains 42.6% by weight acid. Assume that the density is constant and equal to that of water.

The reaction is reversible, and the specific reaction rates may be taken as the same as those used in Example 4-2:



$$k = 4.76 \times 10^{-4} \text{ liter}/(\text{g mole})(\text{min})$$

$$k' = 1.63 \times 10^{-4} \text{ liter}/(\text{g mole})(\text{min})$$

Compute the conversion of acetic acid to ester as a function of time from  $t = 0$  until the last amount of acid is added (120 min).

**Solution** As the conversion is to be based on the acetic acid and there is no acid in the initial charge to the reactor, the proper design equation is Eq. (4-18). Since the rate constants are in molal units, the concentrations will also be expressed in those units.

If  $[H]$ ,  $[OH]$ ,  $[W]$ , and  $[E]$  represent acid, alcohol, water, and ester concentrations, in pound moles per cubic foot, equations similar to Eq. (4-16) for each component are

$$[H] = \frac{F_0(w_H)_0 t(1-x)}{M_H V} \quad [\text{analogous to Eq. (4-16), with } (m_A)_0 = 0]$$

$$[OH] = \frac{(1/M_{OH})(m_{OH})_i - xF_0(w_H)_0 t(1/M_H)}{V}$$

$$[W] = \frac{(1/M_W)F_0(w_W)_0 t + xF_0(w_H)_0 t(1/M_H)}{V}$$

$$[E] = \frac{xF_0(w_H)_0 t(1/M_H)}{V}$$

Substituting these expressions into the rate equations gives a relationship for the net rate of conversion of the acid in terms of  $x$ ,  $t$ , and  $V$ ,



$$r = \frac{k\{F_0(w_H)_0 t(1-x)[(m_{OH})_i(M_{OH}) - xF_0(w_H)_0 t/M_H]\}}{M_H V^2} - k' \frac{x F_0(w_H)_0 t [F_0(w_W)_0 t/M_W + x F_0(w_H)_0 t/M_H]}{M_H V^2} \quad (A)$$

where  $F_0 = 3.92$  lb/min

$$(w_H)_0 = 0.426$$

$$(m_{OH})_i = 400 \text{ lb}$$

$$(w_W)_0 = 1 - 0.426 = 0.574$$

$$M_H = \text{molecular weight acetic acid} = 60$$

$$M_{OH} = \text{molecular weight ethyl alcohol} = 46$$

$$M_W = \text{molecular weight water} = 18$$

The rate constants, expressed as  $\text{ft}^3/(\text{lb mole})(\text{min})$ , become

$$k = 4.76 \times 10^{-4} \frac{1}{28.32} (454) = 7.63 \times 10^{-3}$$

$$k' = 2.62 \times 10^{-3}$$

Substituting these results in Eq. (A) to obtain a working expression for the rate, in lb moles/ $(\text{ft}^3)(\text{min})$ , we have

$$r = \frac{1.28 \times 10^{-2} t(1-x)(8.68 - 0.0278xt)}{60V^2} - \frac{4.37 \times 10^{-3} t^2 x(0.125 + 0.0278x)}{60V^2}$$

or

$$r = \frac{1}{V^2} [21.3 \times 10^{-5} t(1-x)(8.68 - 0.0278xt) - 7.13 \times 10^{-5} t^2 x(0.125 + 0.0278x)] \quad (B)$$

Since the density is assumed constant, Eq. (4-19) is applicable and the reactor volume, in cubic feet, is

$$V = V_0 + \frac{F_0}{\rho} t = \frac{m_0 + F_0 t}{\rho} = \frac{400 + 3.92t}{59.8} = 6.69 + 0.0655t \quad (C)$$

Equation (4-18) may be written

$$F_0(w_H)_0 t dx = rVM_H dt - F_0(w_H)_0 x dt$$

or

$$3.92(0.426)t dx = rV(60) dt - 3.92(0.426)x dt$$

$$t dx = 35.9rV dt - x dt$$

In difference form this expression becomes

$$\Delta(xt) = 35.9(\bar{r}V)_a \Delta t \quad (D)$$

Equations (B), (C), and (D) may now be employed to carry out a stepwise solution. Since the concentration equations have been combined with the rate equation in expression (B), step 3 in the general procedure may be omitted. Let us carry out calculations for the first time increment in detail.

