

Reactors for Measuring Reaction Rates

3.1 | Ideal Reactors

The confines in which chemical reactions occur are called reactors. A reactor can be a chemical reactor in the traditional sense or other entities, for example, a chemical vapor deposition apparatus for making computer chips, an organ of the human body, and the atmosphere of a large city. In this chapter, the discussion of reactors is limited to topics germane to the determination of reaction rates. Later in this text, strategies for attacking the problems of mathematically describing and predicting behavior of reactors in general are presented.

In practice, conditions in a reactor are usually quite different than the ideal requirements used in the definition of reaction rates. Normally, a reactor is not a closed system with uniform temperature, pressure, and composition. These ideal conditions can rarely if ever be met even in experimental reactors designed for the measurement of reaction rates. In fact, reaction rates cannot be measured directly in a closed system. In a closed system, the composition of the system varies with time and the rate is then inferred or calculated from these measurements.

There are several questions that can be put forth about the operation of reactors and they can be used to form the basis of classifying and defining ideal conditions that are desirable for the proper measurements of reaction rates.

The first question is whether the system exchanges *mass* with its surroundings. If it does not, then the system is called a *batch reactor*. If it does, then the system is classified as a *flow reactor*.

The second question involves the exchange of heat between the reactor and its surroundings. If there is no heat exchange, the reactor is then *adiabatic*. At the other extreme, if the reactor makes very good thermal contact with the surroundings it can be held at a constant temperature (in both time and position within the reactor) and is thus *isothermal*.

Table 3.1.1 | Limiting conditions of reactor operation.¹

Event	Limiting conditions	
Exchange of mass	Batch	Flow
Exchange of heat	Isothermal	Adiabatic
Mechanical variables	Constant volume	Constant pressure
Residence time	Unique	Exponential distribution
Space-time behavior	Transient	Stationary

¹From M. Boudart, *Kinetics of Chemical Processes*, Butterworth & Heinemann, 1991, p. 13.

The third question concerns the mechanical variables: pressure and volume. Is the reactor at constant pressure or constant volume? The fourth question is whether the time spent in the reactor by each volume element of fluid is the same. If it is not the same, there may exist a *distribution of residence times* and the opposite extreme of a unique residence time is an exponential distribution.

The fifth question focuses on a particular fixed volume element in the reactor and whether it changes as a function of time. If it does not, then the reactor is said to operate at a stationary state. If there are time variations, then the reactor is operating under transient conditions. A nontrivial example of the transient situation is designed on purpose to observe how a chemically reactive system at equilibrium relaxes back to the equilibrium state after a small perturbation. This type of relaxation experiment can often yield informative kinetic behavior.

The ten possibilities outlined above are collected in Table 3.1.1. Next, ideal reactors will be illustrated in the contexts of the limiting conditions of their operation.

3.2 | Batch and Semibatch Reactors

Consider the ideal batch reactor illustrated in Figure 3.2.1. If it is assumed that the contents of the reactor are perfectly mixed, a material balance on the reactor can be written for a species i as:

$$\begin{array}{ccccccc}
 \frac{dn_i}{dt} & = & 0 & - & 0 & + & (v_i r V) \\
 \text{accumulation} & & \text{input} & & \text{output} & & \text{amount produced by reaction}
 \end{array}$$

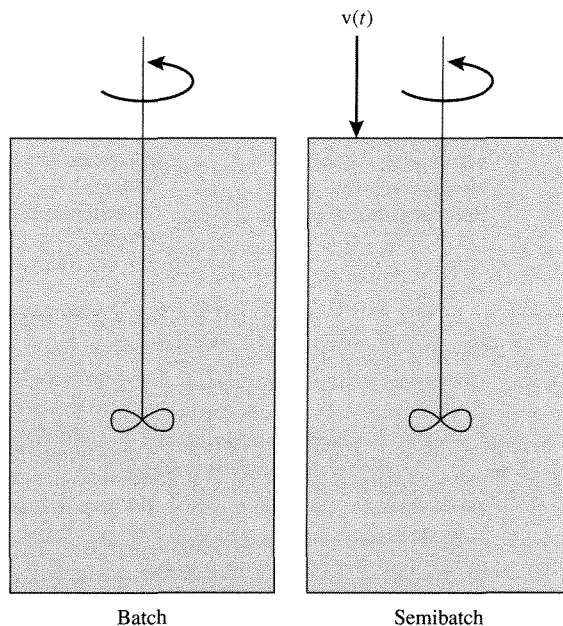
or

$$\frac{dn_i}{dt} = v_i r V \quad \text{with } n_i = n_i^0 \text{ @ } t = 0 \quad (3.2.1)$$

The material balance can also be written in terms of the fractional conversion and it is:

$$n_i^0 \frac{df_i}{dt} = -(v_i r) V^0 (1 + \varepsilon_i f_i) \quad \text{with } f_i = 0 \text{ @ } t = 0 \quad (3.2.2)$$

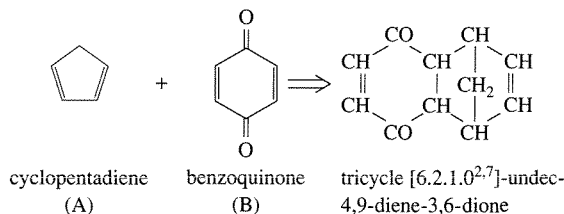
where $|\varepsilon_i| > 0$ for nonconstant volume.

**Figure 3.2.1 |**

Ideal batch and semibatch reactors. $v(t)$ is a volumetric flow rate that can vary with time.

EXAMPLE 3.2.1

An important class of carbon-carbon bond coupling reactions is the Diels-Alder reactions. An example of a Diels-Alder reaction is shown below:



If this reaction is performed in a well-mixed isothermal batch reactor, determine the time necessary to achieve 95 percent conversion of the limiting reactant (from C. Hill, *An Introduction to Chemical Engineering Kinetics and Reactor Design*, Wiley, 1977, p. 259).

Data: $k = 9.92 \times 10^{-6} \text{ m}^3/\text{mol/s}$

$$C_A^0 = 100 \text{ mol/m}^3$$

$$C_B^0 = 80 \text{ mol/m}^3$$

■ Answer

From the initial concentrations, benzoquinone is the limiting reactant. Additionally, since the reaction is conducted in a dilute liquid-phase, density changes can be neglected. The reaction rate is second-order from the units provided for the reaction rate constant. Thus,

$$(\nu_{Br}) = -k(C_B^0)^2(1 - f_B)(\bar{M} - f_B), \bar{M} = C_A^0/C_B^0$$

The material balance on the isothermal batch reactor is:

$$\frac{dn_B}{dt} = \nu_{Br}V$$

with $f_B = 0$ at $t = 0$. Integration of this first-order initial-value problem yields:

$$t = \int_0^{f_B} \frac{d\gamma}{kC_B^0(1 - \gamma)(\bar{M} - \gamma)}$$

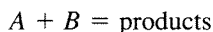
where γ is the integration variable. The integration yields:

$$t = \frac{\ln\left[\left(\frac{\bar{M} - f_B}{1 - f_B}\right)\frac{1}{\bar{M}}\right]}{kC_B^0(\bar{M} - 1)}$$

Using the data provided, $t = 7.9 \times 10^3$ s or 2.2 h to reach 95 percent conversion of the benzoquinone. This example illustrates the general procedure used for solving isothermal problems. First, write down the reaction rate expression. Second, formulate the material balance. Third, substitute the reaction rate expression into the material balance and solve.

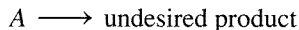
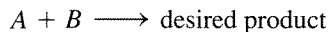
Consider the semibatch reactor schematically illustrated in Figure 3.2.1. This type of reactor is useful for accomplishing several classes of reactions. Fermentations are often conducted in semibatch reactors. For example, the concentration of glucose in a fermentation can be controlled by varying its concentration and flow rate into the reactor in order to have the appropriate times for: (1) the initial growth phase of the biological catalysts, and (2) the period of metabolite production. Additionally, many bioreactors are semibatch even if liquid-phase reactants are not fed to the reactor because oxygen must be continuously supplied to maintain the living catalyst systems (i.e., bacteria, yeast, etc.).

Alternatively, semibatch reactors of the type shown in Figure 3.2.1 are useful for reactions that have the stoichiometry:



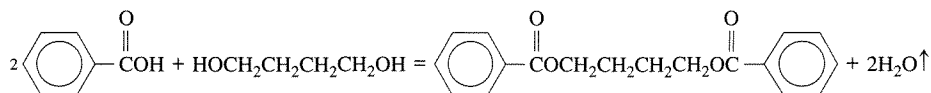
where B is already in the reactor and A is slowly fed. This may be necessary to: (1) control heat release from exothermic reaction, for example, hydrogenations, (2) provide

gas-phase reactants, for example, with halogenations, hydrogenations, or (3) alter reaction selectivities. In the network:

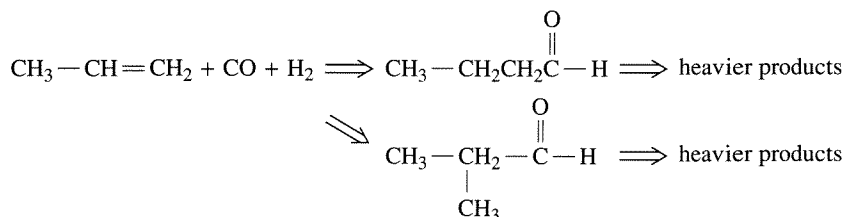


maintaining a constant and high concentration of B would certainly aid in altering the selectivity to the desired product.

In addition to feeding of components into the reactor, if the sign on $v(t)$ is negative, products are continuously removed, for example, reactive distillation. This is done for reactions: (1) that reveal product inhibition, that is, the product slows the reaction rate, (2) that have a low equilibrium constant (removal of product does not allow equilibrium to be reached), or (3) where the product alters the reaction network that is proceeding in the reactor. A common class of reactions where product removal is necessary is ester formation where water is removed,



A very large-scale reaction that utilizes reactive distillation of desired liquid products is the hydroformylation of propene to give butyraldehyde:



A schematic illustration of the hydroformylation reactor is provided in Figure 3.2.2.

The material balance on a semibatch reactor can be written for a species i as:

$$\underbrace{\frac{dn_i}{dt}}_{\text{accumulation}} = \underbrace{v(t)C_i^0(t)}_{\text{input}} - \underbrace{0}_{\text{output}} + \underbrace{(v_i r)V}_{\substack{\text{amount} \\ \text{produced} \\ \text{by reaction}}}$$

or

$$\frac{dn_i}{dt} = (v_i r)V + v(t)C_i^0(t) \quad (3.2.2)$$

where $C_i^0(t)$ is the concentration of species i entering from the input stream of volumetric flow rate $v(t)$.

