

Chapter 5

Ideal Reactors for a Single Reaction

In this chapter we develop the performance equations for a single fluid reacting in the three ideal reactors shown in Fig. 5.1. We call these *homogeneous reactions*. Applications and extensions of these equations to various isothermal and nonisothermal operations are considered in the following four chapters.

In the *batch reactor*, or BR, of Fig. 5.1a the reactants are initially charged into a container, are well mixed, and are left to react for a certain period. The resultant mixture is then discharged. This is an unsteady-state operation where composition changes with time; however, at any instant the composition throughout the reactor is uniform.

The first of the two ideal steady-state flow reactors is variously known as the *plug flow*, *slug flow*, *piston flow*, *ideal tubular*, and *unmixed flow reactor*, and it is shown in Fig. 5.1b. We refer to it as the *plug flow reactor*, or PFR, and to this pattern of flow as *plug flow*. It is characterized by the fact that the flow of fluid through the reactor is orderly with no element of fluid overtaking or mixing with any other element ahead or behind. Actually, there may be lateral mixing of fluid in a plug flow reactor; however, there must be no mixing or diffusion along

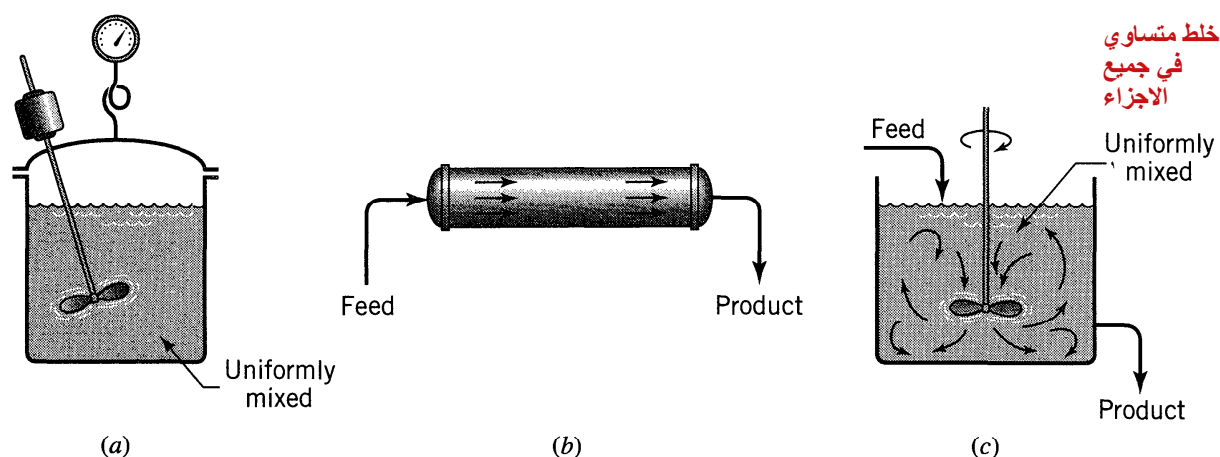


Figure 5.1 The three types of ideal reactors: (a) *batch reactor*, or BR; (b) *plug flow reactor*, or PFR; and (c) *mixed flow reactor*, or MFR.

the flow path. The necessary and sufficient condition for plug flow is for the residence time in the reactor to be the same for all elements of fluid.*

The other ideal steady-state flow reactor is called the mixed reactor, the backmix reactor, the ideal stirred tank reactor, the C^* (meaning C-star), CSTR, or the CFSTR (constant flow stirred tank reactor), and, as its names suggest, it is a reactor in which the contents are well stirred and uniform throughout. Thus, the exit stream from this reactor has the same composition as the fluid within the reactor. We refer to this type of flow as *mixed flow*, and the corresponding reactor the *mixed flow reactor*, or MFR.

These three ideals are relatively easy to treat. In addition, one or other usually represents the best way of contacting the reactants—no matter what the operation. For these reasons, we often try to design real reactors so that their flows approach these ideals, and much of the development in this book centers about them.

In the treatment to follow it should be understood that the term V , called the reactor volume, really refers to the volume of fluid in the reactor. When this differs from the internal volume of reactor, then V_r designates the internal volume of reactor while V designates the volume of reacting fluid. For example, in solid catalyzed reactors with voidage ε we have

$$V = \varepsilon V_r$$

For homogeneous systems, however, we usually use the term V alone.