STEP 1 Choose an initial time increment of 5 min. The initial volume  $V$  is  $6.69 \text{ ft}^3$  (based on the density of water at  $100^\circ\text{C}$ ). The initial rate as computed from Eq. (B) is zero, since at  $t = 0$  there is no acid in the reactor. To obtain a reasonable estimate of  $(\bar{r}V)_a$  with which to start the computations, calculate  $r$  for an average  $t = \frac{\Delta t}{2} = 2.5$  min:

$$\begin{aligned} r &= \left(\frac{1}{6.69}\right)^2 [21.3 \times 10^{-5} (2.5)(1 - 0)(8.68 - 0) - 0] \\ &= 1.04 \times 10^{-4} \text{ lb mole}/(\text{ft}^3)(\text{min}) \end{aligned}$$

Hence the first estimate of  $(\bar{r}V)_a$  is

$$(\bar{r}V)_a = 1.04 \times 10^{-4} (6.69) = 6.94 \times 10^{-4}$$

From Eq. (D),

$$\Delta(tx) = 35.9(6.94 \times 10^{-4})(5) = 0.1250$$

$$t_1 x_1 - 0 = 0.1250$$

or  $x_1 = 0 + 0.0250 = 0.0250$

STEP 2 The reactor volume at the end of the first increment is given by Eq. (C) as

$$V_1 = 6.69 + 0.0655(5) = 7.02 \text{ ft}^3$$

STEP 4 The rate at the end of the increment is obtained from Eq. (B), with  $x = 0.0250$ ,  $t = 5$ , and  $V_1 = 7.02$ :

$$\begin{aligned} r &= \left(\frac{1}{7.02}\right)^2 [21.3 \times 10^{-5}(5) 0.975(8.68 - 0.003) \\ &\quad - 7.13 \times 10^{-5}(0.625)(0.125 + 0.0007)] \\ &= \frac{0.898 \times 10^{-2} - 0.56 \times 10^{-5}}{7.02^2} = 1.82 \times 10^{-4} \end{aligned}$$

STEP 5 At the end of the increment  $\bar{r}V = (1.82 \times 10^{-4})(7.02) = 12.8 \times 10^{-4}$ . At the beginning of the increment ( $t = 0$ )  $\bar{r}V = 0(6.69) = 0$ . Hence the second estimate of  $(\bar{r}V)_a$  is

$$(\bar{r}V)_a = \frac{12.8 \times 10^{-4} + 0}{2} = 6.40 \times 10^{-4}$$

STEP 6 The second estimate of  $\Delta x$  is given by Eq. (D),

$$\Delta(tx) = 35.9(6.40 \times 10^{-4})(5) = 0.115$$

STEP 7 Recalculation of  $(rV)_a$  will not change the value of  $6.40 \times 10^{-4}$  significantly. Hence at the end of the first increment

$$x_1 = \frac{0.115}{5} = 0.0230$$

$$V_1 = 7.02 \text{ ft}^3$$

$$r_1 = 1.82 \times 10^{-4} \text{ lb mole}/(\text{min})(\text{ft}^3)$$

$$(rV)_a = 12.8 \times 10^{-4}$$

For the second increment of 5 min, estimate  $(rV)_a = 18.0 \times 10^{-4}$ . Then the first estimate of  $\Delta x$  is

$$\Delta(tx) = 35.9(18.0 \times 10^{-4})(5) = 0.323$$

$$t_2x_2 - t_1x_1 = t_2x_2 - 0.115 = 0.323$$

$$x_2 = 0.0115 + 0.0323 = 0.0438$$

$$V_2 = 6.69 + 0.0655 \times 10 = 7.34 \text{ ft}^3$$

$$r_2 = \frac{1}{7.34^2} (1.71 \times 10^{-2} - 0.004 \times 10^{-2}) = 3.18 \times 10^{-4}$$

$$(rV)_2 = 23.3 \times 10^{-4}$$

$$(rV)_a = \frac{(12.8 + 23.3) \times 10^{-4}}{2} = 18.1 \times 10^{-4}$$

Since this result is close to the first estimate of  $18.0 \times 10^{-4}$ , further calculations of the rate are unnecessary. At the end of the second increment ( $t = 10$  min)

$$x_2 = 0.044$$

$$V_2 = 7.34 \text{ ft}^3$$

$$r_2 = 3.18 \times 10^{-4}$$

$$(rV)_2 = 23.3 \times 10^{-4}$$

The results for the entire time interval 0 to 120 min, determined by continuing these stepwise calculations,<sup>1</sup> are summarized in Table 4-15.