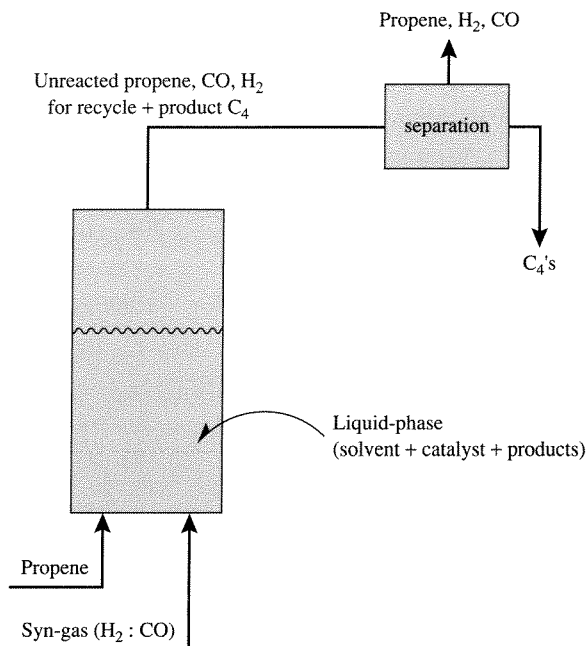
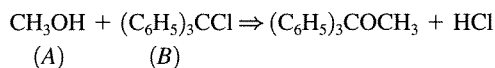


Figure 3.2.2 |
Schematic illustration of a propene hydroformylation reactor.

EXAMPLE 3.2.2

To a well-stirred tank containing 40 mol of triphenylmethylchloride in dry benzene (initial volume is 378 L) a stream of methanol in benzene at 0.054 mol/L is added at 3.78 L/min. A reaction proceeds as follows:



The reaction is essentially irreversible since pyridine is placed in the benzene to neutralize the formed HCl, and the reaction rate is:

$$r = 0.263 C_A^2 C_B \text{ (mol/L/min)}$$

Determine the concentration of the product ether as a function of time (problem adapted from N. H. Chen, *Process Reactor Design*, Allyn and Bacon, Inc., 1983, pp. 176–177).

■ Answer

The material balance equations for n_A and n_B are:

$$\frac{dn_A}{dt} = (0.054 \text{ mol/L})(3.78 \text{ L/min}) - 0.263 C_A^2 C_B V$$

$$\frac{dn_B}{dt} = -0.263 C_A^2 C_B V$$

The volume in the reactor is changing due to the input of methanol in benzene. Thus, the volume in the reactor at any time is:

$$V = 3.78(100 + t)$$

Therefore,

$$\frac{dn_A}{dt} = 0.204 - 0.263 n_A^2 n_B / [3.78(100 + t)]^2$$

$$\frac{dn_B}{dt} = -0.263 n_A^2 n_B / [3.78(100 + t)]^2$$

where

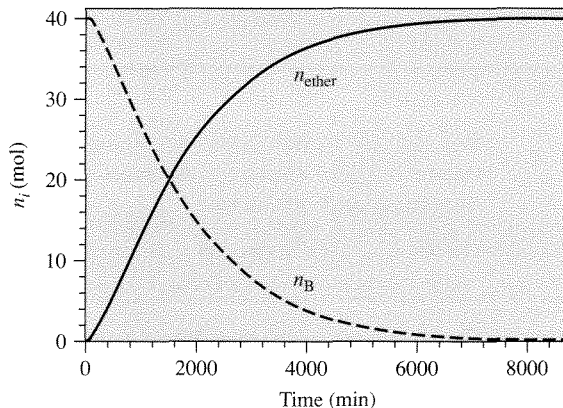
$$n_A^0 = 0 @ t = 0$$

$$n_B^0 = 40 @ t = 0$$

From Equation (1.2.6),

$$n_{\text{ether}} = n_B^0 - n_B$$

since no ether is initially present. The numerical solution to the rate equations gives $n_A(t)$ and $n_B(t)$ from which $n_{\text{ether}}(t)$ can be calculated. The results are plotted below.



For other worked examples of semibatch reactors, see H. S. Fogler, *Elements of Chemical Reaction Engineering*, 3rd ed., Prentice-Hall, 1992, pp. 190–200, and N. H. Chen, *Process Reactor Design*, Allyn and Bacon, Inc., 1983, Chap. 6.

3.3 | Stirred-Flow Reactors

The ideal reactor for the direct measurement of reaction rates is an isothermal, constant pressure, flow reactor operating at steady-state with complete mixing such that the composition is uniform throughout the reactor. This ideal reactor is frequently

called a *stirred-tank reactor*, a *continuous flow stirred-tank reactor (CSTR)*, or a *mixed flow reactor (MFR)*. In this type of reactor, the composition in the reactor is assumed to be that of the effluent stream and therefore all the reaction occurs at this constant composition (Figure 3.3.1).

Since the reactor is at steady-state, the difference in F_i^0 (input) and F_i (output) must be due to the reaction. (In this text, the superscript 0 on flow rates denotes the input to the reactor.) The material balance on a CSTR is written as:

$$\begin{array}{ccccccc} 0 & = & F_i^0 & - & F_i & + & (v_i r)V \\ \text{accumulation} & & \text{input} & & \text{output} & & \text{amount} \\ & & \text{of } i & & \text{of } i & & \text{produced} \\ & & & & & & \text{by reaction} \end{array} \quad (3.3.1)$$

(Note that V is the volume of the reacting system and V_R is the volume of the reactor; both are not necessarily equal.) Therefore, the rate can be measured directly as:

$$v_i r = \frac{F_i - F_i^0}{V} \quad (3.3.2)$$

Equation (3.3.2) can be written for the limiting reactant to give:

$$v_l r = \frac{F_l - F_l^0}{V} \quad (3.3.3)$$

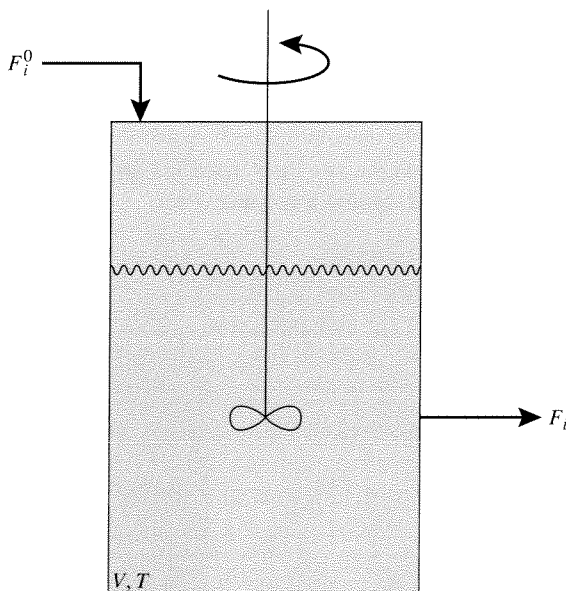


Figure 3.3.1 |

Stirred-flow reactor. The composition of the reacting volume, V , at temperature, T , is the same everywhere and at all times. F_i^0 is the molar flow rate of species i into the reactor while F_i is the molar flow rate of species i out of the reactor.

Recalling the definition of the fractional conversion:

$$f_l = \frac{n_l^0 - n_l}{n_l^0} = \frac{F_l^0 - F_l}{F_l^0} \quad (3.3.4)$$

Substitution of Equation (3.3.4) into Equation (3.3.3) yields:

$$(-v_l)r = \left(\frac{F_l^0}{V}\right)f_l \quad (3.3.5)$$

If $v_l = -1$, then the reaction rate is equal to the number of moles of the limiting reactant fed to the reactor per unit time and per unit volume of the reacting fluid times the fractional conversion. For any product p not present in the feed stream, a material balance on p is easily obtained from Equation (3.3.1) with $F_i^0 = 0$ to give:

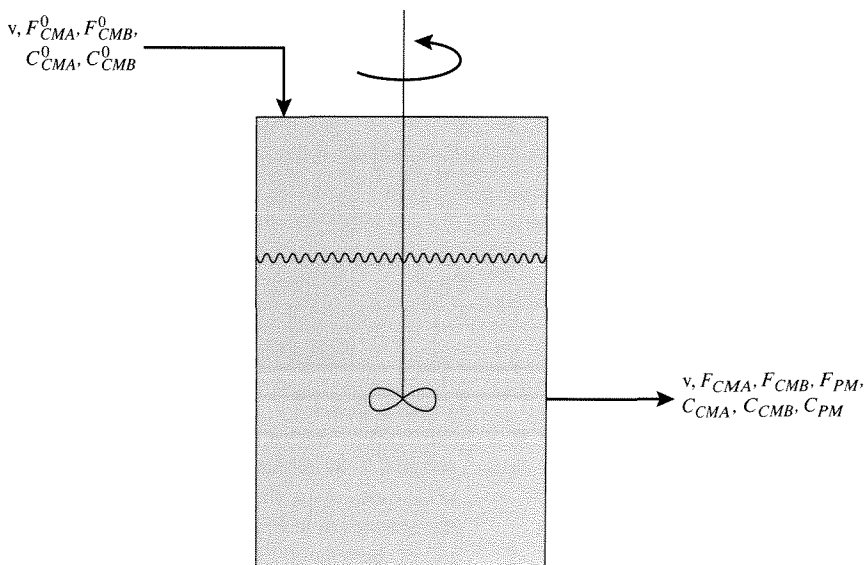
$$v_p r = F_p/V \quad (3.3.6)$$

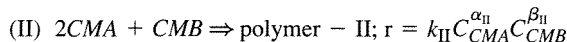
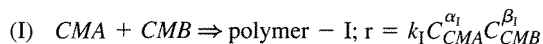
The quantity (F_p/V) is called the space-time yield.

The equations provided above describe the operation of stirred-flow reactors whether the reaction occurs at constant volume or not. In these types of reactors, the fluid is generally a liquid. If a large amount of solvent is used, that is, dilute solutions of reactants/products, then changes in volume can be neglected. However, if the solution is concentrated or pure reactants are used (sometimes the case for polymerization reactions), then the volume will change with the extent of reaction.

EXAMPLE 3.3.1

Write the material balance equation on comonomer A for the steady-state CSTR shown below with the two cases specified for the reaction of comonomer A (CMA) and comonomer B (CMB) to give a polymer (PM).





■ Answer

The material balance equation is:

$$\text{input} = \text{output} - \text{removal by reaction} + \text{accumulation}$$

Since the reactor is at steady-state, there is no accumulation and:

$$F_{CMA}^0 = F_{CMA} - (v_{CMA} r) V$$

For case (I) the material balance is:

$$F_{CMA}^0 = F_{CMA} - (-k_I C_{CMA}^{\alpha_I} C_{CMB}^{\beta_I}) V$$

while case (II) gives:

$$F_{CMA}^0 = F_{CMA} - (-2k_{II} C_{CMA}^{\alpha_{II}} C_{CMB}^{\beta_{II}}) V$$

If changes in the volume due to reaction can be neglected, then the CSTR material balance can be written in terms of concentrations to give (v = volumetric flow rate; that is, volume per unit time):

$$0 = vC_i^0 - vC_i + (v_I r) V \quad (3.3.7)$$

$$(-v_I) r = \frac{C_i^0 - C_i}{(V/v)} \quad (3.3.8)$$

The ratio (V/v) is the volume of mixture in the reactor divided by the volume of mixture fed to the reactor per unit time and is called the *space time*, τ . The inverse of the space time is called the *space velocity*. In each case, the conditions for the volume of the feed must be specified: temperature, pressure (in the case of a gas), and state of aggregation (liquid or gas). Space velocity and space time should be used in preference to “contact time” or “holding time” since there is no unique residence time in the CSTR (see below). Why develop this terminology? Consider a batch reactor. The material balance on a batch reactor can be written [from Equation (3.2.1)]:

$$t = \int_{n_i^0}^{n_i^{\text{final}}} \frac{dn_i}{v_i r V} = C_i^0 \int_0^{f^{\text{final}}} \frac{df_i}{(-v_i) r (1 + \epsilon_i f_i)} \quad (3.3.9)$$

Equation (3.3.9) shows that the time required to reach a given fractional conversion does not depend upon the reactor volume or total amount of reagents. That is to say, for a given fractional conversion, as long as C_i^0 is the same, 1, 2, or 100 mol of i can be converted in the same time. With flow reactors, for a given C_i^0 , the fractional conversion from different sized reactors is the same provided τ is the same. Table 3.3.1 compares the appropriate variables from flow and nonflow reactors.

