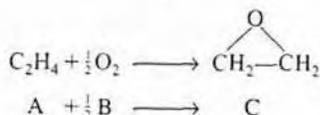


Example 4-6 Calculating X in a Reactor with Pressure Drop

The economics

Approximately 7 billion pounds of ethylene oxide were produced in the United States in 1997. The 1997 selling price was \$0.58 a pound, amounting to a commercial value of \$4.0 billion. Over 60% of the ethylene oxide produced is used to make ethylene glycol. The major end uses of ethylene oxide are antifreeze (30%), polyester (30%), surfactants (10%), and solvents (5%). We want to calculate the catalyst weight necessary to achieve 60% conversion when ethylene oxide is to be made by the vapor-phase catalytic oxidation of ethylene with air.

The uses



Ethylene and oxygen are fed in stoichiometric proportions to a packed-bed reactor operated isothermally at 260°C. Ethylene is fed at a rate of 0.30 lb mol/s at a pressure of 10 atm. It is proposed to use 10 banks of 1½-in.-diameter schedule 40 tubes packed with catalyst with 100 tubes per bank. Consequently, the molar flow rate to each tube is to be 3×10^{-4} lb mol/s. The properties of the reacting fluid are to be considered identical to those of air at this temperature and pressure. The density of the ¼-in.-catalyst particles is 120 lb/ft³ and the bed void fraction is 0.45. The rate law is

$$-r'_A = kP_A^{1/3}P_B^{2/3} \quad \text{lb mol/lb cat} \cdot \text{h}$$

with⁵

$$k = 0.0141 \frac{\text{lb mol}}{\text{atm} \cdot \text{lb cat} \cdot \text{h}} \text{ at } 260^\circ\text{C}$$

Solution**1. Differential mole balance:**

$$F_{A0} \frac{dX}{dW} = -r'_A \quad (\text{E4-6.1})$$

2. Rate law:

$$-r'_A = kP_A^{1/3}P_B^{2/3} = k(C_A RT)^{1/3}(C_B RT)^{2/3} \quad (\text{E4-6.2})$$

$$= kRT C_A^{1/3} C_B^{2/3} \quad (\text{E4-6.3})$$

3. Stoichiometry. Gas-phase, isothermal $v = v_0(1 + \epsilon X)(P_0/P)$:

$$C_A = \frac{F_A}{v} = \frac{C_{A0}(1-X)}{1 + \epsilon X} \left(\frac{P}{P_0} \right) = \frac{C_{A0}(1-X)y}{1 + \epsilon X} \quad \text{where } y = \frac{P}{P_0} \quad (\text{E4-6.4})$$

⁵ *Ind. Eng. Chem.*, 45, 234 (1953).

$$C_B = \frac{F_B}{v} = \frac{C_{A0}(\Theta_B - X/2)}{1 + \varepsilon X} y \quad (\text{E4-6})$$

For stoichiometric feed $\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{1}{2}$

$$C_B = \frac{C_{A0}(1-X)}{2(1+\varepsilon X)} y$$

For isothermal operation, Equation (4-30) becomes

$$\frac{dy}{dW} = -\frac{\alpha}{2y}(1 + \varepsilon X) \quad (\text{E4-7})$$

4. **Combining** the rate law and concentrations:

$$-r'_A = kRT_0 \left[\frac{C_{A0}(1-X)}{1+\varepsilon X} (y) \right]^{1/3} \left[\frac{C_{A0}(1-X)}{2(1+\varepsilon X)} (y) \right]^{2/3} \quad (\text{E4-8})$$

Factoring $(\frac{1}{2})^{2/3}$ and recalling $P_{A0} = C_{A0} RT_0$, we can simplify Equation (E4-6)

$$-r'_A = k' \left(\frac{1-X}{1+\varepsilon X} \right) y \quad (\text{E4-9})$$

where $k' = kP_{A0} (\frac{1}{2})^{2/3} = 0.63kP_{A0}$.

5. **Parameter evaluation per tube** (i.e., divide feed rates by 1000):

Ethylene: $F_{A0} = 3 \times 10^{-4} \text{ lb mol/s} = 1.08 \text{ lb mol/h}$

Oxygen: $F_{B0} = 1.5 \times 10^{-4} \text{ lb mol/s} = 0.54 \text{ lb mol/h}$

I = inerts = N₂: $F_I = 1.5 \times 10^{-4} \text{ lb mol/s} \times \frac{0.79 \text{ mol N}_2}{0.21 \text{ mol O}_2}$

$$F_I = 5.64 \times 10^{-4} \text{ lb mol/s} = 2.03 \text{ lb mol/h}$$

Summing: $F_{T0} = F_{A0} + F_{B0} + F_I = 3.65 \text{ lb mol/h}$

$$y_{A0} = \frac{F_{A0}}{F_{T0}} = \frac{1.08}{3.65} = 0.30$$

$$\varepsilon = y_{A0}\delta = (0.3)(1 - \frac{1}{2} - 1) = -0.15$$

$$P_{A0} = y_{A0}P_0 = 3.0 \text{ atm}$$

$$k' = kP_{A0} (\frac{1}{2})^{2/3} = 0.0141 \frac{\text{lb mol}}{\text{atm} \cdot \text{lb cat} \cdot \text{h}} \times 3 \text{ atm} \times 0.63 = 0.0266 \frac{\text{lb mol}}{\text{h} \cdot \text{lb cat}}$$