5.1 IDEAL BATCH REACTOR

Make a material balance for any component A. For such an accounting we usually select the limiting component. In a batch reactor, since the composition is uniform throughout at any instant of time, we may make the accounting about the whole reactor. Noting that no fluid enters or leaves the reaction mixture during reaction, Eq. 4.1, which was written for component A, becomes

$$\overset{=0}{\cancel{\text{input}}} = \overset{=0}{\cancel{\text{output}}} + \text{disappearance} + \text{accumulation}$$

or

$$+ \left(\begin{array}{c} \text{rate of loss of reactant A} \\ \text{within reactor due to} \\ \text{chemical reaction} \end{array} \right) = - \left(\begin{array}{c} \text{rate of accumulation} \\ \text{of reactant A} \\ \text{within the reactor} \end{array} \right) \quad (1)$$

Evaluating the terms of Eq. 1, we find

$$\begin{array}{l} \text{disappearance of A} \\ \text{by reaction,} \\ \text{moles/time} \end{array} = (-r_A)V = \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})} \right) (\text{volume of fluid})$$

$$\begin{array}{l} \text{accumulation of A,} \\ \text{moles/time} \end{array} = \frac{dN_A}{dt} = \frac{d[N_{A0}(1 - X_A)]}{dt} = -N_{A0} \frac{dX_A}{dt}$$

* The necessary condition follows directly from the definition of plug flow. However, the sufficient condition—that the same residence times implies plug flow—can be established only from the second law of thermodynamics.

By replacing these two terms in Eq. 1, we obtain

$$(-r_A)V = N_{A0} \frac{dX_A}{dt} \quad (2)$$

Rearranging and integrating then gives

$$t = N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)V} \quad (3)$$

This is the general equation showing the time required to achieve a conversion X_A for either isothermal or nonisothermal operation. The volume of reacting fluid and the reaction rate remain under the integral sign, for in general they both change as reaction proceeds.

This equation may be simplified for a number of situations. If the **density of the fluid remains constant**, we obtain

حجم ثابت او یمكن يكون متغير

$$t = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A} = - \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A} \quad \text{for } \varepsilon_A = 0 \quad (4)$$

For all reactions in which the volume of reacting mixture changes proportionately with conversion, such as in single gas-phase reactions with significant **density changes**, Eq. 3 becomes

$$t = N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)V_0(1 + \varepsilon_A X_A)} = C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)(1 + \varepsilon_A X_A)} \quad (5)$$

In one form or another, Eqs. 2 to 5 have all been encountered in Chapter 3. They are applicable to both isothermal and nonisothermal operations. For the latter the variation of rate with temperature, and the variation of temperature with conversion, must be known before solution is possible. Figure 5.2 is a graphical representation of two of these equations.