Table 3.3.1 | Comparison of appropriate variables for flow and nonflow reactors.

Nonflow	Flow
t (time)	τ (time)
$V = V^0(1 + \varepsilon_i f_i)$ (volume)	$v = v^0(1 + \varepsilon_i f_i)$ (volume/time)
$n_i = n_i^0(1 - f_i)$ (mol)	$F_i = F_i^0(1 - f_i)$ (mol/time)

In order to show that there is not a unique residence time in a CSTR, consider the following experiment. A CSTR is at steady state and a tracer species (does not react) is flowing into and out of the reactor at a concentration C^0 . At $t = 0$, the feed is changed to pure solvent at the same volumetric flow. The material balance for this situation is:

$$\frac{dn_i}{dt} = 0 - C_i v \quad (3.3.10)$$

(accumulation) = (input) - (output)

or

$$-V \frac{dC_i}{dt} = C_i v \quad \text{with } C_i = C^0 \text{ at } t = 0.$$

Integration of this equation gives:

$$C = C^0 \exp[-t/\tau] \quad (3.3.11)$$

This exponential decay is typical of first-order processes as shown previously. Thus, there is an exponential distribution of residence times; some molecules will spend little time in the reactor while others will stay very long. The mean residence time is:

$$\langle t \rangle = \frac{\int_0^\infty t C(t) dt}{\int_0^\infty C(t) dt} \quad (3.3.12)$$

and can be calculated by substituting Equation (3.3.11) into Equation (3.3.12) to give:

$$\langle t \rangle = \frac{\int_0^\infty t \exp[-t/\tau] dt}{\int_0^\infty \exp[-t/\tau] dt} \quad (3.3.13)$$

Since

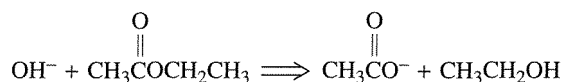
$$\int_0^\infty x \exp[-x] dx = 1$$

$$\langle t \rangle = \frac{\tau^2}{-\tau \exp[-t/\tau] \Big|_0^\infty} = \tau \quad (3.3.14)$$

Thus, the mean residence time for a CSTR is the space time. The fact that $\langle t \rangle = \tau$ holds for reactors of any geometry and is discussed in more detail in Chapter 8.

EXAMPLE 3.3.2

The rate of the following reaction has been found to be first-order with respect to hydroxyl ions and ethyl acetate:



In a stirred-flow reactor of volume $V = 0.602$ L, the following data have been obtained at 298 K [Denbigh et al., *Disc. Faraday Soc.*, **2** (1977) 263]:

flow rate of barium hydroxide solution: 1.16 L/h

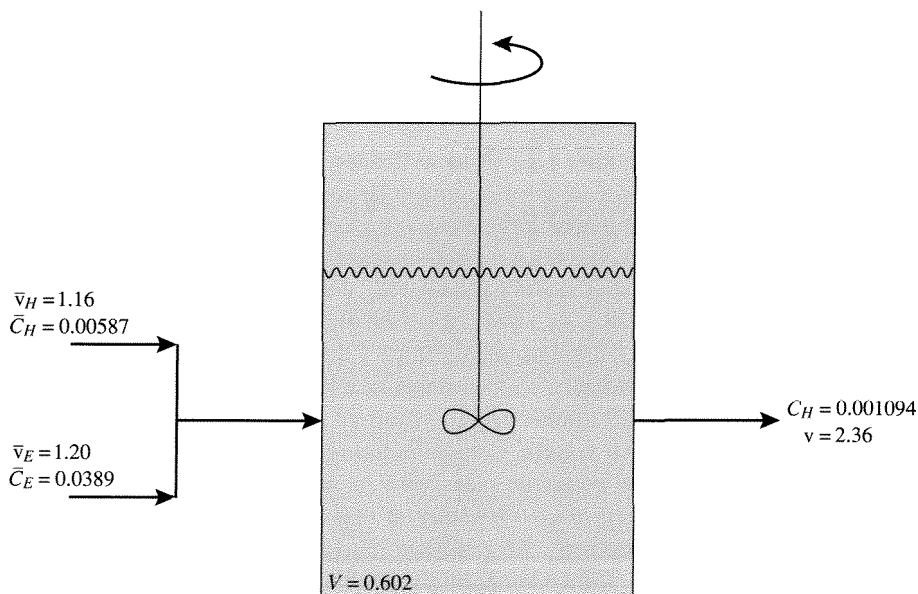
flow rate of ethyl acetate solution: 1.20 L/h

inlet concentration of OH^- : 0.00587 mol/L

inlet concentration of ethyl acetate: 0.0389 mol/L

outlet concentration of OH^- : 0.001094 mol/L

Calculate the rate constant. Changes in volume accompanying the reaction are negligible. (Problem taken from M. Boudart, *Kinetics of Chemical Processes*, Butterworth-Heinemann, Boston, 1991, pp. 23–24.)

■ Answer

Since $\bar{v}_H \cong \bar{v}_E$, the limiting reactant is the hydroxyl ion. Thus, a material balance on OH^- gives:

$$0 = C_H^0 \bar{v} - C_H \bar{v} + (v_r) V$$

where

$$\begin{aligned}v &= \bar{v}_H + \bar{v}_E = 2.36 \text{ L/h} \\C_H^0 &= \bar{C}_H \bar{v}_H / v = 0.00289 \text{ mol/L} \\(-v_H)r &= k C_H C_E\end{aligned}$$

Since the outlet value of C_H is known, the fractional conversion and C_E can be calculated as:

$$f_H = \frac{C_H^0 - C_H}{C_H^0} = \frac{0.00289 - 0.001094}{0.00289} = 0.62$$

and

$$C_E = C_E^0 - C_H^0 f_H = \frac{\bar{C}_E \bar{v}_E}{v} - C_H^0 f_H = 0.0180 \text{ mol/L}$$

Thus,

$$(-v_H)r = \frac{C_H^0 - C_H}{\tau} = \frac{0.00289 - 0.001094}{[0.602/2.36]} = 0.0070 \left(\frac{\text{mol}}{\text{L} \cdot \text{h}} \right)$$

and

$$k = \frac{(-v_H)r}{C_H C_E} = \frac{0.0070}{(0.001094)(0.0180)} = 360 \left(\frac{\text{L}}{\text{mol} \cdot \text{h}} \right)$$

3.4 | Ideal Tubular Reactors

Another type of ideal reactor is the tubular flow reactor operating isothermally at constant pressure and at steady state with a unique residence time. This type of reactor normally consists of a cylindrical pipe of constant cross-section with flow such that the fluid mixture completely fills the tube and the mixture moves as if it were a plug traveling down the length of the tube. Hence the name *plug flow reactor (PFR)*. In a PFR, the fluid properties are uniform over any cross-section normal to the direction of the flow; variations only exist along the length of the reactor. Additionally, it is assumed that *no* mixing occurs between adjacent fluid volume elements either radially (normal to flow) or axially (direction of flow). That is to say each volume element entering the reactor has the same residence time since it does not exchange mass with its neighbors. Thus, the CSTR and the PFR are the two *ideal limits of mixing* in that they are completely mixed and not mixed at all, respectively. *All* real flow reactors will lie somewhere between these two limits.

Since the fluid properties vary over the volume of the reactor, consider a material balance on a section of a steady-state isothermal PFR, dL (see Figure 3.4.1):

$$\begin{aligned}0 &= F_i - (F_i + dF_i) + v_r A_C dL \\(\text{accumulation}) &= (\text{input}) - (\text{output}) + (\text{amount produced by reaction})\end{aligned} \quad (3.4.1)$$

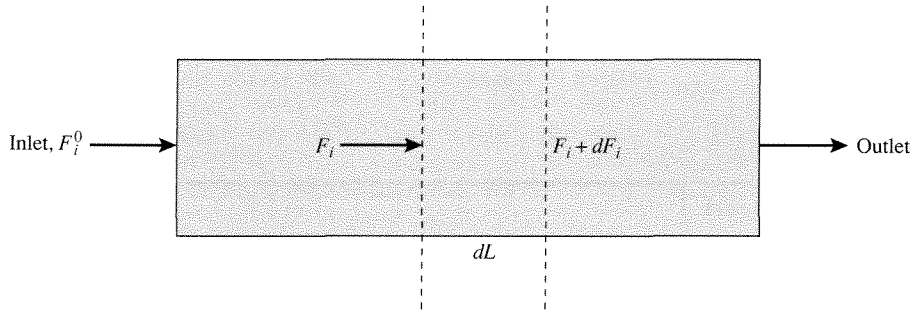


Figure 3.4.1 |
Tubular reactor.

where A_C is the cross-sectional area of the tube. Also, $A_C dL = dV_R$, so Equation (3.4.1) can be written as:

$$\frac{dF_i}{dV_R} = v_i r \quad (3.4.2)$$

or

$$F_i^0 \frac{df_i}{dV_R} = -v_i r \quad (3.4.3)$$

Integration of Equation (3.4.3) gives:

$$\frac{V_R}{F_i^0} = \int_{f_i^0}^{f_i^{\text{outlet}}} \frac{df_i}{(v_i r)} \quad \text{or} \quad \tau = \frac{V_R}{v} = C_i^0 \int_{f_i^0}^{f_i^{\text{outlet}}} \frac{df_i}{(v_i r)} \quad (3.4.4)$$

If changes in volume due to reaction are negligible, then $[F_i = C_i v$; moles of i /time = (moles of i /volume) (volume/time)]:

$$\frac{dC_i}{d\tau} = \frac{dC_i}{d(V_R/v)} = v_i r \quad (3.4.5)$$

Note the analogy to batch reactors that have a unique residence time t and where

$$\frac{dC_i}{dt} = v_i r \quad (3.4.6)$$

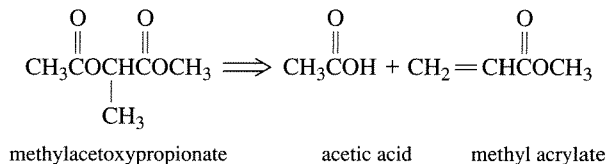
Clearly, the space-time, τ , in the ideal tubular reactor is the same as the residence time in the batch reactor *only* if volume changes are neglectable. This is easy to see from Equation (3.4.2) by substituting $C_i v$ for F_i and recalling that for volume changes $v = v^0 (1 + \varepsilon_i f_i)$:

$$\frac{d}{dV_R} (C_i v) = v \frac{dC_i}{dV_R} + C_i \frac{dv}{dV_R} = v_i r \quad (3.4.7)$$

Thus, if $dv/dV_R = 0$, then there is an analogy between τ and t in a PFR and batch reactor, respectively [Equations (3.4.5) and (3.4.6)], and if $dv/dV_R \neq 0$, then comparison of Equations (3.4.7) and (3.4.6) shows that there is none.