As has been mentioned, when reverse reactions are important, continuous removal of one or more of the reaction products will increase the conversion obtainable in a given time. Thus one reactant could be charged to the reactor, a second reactant could be added continuously, and one of

<sup>1</sup>This solution of the problem is approximate because of the assumption of constant density of the reaction mixture. However, if density-vs-composition data were available, the same stepwise method of calculation could be employed to obtain a more precise solution. Equation (C) would have to be modified to take into account density differences.

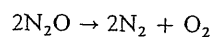
Table 4-15 Semibatch-reactor design for esterification of acetic acid with ethyl alcohol

$t$ , min	$V$ , ft <sup>3</sup>	Conversion of acid	$r$ , lb moles acid reacted/(min)(ft <sup>3</sup> )
0	6.69	0	0
5	7.02	0.023	$1.82 \times 10^{-4}$
10	7.34	0.044	$3.2 \times 10^{-4}$
20	8.00	0.081	$5.2 \times 10^{-4}$
40	9.31	0.138	$7.0 \times 10^{-4}$
60	10.6	0.178	$7.3 \times 10^{-4}$
80	11.9	0.205	$6.9 \times 10^{-4}$
100	13.2	0.224	$6.3 \times 10^{-4}$
120	14.5	0.237	$5.7 \times 10^{-4}$

the products could be withdrawn continuously.<sup>1</sup> This form of semibatch reactor can be treated by modifying the design equation (4-17), the volume equation (4-19), and the expressions for the concentration to take into account the withdrawal of material.

### Problems

- 4-1. Nitrous oxide decomposes approximately according to a second-order rate equation. The specific reaction rate in the forward direction,



is  $k = 977 \text{ cm}^3/(\text{g mole})(\text{sec})$  at  $895^\circ\text{C}$ . Calculate the fraction decomposed at 1.0 and 10 sec. and at 10 min in a constant-volume batch reactor. The rate of the reverse reaction is negligible and the initial pressure (all  $\text{N}_2\text{O}$ ) is 1 atm.

- 4-2. An aqueous solution of ethyl acetate is to be saponified with sodium hydroxide. The initial concentration of ethyl acetate is 5.0 g/liter and that of caustic soda is 0.10 normal. Values of the second-order rate constant, in liters/(g mole)(min), are

$$k = \begin{cases} 23.5 & \text{at } 0^\circ\text{C} \\ 92.4 & \text{at } 20^\circ\text{C} \end{cases}$$

The reaction is essentially irreversible. Estimate the time required to saponify 95% of the ester at  $40^\circ\text{C}$ .

- 4-3. It has been mentioned that gaseous reactions are more suitably carried out on a commercial scale in flow equipment than in batch reactors. Consider the following example. Watson<sup>2</sup> has studied the thermal (noncatalytic) cracking of

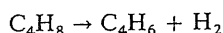
<sup>1</sup>This withdrawal might be accomplished by distillation, for example.

<sup>2</sup>K. M. Watson, *Chem. Eng. Progr.*, **44**, 229 (1948).

butenes at 1 atm pressure in a flow reactor. The rate equation determined from his experimental data is

$$\log k_1 = -\frac{60,000}{4.575T} + 15.27$$

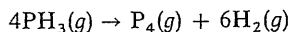
where  $k_1$  = butenes cracked, g moles/(hr)(liter)(atm), and  $T$  is in degrees Kelvin. Although the feed consists of a number of different butenes and the products vary from coke to butadiene, the irreversible reaction may be considered as a first-order one,



It is desired to crack butenes in a batch-type reactor which will operate at 1200°F and will be equipped for efficient agitation. The initial charge to the reactor will consist of 1 lb mole of butenes and 10 lb moles of steam. Under these conditions the change in total moles during the course of the reaction can be neglected. (a) Determine the time required for a conversion of 30% of the butenes. (b) Determine the reactor volume required.