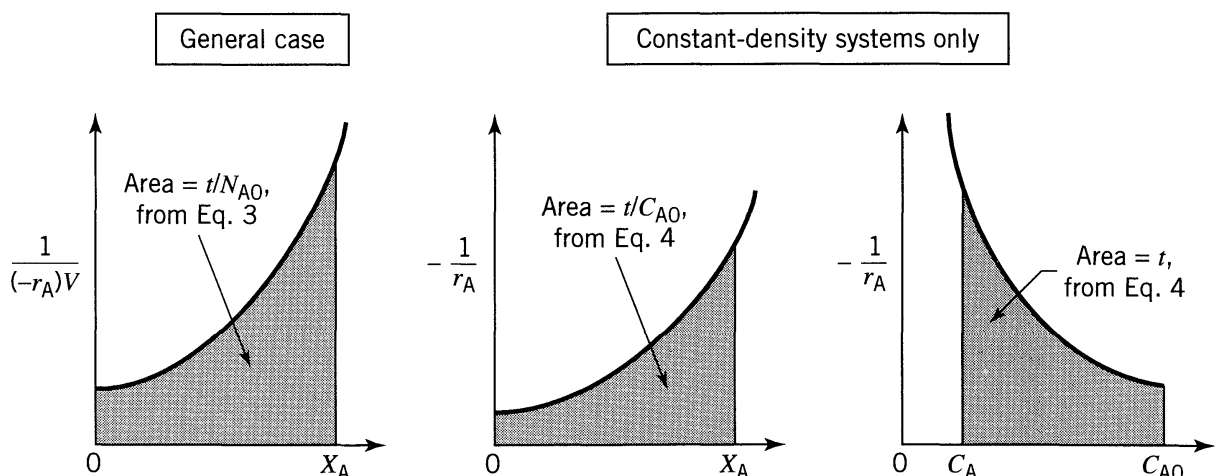


Figure 5.2 Graphical representation of the performance equations for batch reactors, isothermal or nonisothermal.

Space-Time and Space-Velocity

Just as the reaction time t is the natural performance measure for a batch reactor, so are the space-time and space-velocity the proper performance measures of flow reactors. These terms are defined as follows:

Space-time:

الزمن اللازم لمعالجة لحجم معين من المواد المتفاعلة بمقدار حجم المفاعل
الوقت اللازم لمعالجة حجم مفاعل واحد من التغذية المقاسة في ظروف محددة

$$\tau = \frac{1}{s} = \left(\frac{\text{time required to process one reactor volume of feed measured at specified conditions}}{\text{reactor volume of feed measured at specified conditions}} \right) = [\text{time}] \quad (6)$$

Space-velocity:

عدد حجومات المواد المتفاعلة (والتي حجمها بقدر حجم المفاعل) التي يمكن ان يعالجها المفاعل خلال وحدة الزمن
عدد أحجام تغذية المفاعل في ظروف محددة والتي يمكن معالجتها في وقت الوحدة

$$s = \frac{1}{\tau} = \left(\frac{\text{number of reactor volumes of feed at specified conditions which can be treated in unit time}}{\text{reactor volume of feed at specified conditions}} \right) = [\text{time}^{-1}] \quad (7)$$

Thus, a space-velocity of 5 hr^{-1} means that five reactor volumes of feed at specified conditions are being fed into the reactor per hour. A space-time of 2 min means that every 2 min one reactor volume of feed at specified conditions is being treated by the reactor.

Now we may arbitrarily select the temperature, pressure, and state (gas, liquid, or solid) at which we choose to measure the volume of material being fed to the reactor. Certainly, then, the value for space-velocity or space-time depends on the conditions selected. If they are of the stream entering the reactor, the relation between s and τ and the other pertinent variables is

$$\begin{aligned} \tau = \frac{1}{s} &= \frac{C_{A0}V}{F_{A0}} = \frac{\left(\frac{\text{moles A entering}}{\text{volume of feed}} \right) (\text{volume of reactor})}{\left(\frac{\text{moles A entering}}{\text{time}} \right)} \\ &= \frac{V}{v_0} = \frac{(\text{reactor volume})}{(\text{volumetric feed rate})} \end{aligned} \quad (8)$$

It may be more convenient to measure the volumetric feed rate at some standard state, especially when the reactor is to operate at a number of temperatures. If, for example, the material is gaseous when fed to the reactor at high temperature but is liquid at the standard state, care must be taken to specify precisely what state has been chosen. The relation between the space-velocity and space-time for actual feed conditions (unprimed symbols) and at standard conditions (designated by primes) is given by

$$\tau' = \frac{1}{s'} = \frac{C'_{A0}V}{F_{A0}} = \tau \frac{C'_{A0}}{C_{A0}} = \frac{1}{s} \frac{C'_{A0}}{C_{A0}} \quad (9)$$

In most of what follows, we deal with the space-velocity and space-time based on feed at actual entering conditions; however, the change to any other basis is easily made.