In order to calculate α ,

$$\alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_c P_0}$$

we need the superficial mass velocity, G . The mass flow rates of each species are

We can evaluate the **combine** step either

1. Analytically
2. Graphically
3. Numerically, or
4. Using software

Evaluating the pressure drop parameters

$$\dot{m}_{A0} = 1.08 \frac{\text{lb mol}}{\text{h}} \times 28 \frac{\text{lb}}{\text{lb mol}} = 30.24 \text{ lb/h}$$

$$\dot{m}_{B0} = 0.54 \frac{\text{lb mol}}{\text{h}} \times 32 \frac{\text{lb}}{\text{lb mol}} = 17.28 \text{ lb/h}$$

$$\dot{m}_{I0} = 2.03 \frac{\text{lb mol}}{\text{h}} \times 28 \frac{\text{lb}}{\text{lb mol}} = 56.84 \text{ lb/h}$$

The total mass flow rate is

$$\dot{m}_{T0} = 104.4 \frac{\text{lb}}{\text{h}}$$

$$G = \frac{\dot{m}_{T0}}{A_c} = \frac{104.4 \text{ lb/h}}{0.01414 \text{ ft}^2} = 7383.3 \frac{\text{lb}}{\text{h} \cdot \text{ft}^2}$$

Ah ha! The superficial mass velocity, temperature, and pressure are the same as in Example 4-4. Consequently, we can use the value of β_0 calculated in Example 4-4, to calculate α

$$\beta_0 = 0.0775 \frac{\text{atm}}{\text{ft}}$$

$$\begin{aligned} \alpha &= \frac{2\beta_0}{A_c(1-\phi)\rho_c P_0} = \frac{(2)(0.0775) \text{ atm/ft}}{(0.01414 \text{ ft}^2)(0.55)(120 \text{ lb cat/ft}^3)(10 \text{ atm})} \\ &= \frac{0.0166}{\text{lb cat}} \quad (\alpha = 3.656 \times 10^{-5} / \text{g cat}) \end{aligned}$$

6. **Summary.** Combining Equation (E4-6.1) and (E4-6.8) and summarizing

$$\left\{ \begin{array}{l} \frac{dX}{dW} = \frac{k' (1-X)}{F_{A0} (1+\varepsilon X)} y \end{array} \right. \quad (\text{E4-6.9})$$

$$\left\{ \begin{array}{l} \frac{dy}{dW} = -\frac{\alpha(1+\varepsilon X)}{2y} \end{array} \right. \quad (\text{E4-6.10})$$

$$\left\{ \begin{array}{l} k' = 0.0266 \frac{\text{lb mol}}{\text{h lb cat}} \end{array} \right. \quad (\text{E4-6.11})$$

$$\left\{ \begin{array}{l} F_{A0} = 1.08 \text{ lb } \frac{\text{lb mol}}{\text{h}} \end{array} \right. \quad (\text{E4-6.12})$$

$$\left\{ \begin{array}{l} \alpha = \frac{0.0166}{\text{lb cat}} \end{array} \right. \quad (\text{E4-6.13})$$

$$\left\{ \begin{array}{l} \varepsilon = -0.15 \end{array} \right. \quad (\text{E4-6.14})$$

We have the boundary conditions $W = 0$, $X = 0$, and $y = 1.0$, and $W_T = 60$ lb. Here we are guessing an upper limit of the integration to be 60 lb with the expectation that 60% conversion will be achieved within this catalyst weight. If 60% conversion is not achieved, we will guess a higher weight and redo the calculation.

A large number of ordinary differential equation solver software packages (i.e., ODE solvers), which are extremely user friendly, have become available. We

Program examples
Polymath,
MATLAB can be
loaded from the
CD-ROM (see the
Introduction).

Volumetric flow
rate increases
with increasing
pressure drop.

$$f = \frac{v_0}{v}$$

$$y = \frac{P}{P_0}$$



Living Example Problem

There is a
Polymath ODE
tutorial in Chapter 1
Summary Notes.

shall use Polymath⁶ to solve the examples in the printed text. With Polymath, one simply enters Equations (E4-6.9) and (E4-6.10) and the corresponding parameter values [Equations (4-6.11) through (4-6.14)] into the computer with the boundary conditions and they are solved and displayed as shown in Figures E4-6.1 and E4-6.2. Equations (E4-6.9) and (E4-6.10) are entered as differential equations and the parameter values are set using explicit equations. The rate law may be entered as an explicit equation in order to generate a plot of reaction rate as it changes down the length of the reactor, using Polymath's graphing function. The CD-ROM contains all of the MatLab and Polymath solution programs used to solve the example problems, as well as an example using ASPEN. Consequently, one can load the Polymath program directly from the CD-ROM, which has programmed Equations (E4-6.9) through (E4-6.14), and run the program for different parameter values.