(c) Suppose that the feed consists of 10 moles of steam per mole of hydrocarbon, as before, but this time the hydrocarbon fraction contains 60 mole % butenes and 40% butadiene. The butadiene may undergo two reactions: cracking and polymerization to the dimer. Assuming that the rates of these reactions are known, outline a method of determining the conversion of butenes and of butadiene for a given reaction time.

- 4.4. The decomposition of phosphine is irreversible and first order at 650°C,



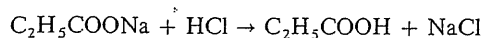
The rate constant ( $\text{sec}^{-1}$ ) is reported as

$$\log k = -\frac{18,963}{T} + 2 \log T + 12.130$$

where  $T$  is in degrees Kelvin. In a closed vessel (constant volume) initially containing phosphine at 1 atm pressure, what will be the pressure after 50, 100, and 500 sec. The temperature is maintained at 650°C.

- 4-5. A first-order homogeneous gas-phase reaction,  $A \rightarrow 3R$ , is first studied in a constant-pressure batch reactor. At a pressure of 2 atm and starting with pure  $A$ , the volume increases by 75% in 15 min. If the same reaction is carried out in a constant-volume reactor, and the initial pressure is 2 atm, how long is required for the pressure to reach 3 atm?
- 4-6. Suppose the initial mixture in Prob. 4-5 consisted of 70 mole %  $A$  and 30 mole % helium (inert) at a total pressure of 2 atm. In a constant-pressure reactor, what would be the increase in volume in 15 min?
- 4-7.<sup>1</sup> A stage in the production of propionic acid,  $\text{C}_2\text{H}_5\text{COOH}$ , is the acidification of a water solution of the sodium salt according to the reaction

<sup>1</sup>From W. F. Stevens, "An Undergraduate Course in Homogeneous Reaction Kinetics," presented at Fourth Summer School for Chemical Engineering Teachers, Pennsylvania State University, June 27, 1955.



The reaction rate may be represented by a second-order reversible equation. Laboratory data on the rate of reaction are obtained by taking 10-ml samples of the reaction solution at varying times and neutralizing the unreacted HCl with 0.515-normal NaOH. The original amount of acid is determined from a sample taken at zero time. The temperature is 50°C, and the initial moles of HCl and C<sub>2</sub>H<sub>5</sub>COONa are the same. The data are as follows:

<i>t</i> , min	0	10	20	30	50	∞
NaOH required, ml	52.5	32.1	23.5	18.9	14.4	10.5

Determine the size of an agitated batch reactor to produce propionic acid at an average rate of 1,000 lb/hr. Twenty minutes is required for charging the reactor and heating to 50°C, and 10 min is necessary for cooling and removing the products. The final conversion is to be 75% of the sodium propionate. The initial charge to the reactor will contain 256 lb of C<sub>2</sub>H<sub>5</sub>COONa and 97.5 lb of HCl per 100 gal. Assume that the density of the reaction mixture is 9.9 lb/gal and remains constant.

- 4-8. The production of carbon disulfide from methane and sulfur vapor can be carried out homogeneously or with a solid catalyst. Also, some solid materials act as a poison, retarding the reaction. The following data were obtained on a flow basis at a constant temperature of 625°C and with an initial reactants ratio of 1 mole of CH<sub>4</sub> to 2 moles of sulfur vapor (considered as S<sub>2</sub>). The first set of data was obtained with the reactor empty (effective volume 67.0 ml), and the second set was obtained after packing the reactor with a granular material (7 mesh) which reduced the void volume to 35.2 ml.

Set	Run	Feed rate, g moles/hr		Production of CS <sub>2</sub> , g moles/hr	Conversion of methane
		CH <sub>4</sub>	S <sub>2</sub>		
1	1	0.417	0.834	0.0531	0.127
	2	0.238	0.476	0.0391	0.164
	3	0.119	0.238	0.0312	0.262
2	1	0.119	0.238	0.0204	0.171
	2	0.178	0.357	0.0220	0.123

Was the granular material acting as a catalyst or as a poison in this case?

- 4-9. Butadiene and steam (0.5 mole steam/mole butadiene) are fed to a tubular-flow reactor which operates at 1180°F and a constant pressure of 1 atm. The reactor is noncatalytic. Considering only the reversible polymerization reaction to the dimer, determine (a) the length of 4-in.-ID reactor required to obtain a conversion of 40% of the butadiene with a total feed rate of 20 lb moles/hr and (b) the space velocity, measured as (liters feed gas)/(hr)(liters reactor volume) (at 1180°F and 1 atm), required to obtain a conversion of 40%.