5.2 STEADY-STATE MIXED FLOW REACTOR

The performance equation for the mixed flow reactor is obtained from Eq. 4.1, which makes an accounting of a given component within an element of volume of the system. But since the composition is uniform throughout, the accounting may be made about the reactor as a whole. By selecting reactant A for consideration, Eq. 4.1 becomes

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

$= 0$

As shown in Fig. 5.3, if $F_{A0} = v_0 C_{A0}$ is the molar feed rate of component A to the reactor, then considering the reactor as a whole we have

input of A, moles/time = $F_{A0}(1 - X_{A0}) = F_{A0}$

output of A, moles/time = $F_A = F_{A0}(1 - X_A)$

disappearance of A by reaction, moles/time = $(-r_A)V = \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})} \right) (\text{volume of reactor})$

Introducing these three terms into Eq. 10, we obtain

$$F_{A0}X_A = (-r_A)V$$

which on rearrangement becomes

or

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{\Delta X_A}{-r_A} = \frac{X_A}{-r_A}$$

$$\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}X_A}{-r_A}$$

any ε_A (11)

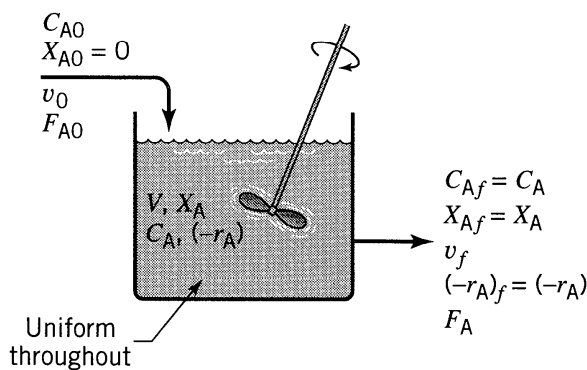


Figure 5.3 Notation for a mixed reactor.

where X_A and r_A are measured at exit stream conditions, which are the same as the conditions within the reactor.

More generally, if the feed on which conversion is based, subscript 0, enters the reactor partially converted, subscript i , and leaves at conditions given by subscript f , we have

$$\frac{V}{F_{A0}} = \frac{\Delta X_A}{(-r_A)_f} = \frac{X_{Af} - X_{Ai}}{(-r_A)_f}$$

or (12)

$$\tau = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}(X_{Af} - X_{Ai})}{(-r_A)_f}$$

For the special case of **constant-density** systems $X_A = 1 - C_A/C_{A0}$, in which case the performance equation for mixed reactors can also be written in terms of concentrations or

or

$\frac{V}{F_{A0}} = \frac{X_A}{-r_A} = \frac{C_{A0} - C_A}{C_{A0}(-r_A)}$ $\tau = \frac{V}{v} = \frac{C_{A0}X_A}{-r_A} = \frac{C_{A0} - C_A}{-r_A}$	$\varepsilon_A = 0$	(13)
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These expressions relate in a simple way the four terms X_A , $-r_A$, V , F_{A0} ; thus, knowing any three allows the fourth to be found directly. In design, then, the size of reactor needed for a given duty or the extent of conversion in a reactor of given size is found directly. In kinetic studies each steady-state run gives, without integration, the reaction rate for the conditions within the reactor. The ease of interpretation of data from a mixed flow reactor makes its use very attractive in kinetic studies, in particular with messy reactions (e.g., multiple reactions and solid catalyzed reactions).

Figure 5.4 is a graphical representation of these mixed flow performance equations. For any specific kinetic form the equations can be written out directly.