It is also interesting to learn what happens to the volumetric flow rate along the length of the reactor. Recalling Equation (3-45),

$$v = v_0(1 + \varepsilon X) \frac{P_0}{P} \frac{T}{T_0} = \frac{v_0(1 + \varepsilon X)(T/T_0)}{P/P_0} \quad (3-45)$$

We let f be the ratio of the volumetric flow rate, v , to the entering volumetric flow rate, v_0 , at any point down the reactor. For isothermal operation Equation (3-45) becomes

$$f = \frac{v}{v_0} = \frac{1 + \varepsilon X}{y} \quad (E4-6.15)$$

TABLE E4-6.1 POLYMATH PROGRAM

ODE REPORT (STIFF)

Differential equations as entered by the user

- [1] $d(X)/d(W) = -\text{raprime}/\text{Fao}$
- [2] $d(y)/d(W) = -\text{alpha}*(1+\text{eps}*X)/2/y$

Explicit equations as entered by the user

- [1] $\text{eps} = -0.15$
- [2] $\text{kprime} = 0.0266$
- [3] $\text{Fao} = 1.08$
- [4] $\text{alpha} = 0.0166$
- [5] $\text{raprime} = -\text{kprime}*(1-X)/(1+\text{eps}*X)*y$
- [6] $f = (1+\text{eps}*X)/y$
- [7] $\text{rate} = -\text{raprime}$

⁶ Developed by Professor M. Cutlip of the University of Connecticut, and Professor M. Shacham of Ben Gurion University. Available from the CACHE Corporation, P.O. Box 7939, Austin, TX 78713.

Figure E4-6.2 shows X , y (i.e., $y = P/P_0$), and f down the length of the reactor. We see that both the conversion and the volumetric flow increase along the length of the reactor while the pressure decreases. For gas-phase reactions with orders greater than zero, this decrease in pressure will cause the reaction rate to be less than in the case of no pressure drop.

Program examples
Polymath,
MATLAB can be
loaded from the
CD-ROM (see the
Introduction).

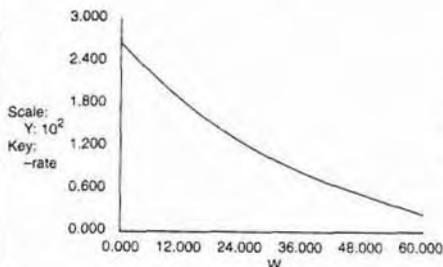


Figure E4-6.1 Reaction rate profile down the PBR.

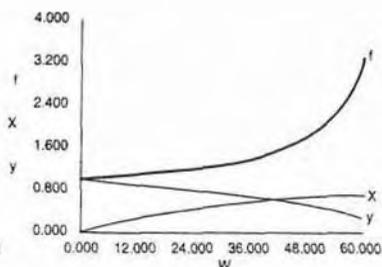


Figure E4-6.2 Output in graphical form from Polymath.

From either the conversion profile (shown in Figure E4-6.2) or the Polymath table of results (not shown in text, but available on the CD), we find 60% conversion is achieved with 44.5-lb catalyst in each tube.

We note from Figure E4-6.2 that the catalyst weight necessary to raise the conversion the last 1% from 65% to 66% (3.5 lb) is 8.5 times more than that (0.41 lb) required to raise the conversion 1% at the reactor's entrance. Also, during the last 5% increase in conversion, the pressure decreases from 3.8 atm to 2.3 atm.

This catalyst weight of 44.5 lb/tube corresponds to a pressure drop of approximately 5 atm. If we had erroneously neglected pressure drop, the catalyst weight would have been found by integrating equation (E4-6.9) with $y = 1$ to give

$$W = \frac{F_{A0}}{k'} \left[(1 + \epsilon) \ln \left(\frac{1}{1-X} - \epsilon X \right) \right] \quad (\text{E4-6.16})$$

$$= \frac{1.08}{0.0266} \times \left[(1 - 0.15) \ln \frac{1}{1 - 0.6} - (-0.15)(0.6) \right] \quad (\text{E4-6.17})$$

$$= 35.3 \text{ lb. of catalyst per tube (neglecting pressure drop) (16 kg/tube)}$$

If we had used this catalyst weight in our reactor we would have had insufficient catalyst to achieve the desired conversion. For this catalyst weight (i.e., 35.300 lb total, 35.3 lb/tube) Figure E4-6.2 gives a conversion of only 53%.