The polymerization reaction is second order and has a specific reaction-rate constant given by

$$\log k = -\frac{5,470}{T} + 8.063$$

where  $k$  is  $C_4H_6$  polymerized, in g moles/(liter)(hr)(atm<sup>2</sup>), and  $T$  is in degrees Kelvin. The reverse (depolymerization) reaction is first order. At 1180°F (911°K) the equilibrium constant for the reaction is 1.27.

- 4-10. A mixture of butenes and steam is to be thermally (noncatalytically) cracked in a tubular-flow reactor at a constant temperature of 1200°F and a constant pressure of 1.0 atm. Although the feed consists of a number of different butenes<sup>1</sup> and the products vary from coke to butadiene, the rate of reaction may be adequately represented by the first-order mechanism

$$r_1 = \frac{\epsilon}{\rho} k_1 p_4$$

$$\log k_1 = -\frac{60,000}{4.575T} + 15.27$$

The rate was determined experimentally in a reactor packed with inert quartz chips, and the reactor to be designed in this problem will also be so packed. The data and notation are as follows:

$r_1$  = g moles butenes cracked/(g quartz chips)(hr)

$\epsilon$  = void fraction = 0.40

$\rho$  = bulk density of bed packed with quartz chips = 1,100 g/liter

$p_4$  = partial pressure of butenes, atm

$T$  = temperature, °K

The ratio of steam to butenes entering the reactor will be 10:1.0 on a molal basis. Under these conditions the change in total number of moles during the course of the reaction can be neglected.

(a) Determine the conversion as a function of size of reactor. Also prepare a plot of conversion of butenes versus two abscissas: (1) lb quartz chips/lb mole butene feed per hr, covering a range of values from 0 to 3,000, and (2) space velocity, defined as (ft<sup>3</sup> feed)/(hr)(ft<sup>3</sup> void volume) at 1200°F. What total volume of reactor would be required for a 20% conversion with a butenes feed rate of 5 lb moles/hr?

(b) Suppose that the feed consists of 10 moles of steam per mole of total hydrocarbons. The hydrocarbon fraction is 60 mole % butenes and 40 mole % butadiene. Consider that the butenes react as in (a) and that the butadiene may undergo two reactions, cracking and polymerization to the dimer. The rate for cracking is

$$r_2 = \frac{\epsilon}{\rho} k_2 p_4'$$

$$\log k_2 = -\frac{30,000}{4.575T} + 7.241$$

<sup>1</sup>See *Chem. Eng. Progr.*, 44, 229 (1948).

where  $r_2$  is butadiene cracked, in g moles/(g quartz chips)(hr), and  $p_4''$  is partial pressure of butadiene, in atmospheres; the rate for polymerization to the dimer is

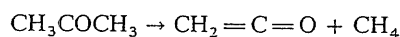
$$r_3 = \frac{\epsilon}{\rho} k_3 (p_4'')^2$$

$$\log k_3 = -\frac{25,000}{4.575T} + 8.063$$

where  $r_3$  is butadiene polymerized, in g moles/(g quartz chips)(hr).

Determine the conversion of butenes and of butadiene as a function of  $W/F$  from 0 to 3,000 lb chips/(lb mole feed per hour). Assume that the total number of moles is constant and neglect all reactions except those mentioned.

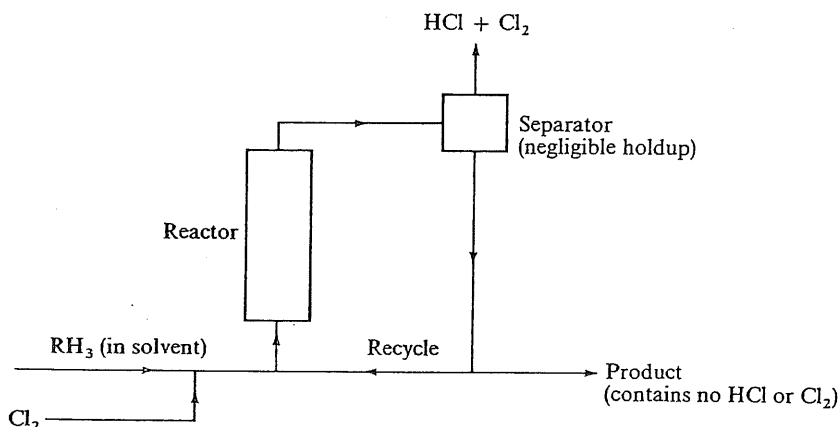
- 4-11. The following conversion data were obtained in a tubular-flow reactor for the gaseous pyrolysis of acetone at 520°C and 1 atmosphere. The reaction is