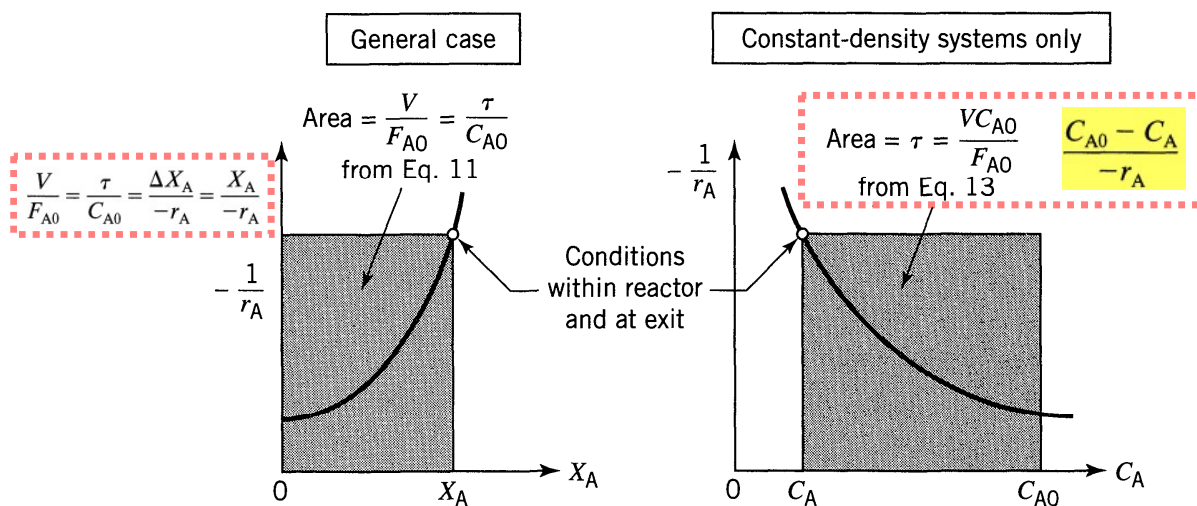


Figure 5.4 Graphical representation of the design equations for mixed flow reactor.

As an example, for constant density systems $C_A/C_{A0} = 1 - X_A$, thus the performance expression for *first-order reaction* becomes

$$k\tau = \frac{X_A}{1 - X_A} = \frac{C_{A0} - C_A}{C_A} \quad \text{for } \varepsilon_A = 0 \quad (14a)$$

On the other hand, for linear expansion

$$V = V_0(1 + \varepsilon_A X_A) \quad \text{and} \quad \frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A}$$

thus for *first-order reaction* the performance expression of Eq. 11 becomes

$$k\tau = \frac{X_A(1 + \varepsilon_A X_A)}{1 - X_A} \quad \text{for any } \varepsilon_A \quad (14b)$$

For *second-order reaction*, $A \rightarrow \text{products}$, $-r_A = kC_A^2$, $\varepsilon_A = 0$, the performance equation of Eq. 11 becomes

$$k\tau = \frac{C_{A0} - C_A}{C_A^2} \quad \text{or} \quad C_A = \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau} \quad (15)$$

Similar expressions can be written for any other form of rate equation. These expressions can be written either in terms of concentrations or conversions. Using conversions is simpler for systems of changing density, while either form can be used for systems of constant density.

EXAMPLE 5.1 REACTION RATE IN A MIXED FLOW REACTOR

One liter per minute of liquid containing A and B ($C_{A0} = 0.10$ mol/liter, $C_{B0} = 0.01$ mol/liter) flow into a mixed reactor of volume $V = 1$ liter. The materials react in a complex manner for which the stoichiometry is unknown. The outlet stream from the reactor contains A, B, and C ($C_{Af} = 0.02$ mol/liter, $C_{Bf} = 0.03$ mol/liter, $C_{Cf} = 0.04$ mol/liter), as shown in Fig. E5.1. Find the rate of reaction of A, B, and C for the conditions within the reactor.

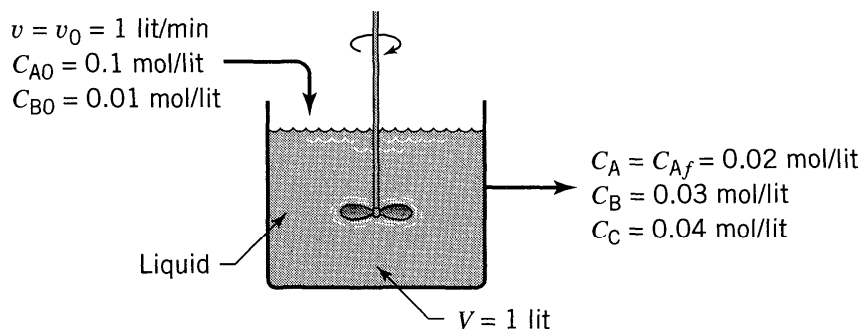


Figure E5.1

SOLUTION

For a liquid in a mixed flow reactor $\varepsilon_A = 0$ and Eq. 13 applies to each of the reacting components, giving for the rate of disappearance:

$$-r_A = \frac{C_{A0} - C_A}{\tau} = \frac{C_{A0} - C_A}{V/v} = \frac{0.10 - 0.02}{1/1} = \underline{\underline{0.08 \text{ mol/liter} \cdot \text{min}}}$$

$$-r_B = \frac{C_{B0} - C_B}{\tau} = \frac{0.01 - 0.03}{1} = \underline{\underline{-0.02 \text{ mol/liter} \cdot \text{min}}}$$

$$-r_C = \frac{C_{C0} - C_C}{\tau} = \frac{0 - 0.04}{1} = \underline{\underline{-0.04 \text{ mol/liter} \cdot \text{min}}}$$