Effect of added
catalyst on
conversion

Neglecting
pressure drop
results in poor
design (here 53%
vs. 60% conversion)

Embarrassing!

4.5.5 Spherical Packed-Bed Reactors



Reference Shelf

Synthesizing a
chemical plant

Always
challenge the
assumptions,
constraints, and
boundaries of the
problem.

Let's consider carrying out this reaction in a spherical reactor similar to one shown in the margin and discussed in detail in the CD-ROM. In a spherical reactor, the cross section varies as we move through the reactor and is greater than in a normal packed-bed reactor. Consequently, the superficial velocity $G = \dot{m}/A_c$ will be smaller. From Equation (4-22), we see that the smaller value of G will give a smaller pressure drop and thus a greater conversion. If 40,000 lb of catalyst in the PBR in Example 4-6 had been used in a spherical reactor, 67% conversion would have been achieved instead of 10% conversion. The equations for calculating conversion in spherical reactors along with an example problem are given in the *Professional Reference Shelf* R4.1 for Chapter 4 on the CD-ROM.

4.6 Synthesizing the Design of a Chemical Plant

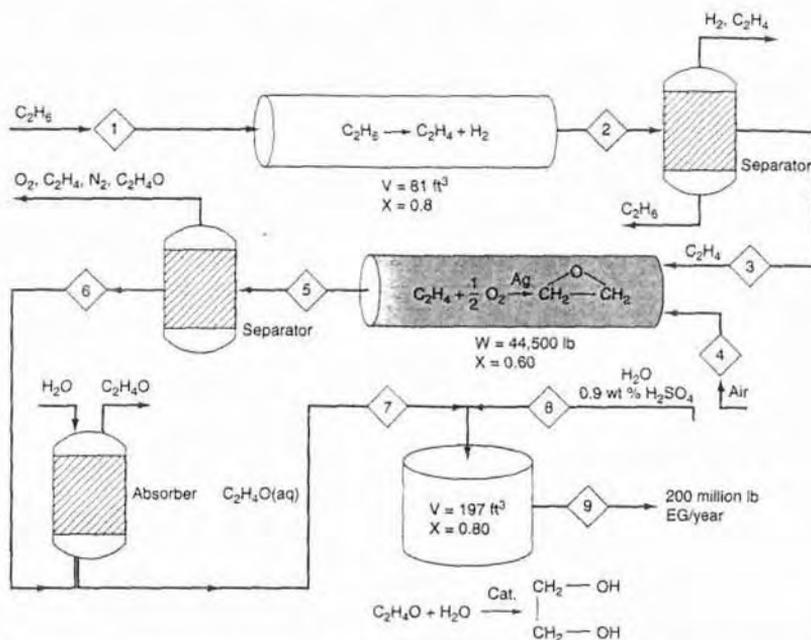
Careful study of the various reactions, reactors, and molar flows of the reactants and products used in the example problems in this chapter reveals that they can be arranged to form a chemical plant to produce 200 million pounds of ethylene glycol from a feedstock of 402 million pounds per year of ethane. The flowsheet for the arrangement of the reactors together with the molar flow rates is shown in Figure 4-10. Here 0.425 lb mol/s of ethane is fed to 100 tubular plug-flow reactors connected in parallel; the total volume is 81 ft³ to produce 0.34 lb mol/s of ethylene (see Example 4-3). The reaction mixture is then fed to a separation unit where 0.04 lb mol/s of ethylene is lost in the separation process in the ethane and hydrogen streams that exit the separator. This process provides a molar flow rate of ethylene of 0.3 lb mol/s, which enters a packed-bed catalytic reactor together with 0.15 lb mol/s of O₂ and 0.564 lb mol/s of N₂. There are 0.18 lb mol/s of ethylene oxide (see Example 4-6) produced in the 1000 pipes arranged in parallel and packed with silver-coated catalyst pellets. There is 60% conversion achieved in each pipe and the total catalyst weight in all the pipes is 44,500 lb. The effluent stream is passed to a separator where 0.03 lb mol/s of ethylene oxide is lost. The ethylene oxide stream is then contacted with water in a gas absorber to produce a 1-lb mol solution of ethylene oxide in water. In the absorption process, 0.022 lb mol of ethylene oxide is lost. The ethylene oxide solution is fed to a 197-ft³ CS together with a stream of 0.9 wt % H₂SO₄ solution to produce ethylene glycol at a rate of 0.102 lb mol/s (see Example 4-2). This rate is equivalent to approximately 200 million pounds of ethylene glycol per year.