Flow rate, g/hr	130.0	50.0	21.0	10.8
Conversion of acetone	0.05	0.13	0.24	0.35

The reactor was 80 cm long and had an inside diameter of 3.3 cm. What rate equation is suggested by these data?

- 4-12. A small pilot plant for the photochlorination of hydrocarbons consists of an ideal tubular-flow reactor which is irradiated, and a recycle system, as shown in the sketch. The HCl produced is separated at the top of the reactor, and the liquid stream is recycled. The  $\text{Cl}_2$  is dissolved in the hydrocarbon (designated as  $\text{RH}_3$ ) before it enters the reactor. It is desired to predict what effect the type of reactor operation will have on the ratio  $[\text{RH}_2\text{Cl}]/[\text{RHCl}_2]$  in the product stream. Determine this ratio, as a function of total conversion of  $\text{RH}_3$ , for two





extremes: zero reflux ratio (ratio of recycle flow rate to product-stream flow rate) and infinite reflux ratio. The concentration of hydrocarbon in the feed entering the reactor is  $[RH_3]_0$ . The hydrocarbon is dissolved in an inert solvent in which  $Cl_2$  is also soluble. There is a stoichiometric excess of  $Cl_2$  fed to the reactor. The reactor operates isothermally, and the HCl product remains in solution until it reaches the separator at the top of the reactor.

Plot curves of  $[RH_2Cl]/[RHCl_2]$  vs conversion for each of the conditions and for three types of kinetics. The reactions are

1.  $RH_3 + Cl_2 \rightarrow RH_2Cl + HCl$
2.  $RH_2Cl + Cl_2 \rightarrow RHCl_2 + HCl$

The three types of kinetics are as follows:

- (a) First order (with equal rate constants), so that the rates of production, in g moles/(vol)(time), are

$$r_{RH_3} = -k_1[RH_3]$$

$$r_{RH_2Cl} = k_1[RH_3] - k_1[RH_2Cl]$$

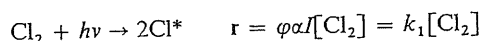
- (b) Second order (with equal rate constants),

$$r_{RH_3} = -k_2[RH_3][Cl_2]$$

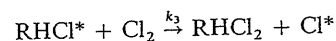
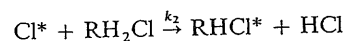
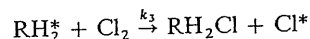
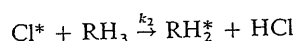
$$r_{RH_2Cl} = k_2[RH_3][Cl_2] - k_2[RH_2Cl][Cl_2]$$

- (c) Chain kinetics, for which the *elementary* steps are

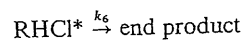
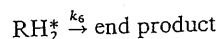
INITIATION



PROPAGATION



TERMINATION



In solving the problem for this case, use the stationary-state hypothesis for the intermediates (free radicals  $Cl^*$ ,  $RH_2^*$ ,  $RHCl^*$ ) to obtain rate equations for  $r_{RH_3}$  and  $r_{RH_2Cl}$  analogous to the rate equations for the first-order and second-order cases. Note that the rate constant for the termination steps is usually much less than that for the propagation steps.

- 4-13. A homogeneous liquid-phase polymerization is carried out in a completely mixed stirred-tank reactor which has an average residence time of 33.6 sec. The concentration of monomer in the feed stream is  $1.0 \times 10^{-3}$  g mole/cm<sup>3</sup>. The polymerization reactions follow a two-step process:

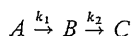
1. An initiation reaction producing an active form of the monomer,  $P_1$ . This reaction has a rate constant  $k_i = 0.10 \text{ sec}^{-1}$ .
2. Propagation reactions, where the monomer reacts with successive polymers of the form  $P_n$ . These are all second order with the same rate constant,  $k_p = 500 \text{ cm}^3/(\text{g mole})(\text{sec})$ .