EXAMPLE 3.4.1

A PFR operating isothermally at 773 K is used to conduct the following reaction:



If a feed of pure methylacetoxypionate enters at 5 atm and at a flow rate of $0.193 \text{ ft}^3/\text{s}$, what length of pipe with a cross-sectional area of 0.0388 ft^2 is necessary for the reaction to achieve 90 percent conversion (from C. G. Hill, *An Introduction to Chemical Engineering Kinetics & Reactor Design*, Wiley, 1977, pp. 266–267)?

$$\text{Data: } k = 7.8 \times 10^9 \exp[-19,200/T] \text{ s}^{-1}$$

■ Answer

From Equation (3.4.2) and $F_A = F_A^0(1 - f_A) = C_A v$:

$$F_A^0 \frac{df_A}{dV_R} = (-v_A)r$$

or

$$\tau = \frac{V_R}{v^0} = C_A^0 \int_0^{f_A=0.9} \frac{df_A}{(-v_A)r}$$

For this gas-phase reaction there is mole change with reaction and

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

Therefore,

$$(-v_A)r = kC_A = k \frac{n_A}{V} = k \frac{n_A^0(1 - f_A)}{V^0(1 + \varepsilon_A f_A)} = kC_A^0 \left[\frac{1 - f_A}{1 + f_A} \right]$$

Combination of the material balance and reaction rate expressions yields:

$$\tau = \frac{1}{k} \int_0^{0.9} \frac{[1 + f_A]}{[1 - f_A]} df_A$$

Integration of this equation yields:

$$k\tau = -2\ln(1 - f_A) - f_A$$

and at 773 K, $k = 0.124 \text{ s}^{-1}$ to give at $f_A = 0.9$:

$$\tau = 29.9 \text{ s}$$

Now, if mole change with reaction is ignored (i.e., $\varepsilon_A = 0$), $\tau = 18.6 \text{ s}$. Notice the large difference in the value of τ when mole change with reaction is properly accounted for in the calculations. Since the gas is expanding with increasing extent of reaction, its velocity through the tube increases. Therefore, τ must be likewise increased to allow for the specified conversion. The reactor volume and length of tube can be calculated as:

$$V_R = \tau v^0 = (29.9)(0.193) = 5.78 \text{ ft}^3$$

and

$$L = V_R/A_C = (5.78 \text{ ft}^3)/(0.0388 \text{ ft}^2) = 149 \text{ ft}$$

EXAMPLE 3.4.2

A first-order reaction occurs in an isothermal CSTR (MFR) and PFR of equal volume. If the space-time is the same in both reactors, which reactor gives the largest space-time yield and why?

■ Answer

Assume that any changes in volume due to reaction can be neglected.

Reactor	Material balance
MFR	$\tau_m = \frac{C_l^0 - C_l}{kC_l}$
PFR	$\tau_p = \int_{C_l^0}^{C_l} \frac{d\bar{C}_l}{k\bar{C}_l} = \frac{1}{k} \ln\left(\frac{C_l^0}{C_l}\right)$

If $\tau_m = \tau_p$ then

$$\frac{1}{k} \left[\frac{C_l^0 - C_l}{C_l} \right]_m = \frac{1}{k} \ln\left(\frac{C_l^0}{C_l}\right)_p$$

Rearranging this equation gives (C_l^p and C_l^m are C_l in the PFR and MFR, respectively):

$$\frac{C_l^0}{C_l^p} = \exp\left[\frac{C_l^0 - C_l^m}{C_l^m}\right]$$

If the approximation:

$$\exp[x] \cong 1 + x + \frac{x^2}{2!} + \dots$$

is used then

$$\frac{C_l^0}{C_l^p} = 1 + \frac{C_l^0 - C_l^m}{C_l^m} + \frac{1}{2} \left(\frac{C_l^0 - C_l^m}{C_l^m} \right)^2 + \dots$$

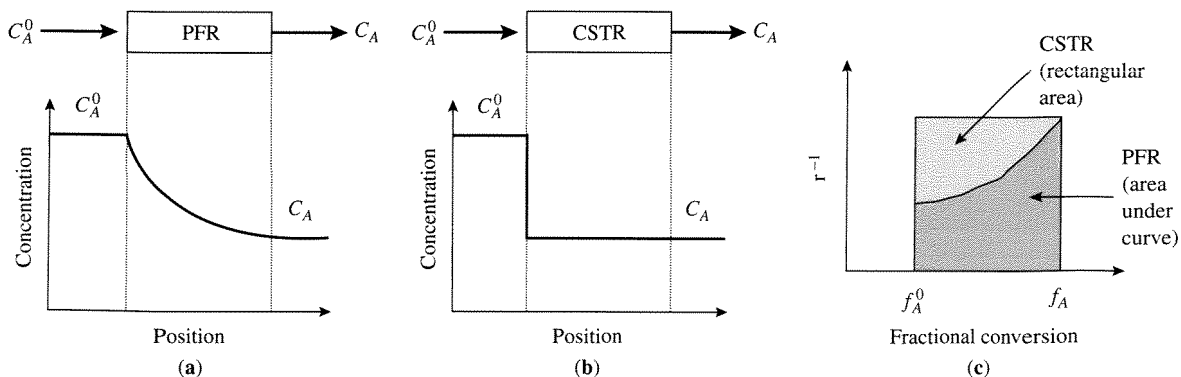
or

$$\frac{C_l^0}{C_l^p} = 1 + \frac{C_l^0}{C_l^m} - 1 + \frac{1}{2} \left(\frac{C_l^0 - C_l^m}{C_l^m} \right)^2 + \dots$$

Thus,

$$C_l^p = C_l^m \left[\frac{1}{1 + \frac{1}{2C_l^0 C_l^m} (C_l^0 - C_l^m)^2 + \dots} \right]$$

Since the term in the bracket will always be less than one, $C_l^p < C_l^m$, indicating that the fractional conversion and hence the space-time yield of the PFR is always higher than the CSTR. The reason for this is that for reaction-rate expressions that follow Rule I (r decreases with time or extent of reaction) the rate is maintained at a higher average value in the PFR than the CSTR. This is easy to rationalize since the concentration of the feed (highest value giving the largest rate) instantaneously drops to the outlet value (lowest value giving the lowest rate) in a CSTR [schematic (b) below] while in the PFR there is a steady progression of declining rate as the fluid element traverses the reactor [schematic (a) below]. In fact, the PFR and the CSTR are the ideal maximum and minimum space-time yield reactor configurations, respectively. This can be demonstrated by plotting the material balance equations for the PFR and CSTR as shown in the schematic (c) below. For the same conversion (i.e., the same outlet f_A), the CSTR always requires a larger reactor volume. In other words, the area in the graph is larger for the CSTR than the PFR.

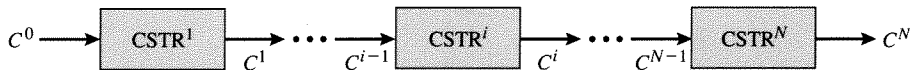


EXAMPLE 3.4.3

Show that a large number of CSTRs in series approaches the behavior of a PFR.

■ Answer

Consider the following series of CSTRs accomplishing a first-order reaction (reactors of equal size).



The material balance for reactor i is:

$$\tau^i = \tau = \frac{C^{i-1} - C^i}{kC^i} \quad \text{or} \quad \frac{C^{i-1}}{C^i} = 1 + k\tau$$

The ratio C^0/C^N can be written as:

$$\frac{C^0}{C^N} = \left(\frac{C^0}{C^1}\right)\left(\frac{C^1}{C^2}\right)\cdots\left(\frac{C^{i-1}}{C^i}\right)\cdots\left(\frac{C^{N-1}}{C^N}\right) = [1 + k\tau]^N$$

because $\tau^i = \tau$ (reactors of equal size). Also,

$$C^N/C^0 = 1 - f$$

giving:

$$C^0/C^N = [1 + k\tau]^N = \frac{1}{1 - f}$$

If $\tau^T = N\tau$, then C^0/C^N can be written as:

$$C^0/C^N = \left[1 + \frac{k\tau^T}{N}\right]^N = 1 + N\left(\frac{k\tau^T}{N}\right) + \frac{N(N-1)}{2!}\left(\frac{k\tau^T}{N}\right)^2 + \cdots \cong e^{k\tau^T}$$

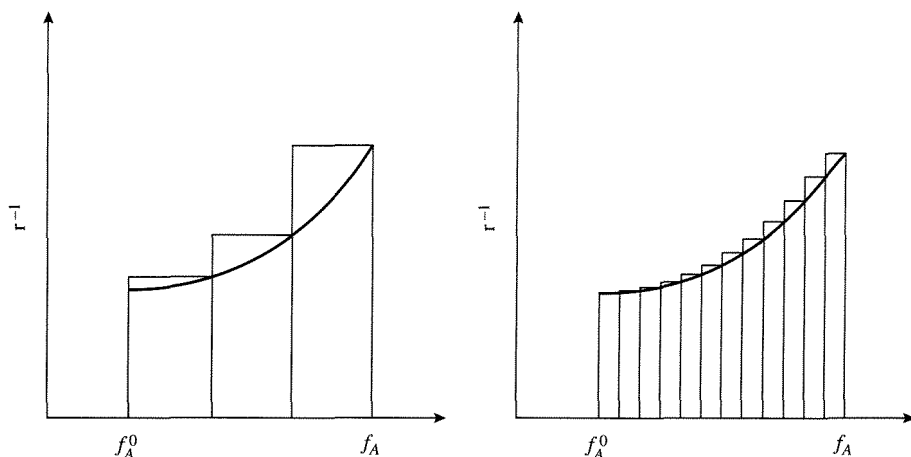
Therefore, as N gets large the series better approximates the exponential and

$$C^0/C^N = e^{k\tau^T}$$

or

$$\tau^T = \frac{1}{k} \ln\left(C^0/C^N\right)$$

which is the material balance for a PFR. This result can be visualized graphically as follows. In Example 3.4.2, r^{-1} was plotted against f_A . Note that if the area under this curve is integrated as illustrated:



the larger number of rectangles that are used to approximate the area under the curve, the less error. Thus, if each rectangle (see Example 3.4.2) represents a CSTR, it is clear that the larger the number of CSTRs in series, the better their overall behavior simulates that of a PFR.

EXAMPLE 3.4.4

Calculate the outlet conversion for a series of CSTRs accomplishing a first-order reaction with $k\tau^T = 5$ and compare the results to that obtained from a PFR.