The profit from a chemical plant will be the difference between income from sales and the cost to produce the chemicals. An approximate formula might be

\$\$\$\$

$$\text{Profit} = \text{Value of products} - \text{Cost of reactants}$$

$$- \text{Operating cost} - \text{Separation costs}$$



Stream	Component ^a	Flow rate (lb mol/s)	Stream	Component ^a	Flow rate (lb mol/s)
1	C ₂ H ₆	0.425	6	EO	0.150
2	C ₂ H ₄	0.340	7	EO	0.128
3	C ₂ H ₄	0.300	8	H ₂ O	0.443
4	Air	0.714	9	EG	0.102
5	EO	0.180			

^aEG, ethylene glycol; EO, ethylene oxide.

Figure 4-10 Production of ethylene glycol.

The operating costs include such costs as energy, labor, overhead, and depreciation of equipment. You will learn more about these costs in your senior design course. While most, if not all, of the streams from the separators could be recycled, let's consider what the profit might be if the streams were to go unrecovered. Also, let's conservatively estimate the operating and other expenses to be \$8 million per year and calculate the profit. Your design instructor might give you a better number. The prices of ethane, sulfuric acid, and ethylene glycol are \$0.04, \$0.043, and \$0.38 per pound, respectively. See www.chemweek.com/ for current prices.

For an ethane feed of 400 million pounds per year and a production rate of 200 million pounds of ethylene glycol per year:

$$\begin{aligned}
 \text{Profit} &= \left[\overbrace{\left(\frac{\$0.38}{\text{lb}} \times 2 \times 10^8 \frac{\text{lb}}{\text{year}} \right)}^{\text{Ethylene glycol cost}} \right] - \left[\overbrace{\left(\frac{\$0.04}{\text{lb}} \times 4 \times 10^8 \frac{\text{lb}}{\text{year}} \right)}^{\text{Ethane cost}} \right] \\
 &\quad - \left[\overbrace{\left(\frac{\$0.043}{\text{lb}} \times 2.26 \times 10^6 \frac{\text{lb}}{\text{year}} \right)}^{\text{Sulfuric acid cost}} \right] - \left[\overbrace{\$8,000,000}^{\text{Operating cost}} \right] \\
 &= \$76,000,000 - \$16,000,000 - \$54,000 - \$8,000,000 \\
 &\cong \$52 \text{ million}
 \end{aligned}$$

Using \$52 million a year as a rough estimate of the profit, you can now make different approximations about the conversion, separations, recycle streams, and operating costs to learn how they affect the profit.

PART 2 Mole Balances Written in Terms of Concentration and Molar Flow Rates

Used for:

- Multiple rxns
- Membranes
- Unsteady state

There are many instances when it is much more convenient to work in terms of the number of moles (N_A , N_B) or molar flow rates (F_A , F_B , etc.) rather than conversion. Membrane reactors and multiple reactions taking place in the gas phase are two such cases where molar flow rates are preferred rather than conversion. We now modify our algorithm by using concentrations for liquids and molar flow rates for gases as our dependent variables. The main difference between the conversion algorithm and the molar flow rate/concentration algorithm is that, in the conversion algorithm, we needed to write a mole balance on only *one species*, whereas in the molar flow rate and concentration algorithm, we must write a mole balance on *each and every species*. This algorithm is shown in Figure 4-11. First we write the mole balances on all species present as shown in Step ①. Next we write the rate law, Step ②, and then we relate the mole balances to one another through the relative rates of reaction as shown in Step ③. Steps ④ and ⑤ are used to relate the concentrations in the rate law to the molar flow rates. In Step ⑥, all the steps are combined by the ODE solver (e.g., Polymath).