(a) Of the total polymer content of the exit stream, what is the weight-fraction distribution of polymer molecules from  $P_1$  to  $P_{10}$ ? (b) For the same reactor and flow rates but another reaction, the initiation rate constant is the same and monomer feed concentration is again  $1.0 \times 10^{-3}$  g mole/cm<sup>3</sup>. The weight-fraction distribution of the total polymer in the exit stream in this case is

Polymer	$P_1$	$P_2$	$P_3$	$P_4$	$P_7$	$P_{10}$	$P_{20}$
Weight fraction	0.0180	0.0314	0.0409	0.0470	0.0546	0.0503	0.0250

What rate constant for the propagation reactions is indicated by these data?

- 4-14. The following irreversible first-order reactions occur at constant density:



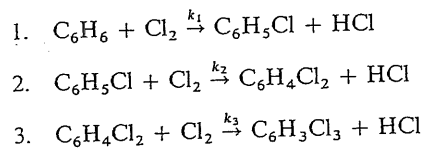
$$k_1 = 0.15 \text{ min}^{-1} \quad k_2 = 0.05 \text{ min}^{-1}$$

This reaction system is to be analyzed in continuous-flow reactors with a volumetric feed rate of 5 ft<sup>3</sup>/min and feed composition  $[A] = [A]_0$  and  $[B] = [C] = 0$ . For the highest production rate of  $B$ , which of the following reactors is preferable?

- (a) A single-stirred tank of volume  $V = 10 \text{ ft}^3$
  - (b) Two stirred tanks in series, each with a volume of 5 ft<sup>3</sup>
  - (c) Two stirred tanks in parallel, each of 5-ft<sup>3</sup> volume and with the feed stream split equally between them
  - (d) A plug-flow (ideal tubular-flow) reactor with a volume of 10 ft<sup>3</sup>
- 4-15. Acetic anhydride is hydrolyzed in three stirred-tank reactors operated in series. The feed flows to the first reactor ( $V = 1$  liter) at a rate of 400 cm<sup>3</sup>/min. The second and third reactors have volumes of 2 and 1.5 liters, respectively. The temperature is 25°C, and at this condition the first-order irreversible rate constant is 0.158 min<sup>-1</sup>. Use a graphical method to calculate the fraction hydrolyzed in the effluent from the third reactor.
- 4-16. Suppose in Prob. 4-15 that the first reactor is operated at 10°C, the second at 40°C, and the third at 25°C. The additional rate constants are 0.0567 min<sup>-1</sup> (at 10°C) and 0.380 min<sup>-1</sup> (at 40°C). Determine the fraction hydrolyzed in the effluent from the third reactor.

- 4-17. Benzene is to be chlorinated in the liquid phase in a kettle-type reactor operated on a steady-state basis. Liquid benzene is added continuously, and the liquid product and gaseous hydrogen chloride are removed continuously. The chlorine gas is bubbled continuously into the liquid reaction mixture in the kettle. The rate of reaction may be assumed large enough that there is no unreacted chlorine in the reaction products. Also, the concentrations of chlorine and HCl in the reaction mixture will be small. The density of the liquid mixture may be assumed constant.

At the constant operating temperature of 55°C the significant reactions are the three substitution ones leading to mono-, di-, and trichlorobenzene. Each reaction is second order and irreversible. The three reactions are



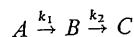
It was noted in Chap. 2 that at 55°C the ratios of the rate constants are

$$\frac{k_1}{k_2} = 8.0$$

$$\frac{k_2}{k_3} = 30$$

Under the proposed operating conditions the composition of the liquid product will be constant for any one run. Different products will be obtained for different ratios of benzene and chlorine fed to the reactor. Compute the composition of the liquid product for the case where 1.4 moles chlorine/mole benzene are fed to the reactor.