■ Answer

Using the equations developed in Example 3.4.3 gives with $k\tau^T = 5$ the following results:

N	$1 - f_A$
1	0.1667
5	0.0310
100	0.0076
1000	0.0068
PFR	0.0067

3.5 | Measurement of Reaction Rates

What are the types of problems that need to be addressed by measuring reaction rates? The answers to this question are very diverse. For example, in the testing of catalysts, a new catalyst may be evaluated for replacement of another catalyst in an existing process or for the development of a new process. Accurate, reliable laboratory reaction rate data are necessary for the design of an industrial reactor

Table 3.5.1 | Rate of reactions in ideal isothermal reactors.

Ideal reactor	General equation		Constant density equation	
Batch	$\frac{1}{V} \frac{dn_l}{dt} = v_l r$	Equation (3.2.1)	$\frac{dC_l}{dt} = v_l r$	
Stirred-flow	$\frac{F_l^0}{V} f_l = (-v_l) r$	Equation (3.3.5)	$\frac{C_l^0 - C_l}{(V/v)} = (-v_l) r$	Equation (3.3.8)
Tubular	$F_l^0 \frac{df_l}{dV_R} = (-v_l) r$	Equation (3.4.3)	$\frac{dC_l}{d(V_R/v)} = v_l r$	Equation (3.4.5)

Nomenclature

- C_l Molar concentration of limiting reactant, mol/volume
 C_l^0 Initial value of C_l
 f_l Fractional conversion of limiting reactant, dimensionless
 n_l Number of moles of limiting reactant, mol
 F_l^0 Initial value of the molar flow rate of limiting reactant, mol/time
 r Reaction rate, mol/volume/time
 v_l Stoichiometric coefficient of limiting reactant, dimensionless
 V Volume of reacting system, volume
 V_R Volume of reactor, volume
 v Volumetric flow rate, volume/time

whether the process is new or old. Another example of why reaction rate data are needed is to make predictions about how large-scale systems behave (e.g., the appearance of ozone holes and the formation of smog). The key issue in all of these circumstances is the acquisition of high-quality reaction rate data. In order to do this, a laboratory-scale reactor must be used. Although deviations from ideal behavior still exist in laboratory reactors, deliberate efforts can be made to approximate ideal conditions as closely as possible. Table 3.5.1 summarizes the material balance equations for the ideal reactors described above. Examples of how these types of reactors are used to measure reaction rates are presented below.

When choosing a laboratory reactor for the measurement of reaction rate data, numerous issues must be resolved. The choice of the reactor is based on the characteristics of the reaction and for all practical matters by the availability of resources (i.e., reactors, analytical equipment, money, etc.). A good example of the issues involved in selecting a laboratory reactor and how they influence the ultimate choice is presented by Weekman [*AIChE J.*, **20** (1974) 833]. Methods for obtaining reaction rate data from laboratory reactors that approximate the ideal reactors listed in Table 3.5.1 are now discussed.

3.5.1 Batch Reactors

A batch reactor by its nature is a transient closed system. While a laboratory batch reactor can be a simple well-stirred flask in a constant temperature bath or a commercial laboratory-scale batch reactor, the direct measurement of reaction rates is not possible from these reactors. The observables are the concentrations of species from which the rate can be inferred. For example, in a typical batch experiment, the concentrations of reactants and products are measured as a function of time. From these data, initial reaction rates (rates at the zero conversion limit) can be obtained by calculating the initial slope (Figure 3.5.1b). Also, the complete data set can be numerically fit to a curve and the tangent to the curve calculated for any time (Figure 3.5.1a). The set of tangents can then be plotted versus the concentration at which the tangent was obtained (Figure 3.5.1c).

If, for example, the reaction rate function is first-order, then a plot of the tangents (dC/dt) versus concentration should be linear with a slope equal to the reaction rate constant and an intercept of zero. It is clear that the accuracy of the

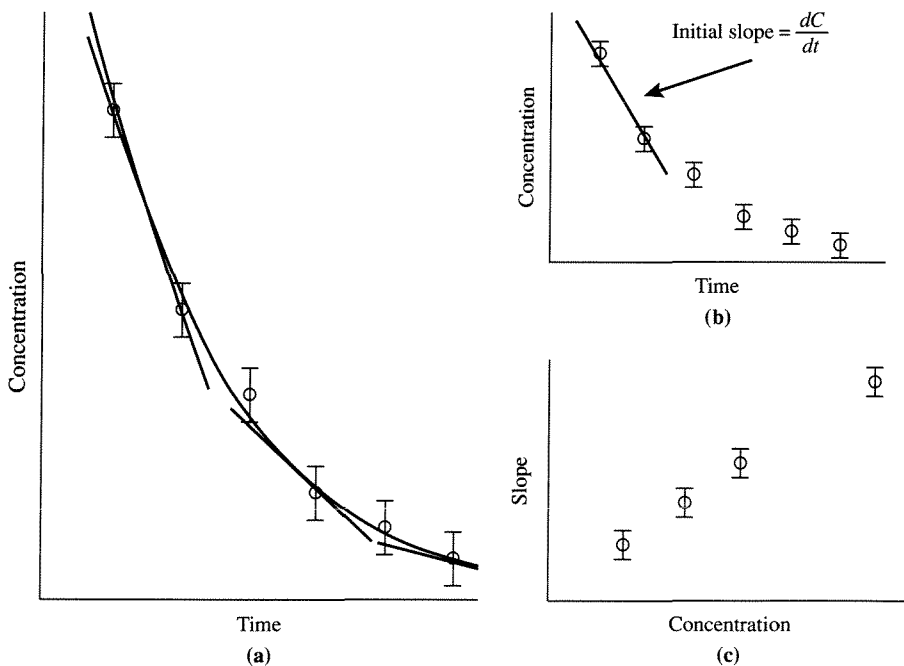


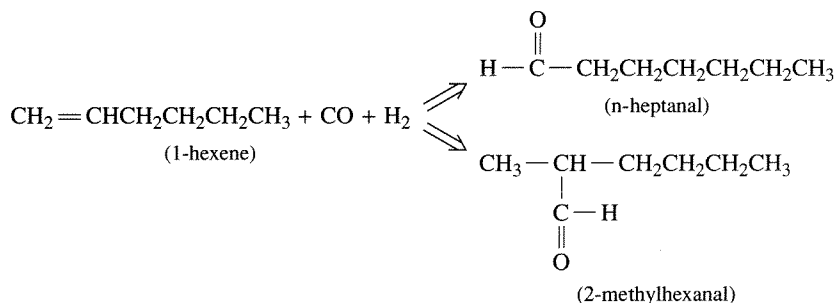
Figure 3.5.1 |

(a) Plot of concentration data versus time, a curve for a numerical fit of the data and lines at tangents to the curve at various times, (b) plot of the initial slope, (c) plot of the slopes of the tangent lines in (a) versus concentrations.

data (size of the error bars) is crucial to this method of determining good reaction rates. The accuracy will normally be fixed by the analytical technique used. Additionally, the greater the number of data points, the better the calculation of the rate. A typical way to measure concentrations is to sample the batch reactor and use chromatography for separation and determination of the amount of each component. In the best cases, this type of procedure has a time-scale of minutes. If the reaction is sufficiently slow, then this methodology can be used. Note, however, that only one datum point is obtained at each extent of reaction (i.e., at each time). If the reaction is fast relative to the time scale for sampling, then often it is not possible to follow the course of the reaction in a batch reactor.

EXAMPLE 3.5.1

P. Butler (Honors Thesis, Virginia Polytechnic Institute and State University, Blacksburg, VA, 1984) investigated the kinetics of the following reaction using rhodium catalysts:

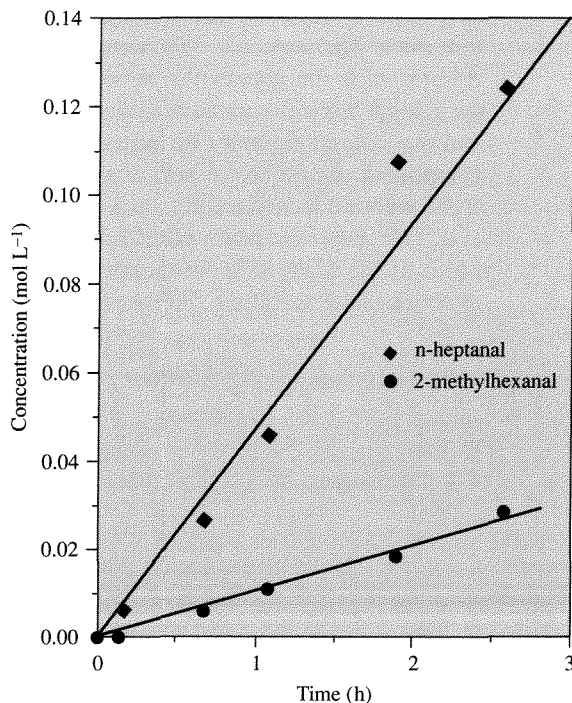


This homogeneous hydroformylation reaction was conducted in a batch reactor, and because of the nature of the catalyst, isomerization reactions of 1-hexene to 2- and 3-hexenes and hydrogenation reactions of hexenes to hexanes and aldehydes to alcohols were minimized. The following data were obtained at 323 K with an initial concentration of 1-hexene at 1 mol/L in toluene and $P_{\text{CO}} = P_{\text{H}_2} = P_{\text{N}_2} (\text{inert}) = 0.33 \text{ atm}$. Calculate the initial rates of formation of the linear, r_N , and branched, r_B , aldehydes from these data.

$t(\text{h})$	n -heptanal (mol/L)	2-methylhexanal (mol/L)
0.17	0.0067	0.0000
0.67	0.0266	0.0058
1.08	0.0461	0.0109
1.90	0.1075	0.0184
2.58	0.1244	0.0279

■ Answer

Plot the concentration data as follows:



The slopes of the lines shown in the plot give $r_N = 0.0515 \text{ mol/L/h}$ and $r_B = 0.0109 \text{ mol/L/h}$ (from linear regression).

EXAMPLE 3.5.2

Butler obtained the initial rate data given in the following table in a manner analogous to that illustrated in Example 3.5.1. Show that a reaction rate expression that follows Rules III and IV can be used to describe these data.

P_{CO} (atm)	P_{H_2} (atm)	$C_{1-\text{hexene}}$ (mol/L)	T (K)	r_N	r_B
0.50	0.50	1.00	323	0.0280	0.0074
0.33	0.33	1.00	323	0.0430	0.0115
0.66	0.33	1.00	323	0.0154	0.0040
0.33	0.33	1.00	313	0.0156	0.0040
0.33	0.33	1.00	303	0.0044	0.0016
0.33	0.33	0.45	323	0.0312	0.0069
0.33	0.33	1.00	323	0.0410	0.0100

■ Answer

An empirical expression of the rate takes the form:

$$r = k \exp[-E/(R_g T)] P_{\text{CO}}^{\alpha_1} P_{\text{H}_2}^{\alpha_2} C_{1-\text{hexene}}^{\alpha_3}$$

and was used to correlate the data to give (R_g in cal):

$$\begin{aligned} r_N &= 2.0 \times 10^{13} \exp[-22,200/(R_g T)] P_{\text{CO}}^{-1.5} P_{\text{H}_2}^{0.45} C_{1-\text{hexene}}^{0.40} \\ r_B &= 4.9 \times 10^{10} \exp[-19,200/(R_g T)] P_{\text{CO}}^{-1.5} P_{\text{H}_2}^{0.45} C_{1-\text{hexene}}^{0.64} \end{aligned}$$

Ideally, much more data are required in order to obtain a higher degree of confidence in the reaction rate expressions. However, it is clear from Examples 3.5.1 and 3.5.2 how much experimental work is required to do so. Also, note that these rates are *initial* rates and cannot be used for integral conversions.