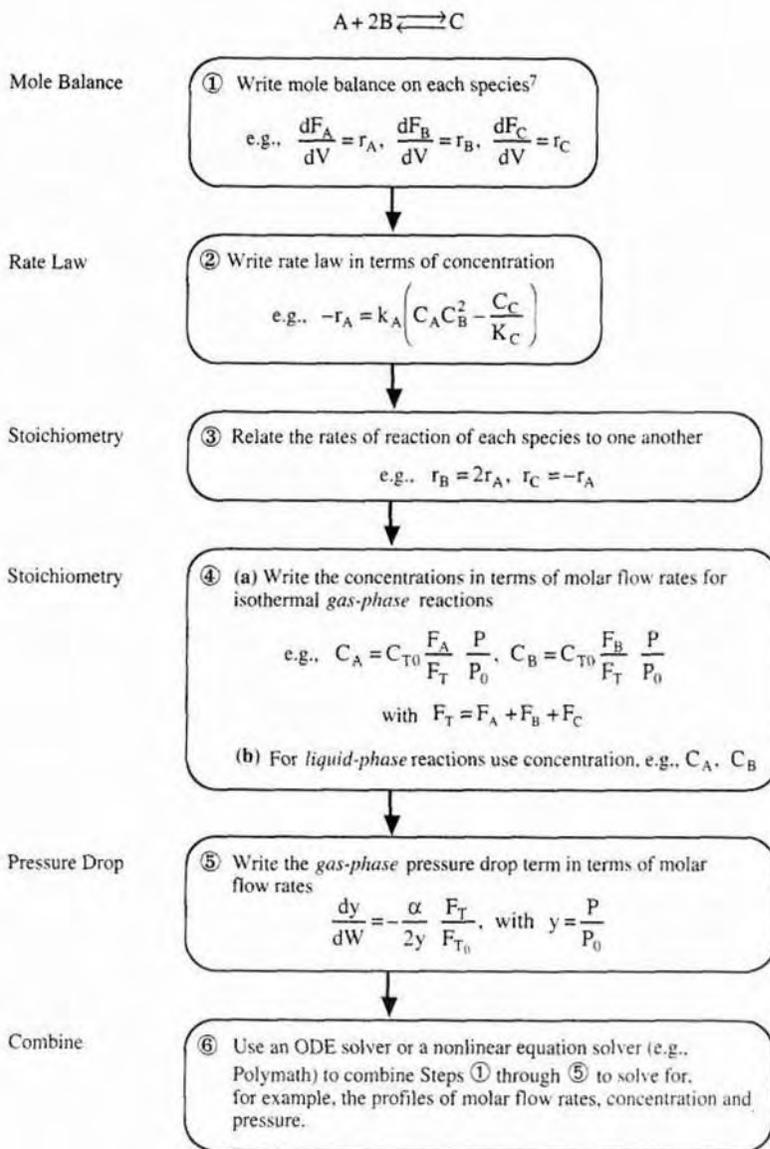


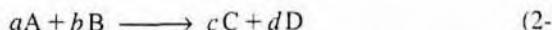
Figure 4-11 Isothermal reaction design algorithm for mole balances.

⁷ For a PBR, use $\frac{dF_A}{dW} = r'_A, \frac{dF_B}{dW} = r'_B, \frac{dF_C}{dW} = r'_C$.

4.7 Mole Balances on CSTRs, PFRs, PBRs, and Batch Reactors

4.7.1 Liquid Phase

For liquid-phase reactions in which there is no volume change, concentration is the preferred variable. The mole balances for the generic reaction



are shown in Table 4-5 in terms of concentration for the four reactor types we have been discussing. We see from Table 4-5 that we have only to specify the parameter values for the system (C_{A0} , v_0 , etc.) and for the rate law parameter (e.g., k_A , α , β) to solve the coupled ordinary differential equations for either PFR, PBR, or batch reactors or to solve the coupled algebraic equations for CSTR.

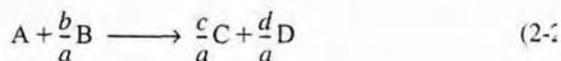


TABLE 4-5. MOLE BALANCES FOR LIQUID-PHASE REACTIONS

Batch	$\frac{dC_A}{dt} = r_A$	and	$\frac{dC_B}{dt} = \frac{b}{a}r_A$
CSTR	$V = \frac{v_0(C_{A0} - C_A)}{-r_A}$	and	$V = \frac{v_0(C_{B0} - C_B)}{-(b/a)r_A}$
PFR	$v_0 \frac{dC_A}{dV} = r_A$	and	$v_0 \frac{dC_B}{dV} = \frac{b}{a}r_A$
PBR	$v_0 \frac{dC_A}{dW} = r'_A$	and	$v_0 \frac{dC_B}{dW} = \frac{b}{a}r'_A$

4.7.2 Gas Phase

The mole balances for gas-phase reactions are given in Table 4-6 in terms of number moles (batch) or molar flow rates for the generic rate law for the

generic reaction Equation (2-1). The molar flow rates for each species F_j are obtained from a mole balance on each species, as given in Table 4-6. For example, for a plug-flow reactor

Must write a mole balance on each species

$$\frac{dF_j}{dV} = r_j \quad (1-11)$$

The generic power law rate law is

Rate law

$$-r_A = k_A C_A^\alpha C_B^\beta$$

To relate concentrations to molar flow rates, recall Equation (3-42), with $y = P/P_0$

Stoichiometry

$$C_j = C_{T0} \frac{F_j}{F_T} \frac{T_0}{T} y \quad (3-42)$$

The pressure drop equation, Equation (4-28), for isothermal operation ($T = T_0$) is

$$\frac{dy}{dW} = \frac{-\alpha}{2y} \frac{F_T}{F_{T0}} \quad (4-28)$$

The total molar flow rate is given as the sum of the flow rates of the individual species:

$$F_T = \sum_{j=1}^n F_j$$

when species A, B, C, D, and I are the only ones present. Then

$$F_T = F_A + F_B + F_C + F_D + F_I$$

We now combine all the preceding information as shown in Table 4-6.