- 4-18. Reconsider Prob. 4-17 for the case where, instead of a single reactor, a two-reactor system is used. The liquid stream enters the first reactor (as pure benzene) and flows from the first reactor to the second, and finally the product is withdrawn from the second reactor. Gaseous hydrogen chloride is withdrawn from each reactor. Plot the composition of the product vs moles of total chlorine added per mole of benzene. Cover a range of the latter variable from 0 to 2.5. One-half the total chlorine is added to each reactor.
- 4-19. The successive irreversible reactions



are first order. They are carried out in a series of identical stirred-tank reactors operating at the same temperature and at constant density. Derive an expression for the number of reactors needed to give the maximum concentration of  $B$  in the effluent in terms of the total average residence time and the rate constants. The feed stream contains no  $B$  or  $C$ . What is the number for the specific case where  $k_2 = 0.1 \text{ hr}^{-1}$ ,  $k_1 = 0.05 \text{ hr}^{-1}$ , and the total residence time is 1.5 hr.

- 4-20. A constant-density reaction is carried out in a stirred-tank reactor of volume  $V$ .

The reaction is first order and irreversible, with a rate constant  $k_1$ . The volumetric feed rate is  $Q$ . Under these conditions the conversion in the product stream is  $x_1$  [given by Eq. (4-7)].

(a) If one-half of the product stream is recycled and the makeup feed rate is reduced to  $Q/2$ , what will be the change in conversion in the product stream? What will be the change in the production rate of the product? (b) If one-half of the product stream is recycled, but the fresh-feed rate is maintained equal to  $Q$ , what will be the effects on the conversion and production rate?

- 4-21. Two stirred tanks of volume  $V_1$  and  $2V_1$  are available for carrying out a first-order irreversible reaction at constant density and temperature. If the flow rate of the feed stream is  $Q$ , which of the following arrangements would give the highest production rate of product?

- (a) Parallel operation of the two reactors, with equal average residence times in each  
 (b) Parallel operation, with different average residence times  
 (c) Series operation, with the feed stream entering the larger reactor  
 (d) Series operation, with the feed entering the smaller reactor

- 4-22. Repeat Example 4-12 with the modification that the effluent from the first reactor is fed to a second reactor. The second reactor originally contains 10 liters of an anhydride solution of concentration  $0.50 \times 10^{-4}$  g mole/cm<sup>3</sup>. Product is withdrawn from reactor 2 at a constant rate of 2 liters/min. Temperatures in both are 40°C, and all other conditions are the same as in Example 4-12.

(a) Determine the concentration of anhydride in the solution leaving the second reactor from zero time until steady-state conditions are reached. (b) Suppose that reactor 2 was originally empty and that its capacity is 10 liters. After it is filled, product is withdrawn at the rate of 2 liters/min. What would be the concentration of the first anhydride solution leaving the second reactor?

- 4-23. Ethyl acetate is to be produced in a 100-gal reactor. The reactor originally holds 100 gal of solution containing 20% by weight ethanol and 35% by weight acetic acid. Its density is 8.7 lb/gal; assume that this value remains constant for all compositions. The reactor is heated to 100°C and this temperature is maintained. Pure ethanol is added at a rate of 2 gpm (17.4 lb/min). Solution is withdrawn at the same volumetric rate. At this level the rate data are

$$r = k[H][OH] \quad k = 4.76 \times 10^{-4} \text{ liter}/(\text{g mole})(\text{min})$$

$$r' = k'[E][W] \quad k' = 1.63 \times 10^{-4} \text{ liter}/(\text{g mole})(\text{min})$$

where  $H$ ,  $OH$ ,  $W$ , and  $E$  refer to acid, alcohol, water, and ester. The concentrations are expressed in gram moles per liter.

Determine the concentration of ester in the product stream for time values from 0 to 1 hr. What is the percent conversion of the total amount of ethanol added? Assume that no water is vaporized in the reactor.

- 4-24. Ethyl acetate is to be saponified by adding a 0.05-normal solution of sodium hydroxide continuously to a kettle containing the ethyl acetate. The reactor

is initially charged with 100 gal of an aqueous solution containing 10 g ethyl acetate/liter. The sodium hydroxide solution is added at a rate of 1.0 gpm until stoichiometric amounts are present. The reaction is relatively fast and irreversible, with a specific reaction rate of 92 liters/(g mole)(min) at 20°C. Assuming that the contents of the kettle are well mixed, determine the concentration of unreacted ethyl acetate as a function of time. At what time will this concentration be a maximum?