3.5.2 Flow Reactors

As pointed out previously, the use of flow reactors allows for the direct measurement of reaction rates. At steady state (unlike the batch reactor), the time scales of the analytical technique used and the reaction are decoupled. Additionally, since numerous samples can be acquired at the same conditions, the accuracy of the data dramatically increases.

Consider the following problem. In the petrochemical industry, many reactions are oxidations and hydrogenations that are very exothermic. Thus, to control the temperature in an industrial reactor the configuration is typically a bundle of tubes (between 1 and 2 inches in diameter and thousands in number) that are bathed in a heat exchange fluid. The high heat exchange surface area per reactor volume allows the large heat release to be effectively removed. Suppose that a new catalyst is to be prepared for ultimate use in a reactor of this type to conduct a gas-phase reaction. How are appropriate reaction rate data obtained for this situation?

Consider first the tubular reactor. From the material balance (Table 3.5.1), it is clear that in order to solve the mass balance the functional form of the rate expression must be provided because the reactor outlet is the *integral* result of reaction over the volume of the reactor. However, if only initial reaction rate data were required, then a tubular reactor could be used by noticing that if the differentials are replaced by deltas, then:

$$F_i^0 \frac{\Delta f_i}{\Delta V_R} = (-v_i) r \Big|_{C_i^0} \quad (3.5.1)$$

Thus, a small tubular reactor that gives differential conversion (i.e., typically below 5 percent) can yield a point value for the reaction rate. In this case, the reaction rate is evaluated at C_i^0 . Actually, the rate could be better calculated with the arithmetic mean of the inlet and outlet concentrations:

$$C_i = \frac{C_i^0 + C_i^{\text{exit}}}{2}$$

However, since $C_i^0 \cong C_i^{\text{exit}}$ the inlet concentration is often used.

EXAMPLE 3.5.3

For the generic reaction $A \Rightarrow B$ the following three reaction rate expressions were proposed to correlate the initial rate data obtained. Describe how a differential tubular reactor could be used to discriminate among these models:

$$r_1 = \frac{k_1 C_A}{1 + k_2 C_B}$$

$$r_2 = \frac{k_3 C_A}{1 + k_4 C_B + k_5 C_A}$$

$$r_3 = \frac{k_6 C_A}{1 + k_7 C_A}$$

■ Answer

If initial rate data are obtained, and if there is no B in the feed stream, then the concentration of B at low conversion is small. Thus, at these conditions the rate expressions are:

$$r_1 = k_1 C_A$$

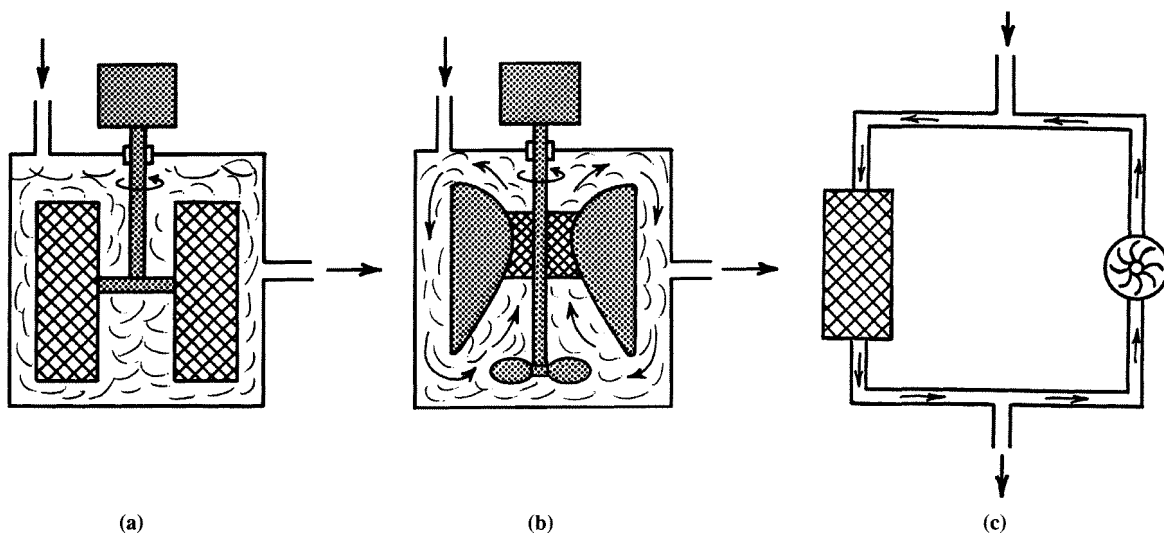
$$r_2 = \frac{k_3 C_A}{1 + k_5 C_A}$$

$$r_3 = \frac{k_6 C_A}{1 + k_7 C_A}$$

Clearly r_1 can be distinguished from r_2 and r_3 by varying C_A such that a plot of r versus C_A can be obtained. Now suppose that r_1 does not describe the data. In a second set of experiments, B can be added to the feed in varying amounts. If r_3 is the correct rate expression, then the measured rates will not change as C_B is varied. If there is a dependence of the observed rate on the concentration of feed B , then r_3 cannot describe the data.

Returning to the problem of obtaining reaction rate data from a new catalyst for a gas-phase reaction, if reaction rates are desired over the complete range of the extent of the reaction, the differential fixed bed is not an appropriate laboratory reactor for this purpose. However, the ideal stirred-flow reactor can accomplish this objective. By varying τ , r can be directly obtained (see Table 3.5.1) at any extent of reaction. The problem with a gas phase reaction is the mixing. If the reaction occurs in the liquid phase, thorough mixing can be achieved with high agitation in many cases. With gases the situation is more difficult. To overcome this, several reactor types have been developed and are commercially available on laboratory scale.

Referring to Figure 3.5.2, the Carberry reactor contains paddles in which the catalyst is mounted and the paddles are rapidly rotated via connection to a control shaft in order to obtain good mixing between the gas phase and the catalyst. A Berty reactor consists of a stationary bed of catalyst that is contacted via circulation of the gas phase by impeller blades. The quality of mixing in this type of configuration

**Figure 3.5.2 |**

Stirred contained solids reactors. [Reproduced from V. W. Weekman, Jr., *AIChE J.*, **20** (1974) p. 835, with permission of the American Institute of Chemical Engineers. Copyright © 1974 AIChE. All rights reserved.] (a) Carberry reactor, (b) Berty reactor (internal recycle reactor), (c) external recycle reactor.

depends on the density of the gas. For low densities (i.e., low pressures), the mixing is poor. Thus, Berty-type internal recycle reactors are most frequently used for reactions well above atmospheric pressure. For low-pressure gas circulation, external recycle can be employed via the use of a pump. At high recycle, these reactors approximate the behavior of a CSTR. This statement is proven below. Thus, these types of laboratory reactors have become the workhorses of the petrochemical industry for measuring accurate reaction rate data.

Consider a generic recycle reactor schematically illustrated in Figure 3.5.3. First, denote R as the recycle ratio. The recycle ratio is defined as the volume of fluid returning to the reaction chamber entrance divided by the volume of fluid leaving the system. Simple material balances around the mixing point prior to the entrance of the reaction volume give:

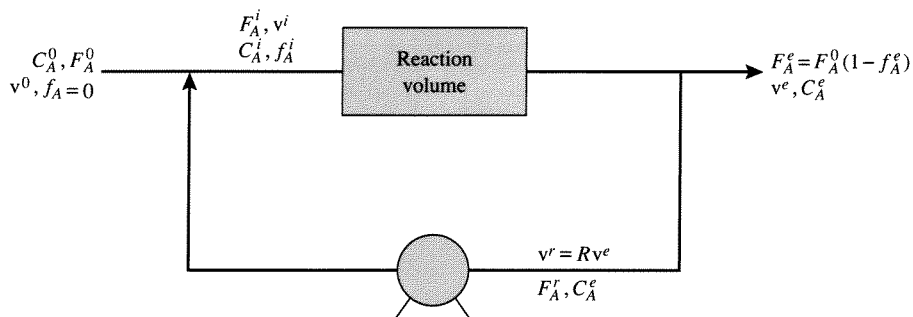
$$v^i = v^0 + v^r \quad (3.5.2)$$

and

$$C_A^i v^i = C_A^i (v^0 + v^r) = C_A^0 v^0 + C_A^e v^r \quad (3.5.3)$$

If the density of the fluid is constant then $v^e = v^0$ and $v^r = Rv^0$. Using these relationships with Equation (3.5.3) gives:

$$C_A^i (v^0 + Rv^0) = C_A^0 v^0 + C_A^e Rv^0 \quad (3.5.4)$$

**Figure 3.5.3 |**

Schematic diagram of a general recycle reactor. Superscripts *i*, *e*, and *r* refer to inlet, exit, and recycle. *R* is the recycle ratio.

or

$$C_A^i = \frac{C_A^0}{1+R} + \frac{RC_A^e}{1+R} \quad (3.5.5)$$

Notice that if $R \rightarrow \infty$, $C_A^i \rightarrow C_A^e$ or the result obtained from an ideal CSTR. Also, if $R \rightarrow 0$, $C_A^i \rightarrow C_A^0$, the inlet to the reaction volume. Thus, by fixing the value of *R*, the recycle reactor can behave like the two ideal limiting reactors (i.e., the CSTR and PFR, or anywhere between these limits). To see this further, a complete material balance on the reactor can be derived from Equation (3.4.2) and is:

$$\frac{dF_A}{dV_R} = v_A r \quad (3.5.6)$$

However, since

$$\begin{aligned} F_A &= vC_A \\ C_A &= C_A^0 \left(\frac{1 - f_A}{1 + \varepsilon_A f_A} \right) \\ v &= v^e + v^r = (R + 1)v^e = (R + 1)v^0(1 + \varepsilon_A f_A) \end{aligned}$$

then

$$\begin{aligned} F_A &= v^0 C_A^0 (R + 1)(1 - f_A) = F_A^0 (R + 1)(1 - f_A) \\ -dF_A &= F_A^0 (R + 1) df_A \end{aligned} \quad (3.5.7)$$

Substitution of Equation (3.5.7) into Equation (3.5.6) gives:

$$\frac{V_R}{F_A^0} = (R + 1) \int_{f_A^i}^{f_A^e} \frac{df_A}{(-v_A)r} \quad (3.5.8)$$

Now, f_A^i must be related to inlet and/or outlet variables for ease of evaluation from readily measurable parameters. To do so, notice that

$$C_A^i = \frac{F_A^i}{v^i} = \frac{F_A^0 + F_A^r}{v^0 + v^r} = \frac{F_A^0 + v^r C_A^e}{v^0 + v^r} = \frac{F_A^0 + R v^e C_A^e}{v^0 + R v^e}$$