4.8 Microreactors

Microreactors are emerging as a new technology in CRE. Microreactors are characterized by their high surface area-to-volume ratios in their microstructured regions that contain tubes or channels. A typical channel width might be 100 μm with a length of 20,000 μm (2 cm). The resulting high surface area-to-volume ratio (ca. 10,000 m^2/m^3) reduces or even eliminates heat and mass

TABLE 4-6. ALGORITHM FOR GAS-PHASE REACTIONS

$$aA + bB \longrightarrow cC + dD$$

Batch	CSTR	PFR
$\frac{dN_A}{dt} = r_A V$	$V = \frac{F_{A0} - F_A}{-r_A}$	$\frac{dF_A}{dV} = r_A$
$\frac{dN_B}{dt} = r_B V$	$V = \frac{F_{B0} - F_B}{-r_B}$	$\frac{dF_B}{dV} = r_B$
$\frac{dN_C}{dt} = r_C V$	$V = \frac{F_{C0} - F_C}{-r_C}$	$\frac{dF_C}{dV} = r_C$
$\frac{dN_D}{dt} = r_D V$	$V = \frac{F_{D0} - F_D}{-r_D}$	$\frac{dF_D}{dV} = r_D$

2. Rate Law:

$$-r_A = k_A C_A^\alpha C_B^\beta$$

3. Stoichiometry:

Relative rates of reaction:

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}$$

then

$$r_B = \frac{b}{a} r_A \quad r_C = -\frac{c}{a} r_A \quad r_D = -\frac{d}{a} r_A$$

Concentrations:

$$C_A = C_{T0} \frac{F_A T_0}{F_T T} y \quad C_B = C_{T0} \frac{F_B T_0}{F_T T} y$$

$$C_C = C_{T0} \frac{F_C T_0}{F_T T} y \quad C_D = C_{T0} \frac{F_D T_0}{F_T T} y$$

$$\frac{dy}{dW} = \frac{-\alpha F_T T}{2y F_{T0} T_0}, \quad y = \frac{P}{P_0}$$

Total molar flow rate: $F_T = F_A + F_B + F_C + F_D + F_I$ **4. Combine:** For an isothermal operation of a PBR with no ΔP

$$\frac{dF_A}{dV} = -k_A C_{T0}^{a+b} \left(\frac{F_A}{F_T}\right)^a \left(\frac{F_B}{F_T}\right)^b \quad \frac{dF_B}{dV} = -\frac{b}{a} k_A C_{T0}^{a+b} \left(\frac{F_A}{F_T}\right)^a \left(\frac{F_B}{F_T}\right)^b$$

$$\frac{dF_C}{dV} = \frac{c}{a} k_A C_{T0}^{a+b} \left(\frac{F_A}{F_T}\right)^a \left(\frac{F_B}{F_T}\right)^b \quad \frac{dF_D}{dV} = \frac{d}{a} k_A C_{T0}^{a+b} \left(\frac{F_A}{F_T}\right)^a \left(\frac{F_B}{F_T}\right)^b$$

1. Specify parameter values: $k_A, C_{T0}, \alpha, \beta, T_0, a, b, c, d$ 2. Specify entering numbers: $F_{A0}, F_{B0}, F_{C0}, F_{D0}$ and final values: V_{final} **5. Use an ODE solver.**

Gas phase

Advantages of
microreactors

transfer resistances often found in larger reactors. Consequently, surface-catalyzed reactions can be greatly facilitated, hot spots in highly exothermic reactions can be eliminated, and in many cases highly exothermic reactions can be carried out isothermally. These features provide the opportunity for microreactors to be used to study the intrinsic kinetics of reactions. Another advantage of microreactors is their use in the production of toxic or explosive intermediates where a leak or microexplosion for a single unit will do minimal damage because of the small quantities of material involved. Other advantages include shorter residence times and narrower residence time distributions.

Figure 4-12 shows (a) a microreactor with heat exchanger and (b) a microplant with reactor, valves, and mixers. Heat, Q , is added or taken away by the fluid flowing perpendicular to the reaction channels as shown in Figure 4-12(a). Production in microreactor systems can be increased simply by adding more units in parallel. For example, the catalyzed reaction



required only 32 microreaction systems in parallel to produce 2000 tons/yr of acetate!

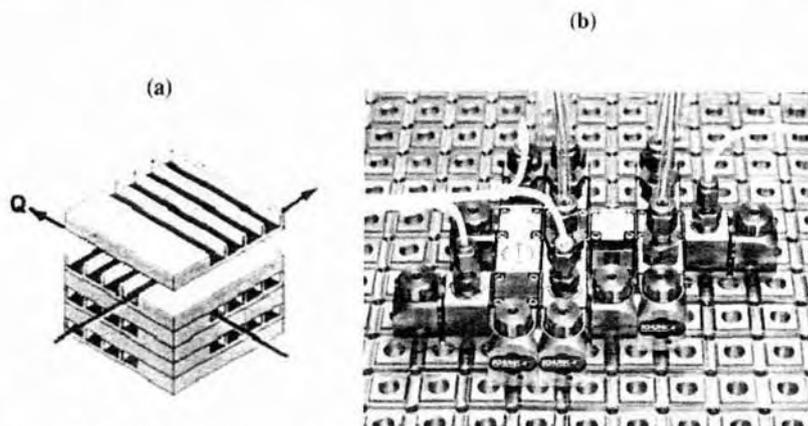


Figure 4-12 Microreactor (a) and Microplant (b). Courtesy of Ehrfeld, Hessel, and Löwe, *Microreactors: New Technology for Modern Chemistry* (Wiley-VCH, 2000).