Thus A is disappearing while B and C are being formed. ■

EXAMPLE 5.2 KINETICS FROM A MIXED FLOW REACTOR

Pure gaseous reactant A ($C_{A0} = 100$ millimol/liter) is fed at a steady rate into a mixed flow reactor ($V = 0.1$ liter) where it dimerizes ($2A \rightarrow R$). For different gas feed rates the following data are obtained:

Run number	1	2	3	4
v_0 , liter/hr	10.0	3.0	1.2	0.5
C_{Af} , millimol/liter	85.7	66.7	50	33.4

Find a rate equation for this reaction.

SOLUTION

For this stoichiometry, $2A \rightarrow R$, the expansion factor is

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

and the corresponding relation between concentration and conversion is

$$\frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A} = \frac{1 - X_A}{1 - \frac{1}{2} X_A}$$

or

$$X_A = \frac{1 - C_A/C_{A0}}{1 + \varepsilon_A C_A/C_{A0}} = \frac{1 - C_A/C_{A0}}{1 - C_A/2C_{A0}}$$

The conversion for each run is then calculated and tabulated in column 4 of Table E5.2.

$$\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}X_A}{-r_A}$$

Table E5.2

Run	Given		X_A	Calculated		
	v_0	C_A		$(-r_A) = \frac{v_0 C_{A0} X_A}{V}$	$\log C_A$	$\log (-r_A)$
1	10.0	85.7	0.25	$\frac{(10)(100)(0.25)}{0.1} = 2500$	1.933	3.398
2	3.0	66.7	0.50	1500	1.824	3.176
3	1.2	50	0.667	800	1.699	2.903
4	0.5	33.3	0.80	400	1.522	2.602

From the performance equation, Eq. 11, the rate of reaction for each run is given by

$$(-r_A) = \frac{v_0 C_{A0} X_A}{V}, \quad \left[\frac{\text{millimol}}{\text{liter} \cdot \text{hr}} \right]$$

These values are tabulated in column 5 of Table E5.2.

Having paired values of r_A and C_A (see Table E5.2) we are ready to test various kinetic expressions. Instead of separately testing for first-order (plot r_A vs. C_A), second-order (plot r_A vs. C_A^2), etc., let us test directly for n th-order kinetics. For this take logarithms of $-r_A = kC_A^n$, giving

$$\log(-r_A) = \log k + n \log C_A$$

For n th-order kinetics this data should give a straight line on a $\log(-r_A)$ vs. $\log C_A$ plot. From columns 6 and 7 of Table E5.2 and as shown in Fig. E5.2, the

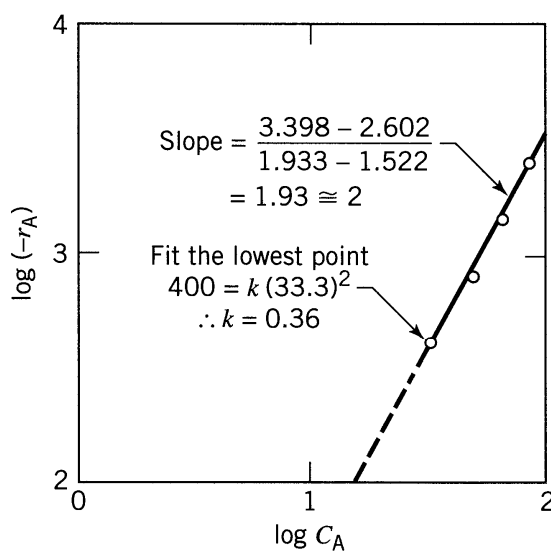


Figure E5.2

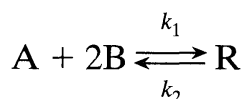
four data points are reasonably represented by a straight line of slope 2, so the rate equation for this dimerization is

$$\underline{-r_A = \left(0.36 \frac{\text{liter}}{\text{hr} \cdot \text{millimol}}\right) C_A^2, \quad \left[\frac{\text{millimol}}{\text{liter} \cdot \text{hr}}\right]}$$

Comment. If we ignore the density change in our analysis (or put $\varepsilon_A = 0$ and use $C_A/C_{A0} = 1 - X_A$) we end up with an incorrect rate equation (reaction order $n \cong 1.6$) which when used in design would give wrong performance predictions.