In terms of f_A , C_A^i is then

$$C_A^i = \frac{F_A^0 + R F_A^0 (1 - f_A^e)}{v^0 + R v^0 (1 + \varepsilon_A f_A^e)} = \frac{F_A^0}{v^0} \left[\frac{1 + R(1 - f_A^e)}{1 + R(1 + \varepsilon_A f_A^e)} \right]$$

Thus,

$$\frac{C_A^i}{C_A^0} = \frac{1 + R - R f_A^e}{1 + R + R \varepsilon_A f_A^e} = \frac{1 - f_A^i}{1 + \varepsilon_A f_A^i}$$

Solving this equation for f_A^i gives:

$$f_A^i = \frac{R \varepsilon_A f_A^e + R f_A^e}{1 + R + \varepsilon_A + \varepsilon_A R} = \frac{R f_A^e}{1 + R} \quad (3.5.9)$$

Substitution of Equation (3.5.9) into Equation (3.5.8) yields:

$$\frac{V_R}{F_A^0} = (R + 1) \int_{f_A^e}^{f_A^i} \frac{df_A}{\frac{R f_A^e}{1 + R} (-v_A) r} \quad (3.5.10)$$

Clearly, if $R \rightarrow 0$, then Equation (3.5.10) reduces to the material balance for a PFR. However, it is not straightforward to recognize that Equation (3.5.10) reduces to the material balance for a CSTR as $R \rightarrow \infty$. To do so, notice that the bottom limit on the integral goes to f_A^e as $R \rightarrow \infty$. To obtain the value for the integral as $R \rightarrow \infty$, Leibnitz's Rule must be used, and it is:

$$\frac{d}{d\alpha} \int_{\varphi_1(\alpha)}^{\varphi_2(\alpha)} \bar{H}(x, \alpha) dx = \int_{\varphi_1(\alpha)}^{\varphi_2(\alpha)} \frac{\partial \bar{H}}{\partial \alpha} dx + \bar{H}(\varphi_2, \alpha) \frac{d\varphi_2}{d\alpha} - \bar{H}(\varphi_1, \alpha) \frac{d\varphi_1}{d\alpha}$$

Taking the limit of Equation (3.5.10) as $R \rightarrow \infty$ gives (L'Hopital's Rule):

$$\lim_{R \rightarrow \infty} \left(\frac{V_R}{F_A^0} \right) = \lim_{R \rightarrow \infty} \frac{\int_{f_A^e}^{f_A^i} \frac{df_A}{\frac{R f_A^e}{1 + R} (-v_A) r}}{\frac{1}{R + 1}}$$

To evaluate the numerator, use Leibnitz's Rule:

$$\frac{d}{dR} \int_{f_A^e}^{f_A^i} \frac{df_A}{\frac{R f_A^e}{1 + R} (-v_A) r} = \int_{f_A^e}^{f_A^i} \frac{\partial}{\partial R} \left[\frac{df_A}{(-v_A) r} \right] + \frac{1}{(-v_A) r} \bigg|_{f_A^e} \frac{df_A^e}{dR} - \frac{1}{(-v_A) r} \bigg|_{f_A^i} \frac{d}{dR} \left(\frac{R f_A^e}{1 + R} \right)$$

The first and second terms on the right-hand side of this equation are zero. Therefore,

$$\lim_{R \rightarrow \infty} \frac{V_R}{F_A^0} = \frac{-\frac{1}{(-v_A)r} \left| \frac{Rf_A^e}{1+R} \left[\frac{f_A^e}{(1+R)^2} \right] \right|}{-\frac{1}{(1+R)^2}} = \frac{f_A^e}{(-v_A)r|_{f_A^e}}$$

Note that this equation is the material balance for a CSTR (see Table 3.5.1). Thus, when using any recycle reactor for the measurement of reaction rate data, the effect of stirring speed (that fixes recirculation rates) on extent of reaction must be investigated. If the outlet conditions do not vary with recirculation rates, then the recycle reactor can be evaluated as if it were a CSTR.

EXAMPLE 3.5.4

Al-Saleh et al. [*Chem. Eng. J.*, **37** (1988) 35] performed a kinetic study of ethylene oxidation over a silver supported on alumina catalyst in a Berty reactor. At temperatures between 513–553 K and a pressure of 21.5 atm, the observed reaction rates (calculated using the CSTR material balance) were independent of the impeller rotation speed in the range 350–1000 rpm (revolutions per minute). A summary of the data is:

Temperature (K)	v^0 [L(h) ⁻¹]	f_{total}	Reaction rate $\times 10^4$ (mol gcat ⁻¹ h ⁻¹)	
			r_{EO}	r_{CO_2}
553	51.0	0.340	3.145	2.229
553	106.0	0.272	5.093	2.676
553	275.0	0.205	9.336	3.564
533	9.3	0.349	0.602	0.692
533	51.0	0.251	2.661	1.379
533	106.0	0.218	4.590	1.582
533	275.0	0.162	8.032	2.215
513	9.3	0.287	0.644	0.505
513	51.0	0.172	1.980	0.763
513	106.0	0.146	3.262	0.902
513	275.0	0.074	3.664	0.989

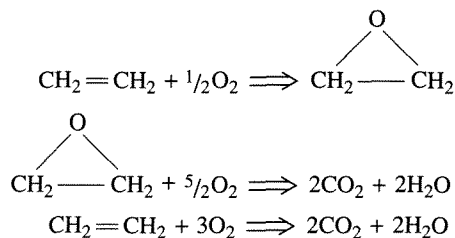
Derive the equations necessary to determine r_{EO} (rate of production of ethylene oxide) and r_{CO_2} (rate of production of CO₂). Assume for this example that the volumetric flow rate is unaffected by the reactions.

■ Answer

From Equation (3.3.6):

$$r_p = v_p r = F_p/V$$

Since the reaction rates are reported on a per mass of catalyst basis rather than per volume, V is replaced with W (the mass of catalyst in the reactor). The reaction network is:



For the molar flow rates,

$$F_{\text{EO}} = F_{\text{E}}^0 \left[\frac{C_{\text{EO}}^{\text{outlet}}}{C_{\text{E}}^0} \right]$$

$$F_{\text{CO}_2} = F_{\text{E}}^0 \left[\frac{C_{\text{CO}_2}^{\text{outlet}}}{C_{\text{E}}^0} \right]$$

where F_{E}^0 is the inlet molar flow rate of ethylene and C_{E}^0 is the inlet concentration of ethylene. Thus, the material balance equations are:

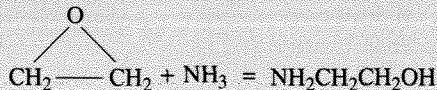
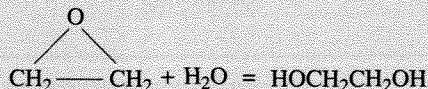
$$r_{\text{EO}} = \frac{F_{\text{E}}^0}{W} \left[\frac{C_{\text{EO}}^{\text{outlet}}}{C_{\text{E}}^0} \right]$$

$$r_{\text{CO}_2} = \frac{F_{\text{E}}^0}{W} \left[\frac{C_{\text{CO}_2}^{\text{outlet}}}{C_{\text{E}}^0} \right]$$

Notice that F_{E}^0 , W , and C_{E}^0 are all fixed for a particular experiment. Thus, measurement of the concentrations in the outlet stream directly yield values for the observed rates.

VIGNETTE 3.5.1

Ethylene oxide (EO) is one of the largest volume chemicals produced from ethylene. The reason for its importance lies in its ability for ethoxylation of other molecules. Reactions of EO are based on the ring opening by a nucleophilic molecule such as water, alcohols, ammonia, amines, carboxylic acids, phenols, or mercaptans. For example, ring-opening reactions of EO with water and ammonia give ethylene glycol and ethanolamines, respectively:



These products are manufactured at very large scale; for example, ethylene glycol production is in the millions of tons per year in the United States alone and is used as a heat transfer fluid such as antifreeze in the radiators of automobiles. With such large-scale use of EO, it is important that the selectivity to EO be as high as possible. Today, after years of catalyst optimization and advances in reactor technology, commercial Ag/Al₂O₃ catalysts give selectivities above 90 percent.

EXAMPLE 3.5.5

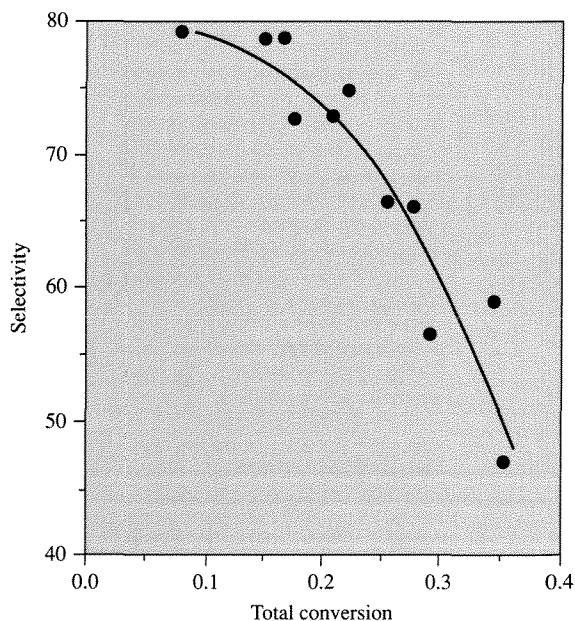
Using the data in Example 3.5.4 calculate the selectivity defined as the ratio of the moles of EO produced per mole of ethylene consumed times 100 percent, and plot the selectivity versus conversion.

Answer

The selectivity can be calculated as:

$$s_{\text{EO}} = \left[\frac{r_{\text{EO}}}{r_{\text{EO}} + r_{\text{CO}_2}} \right] \times 100\%$$

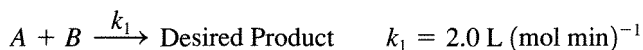
From the plot shown below, the selectivity declines as the conversion is increased because of combustion reactions that produce carbon dioxide.



In addition to the laboratory-scale reactors described here, there are numerous more specialized reactors in use. However, as mentioned previously, the performance of these reactors must lie somewhere between the mixing limits of the PFR and the CSTR. Additionally, when using small laboratory reactors, it is often difficult to maintain ideal mixing conditions, and the state of mixing should always be verified (see Chapter 8 for more details) prior to use. A common problem is that flow rates sufficiently large to achieve PFR behavior cannot be obtained in a small laboratory system, and the flow is laminar rather than turbulent (necessary for PFR behavior). If such is the case, the velocity profile across the reactor diameter is parabolic rather than constant.

Exercises for Chapter 3

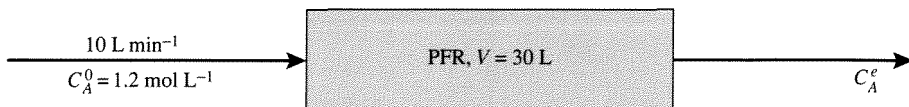
1. The space time necessary to achieve 70 percent conversion in a CSTR is 3 h. Determine the reactor volume required to process $4 \text{ ft}^3 \text{ min}^{-1}$. What is the space velocity for this system?
2. The following parallel reactions take place in a CSTR:



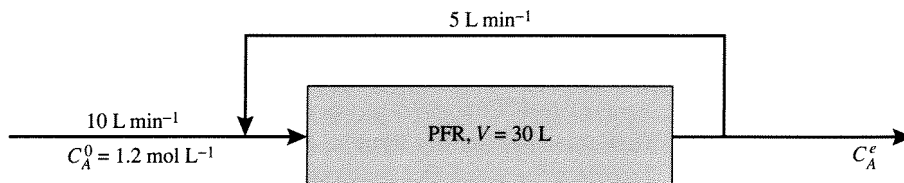
If a liquid stream of A (4 mol L^{-1} , 50 L min^{-1}) and a liquid stream of B (2 mol L^{-1} , 50 L min^{-1}) are co-fed to a 100 L reactor, what are the steady-state effluent concentrations of A and B?

3. The irreversible reaction $2A \rightarrow B$ takes place in the gas phase in a constant temperature plug flow reactor. Reactant A and diluent gas are fed in equimolar ratio, and the conversion of A is 85 percent. If the molar feed rate of A is doubled, what is the conversion of A assuming the feed rate of diluent is unchanged?
4. Consider the reversible first-order reaction of $A \rightleftharpoons B$ in a CSTR of volume $V = 2 \text{ L}$ with forward and reverse rate constants of $k_1 = 2.0 \text{ min}^{-1}$ and $k_{-1} = 1.0 \text{ min}^{-1}$. At time $t = 0$, the concentrations of A and B in the tank are both zero. The incoming stream of A has a volumetric flow rate of 3 L min^{-1} at concentration $C_A^0 = 2 \text{ mol L}^{-1}$. Find the concentrations of A and B as functions of time. You do not need a computer to solve this problem.
5. Consider the liquid phase reaction: $A \Rightarrow \text{products}$ with rate $r = 0.20 C_A^2$ ($\text{mol L}^{-1} \text{ min}^{-1}$) that takes place in a PFR of volume 30 L.

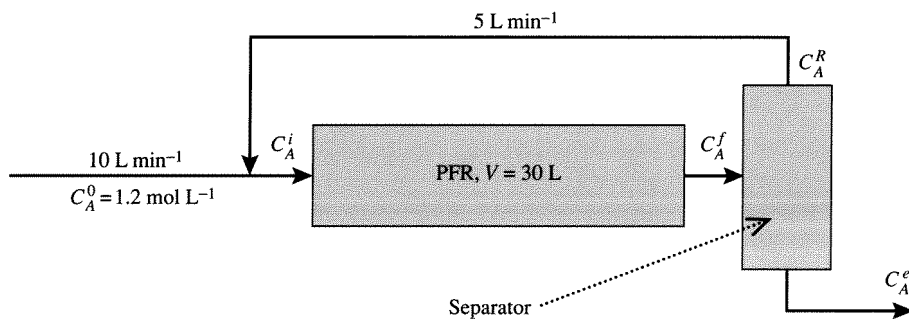
(a) What is the concentration of A (C_A^c) exiting the PFR?



(b) What is C_A^e in a PFR with recycle shown below?

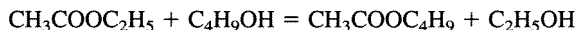


(c) Now, add a separator to the system. Find C_A^e , C_A^R , C_A^i and C_A^f . For the separator, assume $C_A^R = 5C_A^e$.



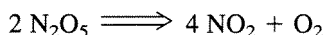
(Problem provided by Prof. J. L. Hudson, Univ. of Virginia.)

6. (Adapted from H. S. Fogler, *Elements of Chemical Reaction Engineering*, 3rd ed., Prentice Hall, Upper Saddle River, NJ, 1999.) Pure butanol is fed into a semibatch reactor containing pure ethyl acetate to produce butyl acetate and ethanol in the reversible reaction:

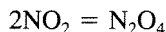


The reaction rate can be expressed in the Guldberg-Waage form. The reaction is carried out isothermally at 300 K. At this temperature, the equilibrium constant is 1.08 and the forward rate constant is $9.0 \times 10^{-5} \text{ L (mol s)}^{-1}$. Initially, there are 200 L of ethyl acetate in the reactor and butanol is fed at a rate of 0.050 L s^{-1} . The feed and initial concentrations of butanol and ethyl acetate are 10.93 mol L^{-1} and 7.72 mol L^{-1} , respectively.

- Plot the equilibrium conversion of ethyl acetate as a function of time.
 - Plot the conversion of ethylacetate, the rate of reaction, and the concentration of butanol as a function of time.
7. Dinitrogen pentoxide decomposes at 35°C with a first-order rate constant of $8 \times 10^{-3} \text{ min}^{-1}$ [F. Daniels and E. H. Johnston, *J. Am. Chem. Soc.*, **43** (1921) 53] according to:

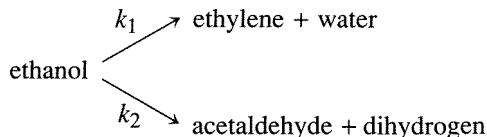


However, the product NO_2 rapidly dimerizes to N_2O_4 :



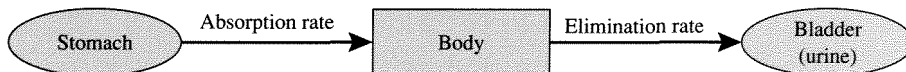
If the decomposition reaction is carried out in a constant volume at 35°C , plot the pressure rise in the reactor as a function of time, for an initial charge of pure N_2O_5 at 0.4 atm. Assume that the dimerization reaction equilibrates immediately. The equilibrium constant of the NO_2 dimerization reaction at 35°C is 3.68. Assume ideal behavior.

8. Ethanol can decompose in a parallel pathway:



Assume that the reaction rates are both first-order in ethanol and that no products are initially present. After 100 s in a constant volume system, there is 30 percent of the ethanol remaining and the mixture contains 13.7 percent ethylene and 27.4 percent acetaldehyde. Calculate the rate constants k_1 and k_2 .

9. Compound A is converted to B in a CSTR. The reaction rate is first-order with a reaction rate constant of 20 min^{-1} . Compound A enters the reactor at a flow rate of $12 \text{ m}^3/\text{min}$ (concentration of 2.0 kmol/m^3). The value of the product B is \$1.50 per kmol and the cost of reactor operation is \$2.50 per minute per cubic meter. It is not economical to separate unconverted A to recycle it back to the feed. Find the maximum profit.
10. A very simplified model for the dynamical processes occurring when an animal is given a drug can be represented by the single compartmental model shown below:



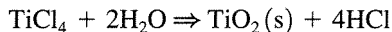
Upon administration of the drug, there is absorption into the body. Subsequently, the drug is converted to metabolites and/or is physically eliminated. As a result, the amount of drug in the body at any time is the net transient response to these input and output processes.

Find the maximum “body” alcohol level in grams and the time when it occurs for a 70 kg human who quickly consumes one can of beer. Assume the absorption and elimination rates are first-order.

Data: The mass of one can of beer is 400 g and contains 5 wt. % alcohol.

$$\begin{aligned} k_{\text{absorption}}/k_{\text{elimination}} &= 5 \\ k_{\text{elimination}} &= 0.008 \text{ min}^{-1} \end{aligned}$$

11. Titanium dioxide particles are used to brighten paints. They are produced by gas-phase oxidation of TiCl_4 vapor in a hydrocarbon flame. The dominant reaction is hydrolysis,



The reaction rate is first-order in TiCl_4 and zero-order in H_2O . The rate constant for the reaction is:

$$k = 8.0 \times 10^4 \exp \left[-\frac{88000 \text{ J/mol}}{R_g T} \right] \text{ s}^{-1}$$

The reaction takes place at 1200 K in a constant pressure flow reactor at 1 atm pressure ($1.01 \times 10^5 \text{ Pa}$). The gas composition at the entrance to the reactor is:

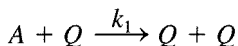
CO_2	8%
H_2O	8%
O_2	5%
TiCl_4	3%
N_2	remainder

- What space time is required to achieve 99 percent conversion of the TiCl_4 to TiO_2 ?
- The reactor is 0.2 m diameter and 1.5 m long. Assuming that the reactor operates 80 percent of the time, how many kilograms of TiO_2 can be produced per year? (The molecular weight of TiO_2 is 80 g/mol.)

$$R_g = 8.3144 \text{ J/mol/K}$$

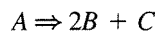
(Problem provided by Richard Flagan, Caltech.)

12. The autocatalytic reaction of A to form Q is one that accelerates with conversion. An example of this is shown below:



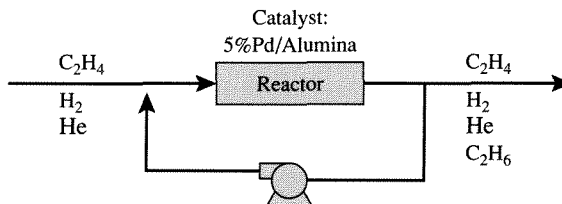
However, the rate decreases at high conversion due to the depletion of reactant A . The liquid feed to the reactor contains 1 mol L^{-1} of A and 0.1 mol L^{-1} of Q .

- To reach 50 percent conversion of A in the smallest reactor volume, would you use a PFR or a CSTR? Support your answer with appropriate calculations.
 - To reach 95 percent conversion of A in the smallest reactor volume, would you use a PFR or a CSTR? Support your answer with appropriate calculations.
 - What is the space time needed to convert 95 percent of A in a CSTR if $k_1 = 1 \text{ L (mol s)}^{-1}$?
13. The irreversible, first-order, gas-phase reaction



takes place in a constant volume batch reactor that has a safety disk designed to rupture when the pressure exceeds 1000 psi. If the rate constant is 0.01 s^{-1} , how long will it take to rupture the safety disk if pure A is charged into the reactor at 500 psi?

14. If you have a CSTR and a PFR (both of the same volume) available to carry out an irreversible, first-order, liquid-phase reaction, how would you connect them in series (in what order) to maximize the conversion?
15. Find the minimum number of CSTRs connected in series to give an outlet conversion within 5 percent of that achieved in a PFR of equal total volume for:
 - (a) first-order irreversible reaction of A to form B, $k\tau_{\text{PFR}} = 1$
 - (b) second-order irreversible reaction of A to form B, $kC_A^0\tau_{\text{PFR}} = 1$.
16. Davis studied the hydrogenation of ethylene to ethane in a catalytic recycle reactor operated at atmospheric pressure (R. J. Davis, Ph.D. Thesis, Stanford University, 1989.) The recycle ratio was large enough so that the reactor approached CSTR behavior. Helium was used as a diluent to adjust the partial pressures of the gases. From the data presented, estimate the orders of the reaction rate with respect to ethylene and dihydrogen and the activation energy of the reaction.



Hydrogenation of ethylene over 50 mg of Pd/alumina catalyst.

Reaction temperature (K)	Inlet flow C_2H_4 (mL min^{-1} STP)	Inlet flow H_2 (mL min^{-1} STP)	Inlet flow He (mL min^{-1} STP)	Conversion of C_2H_4 (%)
193	1.0	20	80	25.1
193	1.0	10	90	16.2
193	1.0	40	60	35.4
193	2.5	20	78.5	8.55
193	5.0	20	76	4.17
175	1.0	20	80	3.14