EXAMPLE 5.3 MIXED FLOW REACTOR PERFORMANCE

The elementary liquid-phase reaction



with rate equation

$$-r_A = -\frac{1}{2}r_B = (12.5 \text{ liter}^2/\text{mol}^2 \cdot \text{min})C_A C_B^2 - (1.5 \text{ min}^{-1})C_R, \quad \left[\frac{\text{mol}}{\text{liter} \cdot \text{min}}\right]$$

is to take place in a 6-liter steady-state mixed flow reactor. Two feed streams, one containing 2.8 mol A/liter and the other containing 1.6 mol B/liter, are to be introduced at equal volumetric flow rates into the reactor, and 75% conversion of limiting component is desired (see Fig. E5.3). What should be the flow rate of each stream? Assume a constant density throughout.

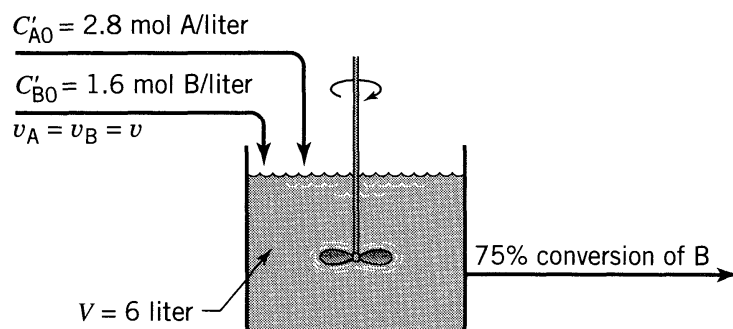


Figure E5.3

SOLUTION

The concentration of components in the mixed feed stream is

$$C_{A0} = 1.4 \text{ mol/liter}$$

$$C_{B0} = 0.8 \text{ mol/liter}$$

$$C_{R0} = 0$$

These numbers show that B is the limiting component, so for 75% conversion of B and $\varepsilon = 0$, the composition in the reactor and in the exit stream is

$$C_A = 1.4 - 0.6/2 = 1.1 \text{ mol/liter}$$

$$C_B = 0.8 - 0.6 = 0.2 \text{ mol/liter} \quad \text{or} \quad 75\% \text{ conversion}$$

$$C_R = 0.3 \text{ mol/liter}$$

Writing the rate and solving the problem in terms of B we have at the conditions within the reactor

$$\begin{aligned} -r_B &= 2(-r_A) = (2 \times 12.5)C_A C_B^2 - (2 \times 1.5)C_R \\ &= \left(25 \frac{\text{liter}^2}{\text{mol}^2 \cdot \text{min}}\right) \left(1.1 \frac{\text{mol}}{\text{liter}}\right) \left(0.2 \frac{\text{mol}}{\text{liter}}\right)^2 - (3 \text{ min}^{-1}) \left(0.3 \frac{\text{mol}}{\text{liter}}\right) \\ &= (1.1 - 0.9) \frac{\text{mol}}{\text{liter} \cdot \text{min}} = 0.2 \frac{\text{mol}}{\text{liter} \cdot \text{min}} \end{aligned}$$

For no density change, the performance equation of Eq. 13 gives

$$\tau = \frac{V}{v} = \frac{C_{B0} - C_B}{-r_B}$$

Hence the volumetric flow rate into and out of the reactor is

$$\begin{aligned} v &= \frac{V(-r_B)}{C_{B0} - C_B} \\ &= \frac{(6 \text{ liter})(0.2 \text{ mol/liter} \cdot \text{min})}{(0.8 - 0.6) \text{ mol/liter}} = \underline{\underline{6 \text{ liter/min}}} \end{aligned}$$

or

$$\underline{\underline{3 \text{ liter/min of each of the two feed streams}}}$$