Microreactors are also used for the production of specialty chemicals, combinatorial chemical screening, lab-on-a-chip, and chemical sensors. In modeling microreactors, we will assume they are either in plug flow for which the mole balance is

$$\frac{dF_A}{dV} = r_A \quad (1-12)$$

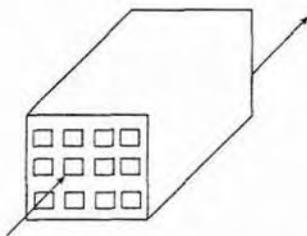
or in laminar flow, in which case we will use the segregation model discussed in Chapter 13. For the plug-flow case, the algorithm is described in Figure 4-11.

Example 4-7 Gas-Phase Reaction in a Microreactor—Molar Flow Rates

The gas-phase reaction



is carried out at 425°C and 1641 kPa (16.2 atm). Pure NOCl is to be fed, and the reaction follows an elementary rate law.⁸ It is desired to produce 20 tons of NO per year in a microreactor system using a bank of ten microreactors in parallel. Each microreactor has 100 channels with each channel 0.2 mm square and 250 mm length.



Plot the molar flow rates as a function of volume down the length of the reactor. The volume of each channel is 10^{-5} dm^3 .

Additional Information

To produce 20 tons per year of NO at 85% conversion would require a feed rate of 0.0226 mol/s of NOCl, or $2.26 \times 10^{-5} \text{ mol/s}$ per channel. The rate constant is

$$k = 0.29 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 500 \text{ K with } E = 24 \frac{\text{kcal}}{\text{mol}}$$

Solution

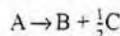
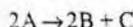
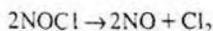
For one channel,

Find V .

$$F_{A0} = \frac{22.6 \mu\text{mol}}{\text{s}} \longrightarrow \text{[Microreactor]} \longrightarrow F_B = \frac{19.2 \mu\text{mol}}{\text{s}}, \quad X = 0.85, \quad V =$$

⁸ J. B. Butt, *Reaction Kinetics and Reactor Design*, 2nd ed. (New York: Marcel Dekker, 2001), p. 153.

Although this particular problem could be solved using conversion, we shall illustrate how it can also be solved using molar flow rates as the variable in the mole balance. We first write the reaction in symbolic form and then divide by the stoichiometric coefficient of the limiting reactant, NOCl.



1. Mole balances on species A, B, and C:

$$\frac{dF_A}{dV} = r_A \quad (\text{E4-7.1})$$

$$\frac{dF_B}{dV} = r_B \quad (\text{E4-7.2})$$

$$\frac{dF_C}{dV} = r_C \quad (\text{E4-7.3})$$

2. Rate law:

$$-r_A = kC_A^2, \quad k = 0.29 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \quad (\text{E4-7.4})$$

3. Stoichiometry: Gas phase with $T = T_0$ and $P = P_0$, then $v = v_0 \frac{F_T}{F_{T0}}$

a. Relative rates

$$\frac{r_A}{-1} = \frac{r_B}{1} = \frac{r_C}{\frac{1}{2}}$$

$$r_B = -r_A$$

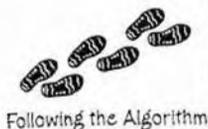
$$r_C = -\frac{1}{2}r_A$$

b. Concentration

Applying Equation (3-42) to species A, B, and C, the concentrations are

$$C_A = C_{T0} \frac{F_A}{F_T}, \quad C_B = C_{T0} \frac{F_B}{F_T}, \quad C_C = C_{T0} \frac{F_C}{F_T} \quad (\text{E4-7.5})$$

$$\text{with } F_T = F_A + F_B + F_C$$



Following the Algorithm

4. **Combine:** the rate law in terms of molar flow rates is

$$-r_A = k_A C_{T0}^2 \left(\frac{F_A}{F_T} \right)^2$$

combining all

$$\frac{dF_A}{dV} = k_A C_{T0}^2 \left(\frac{F_A}{F_T} \right)^2 \quad (\text{E4-7.6})$$

$$\frac{dF_B}{dV} = k_A C_{T0}^2 \left(\frac{F_A}{F_T} \right)^2 \quad (\text{E4-7.7})$$

$$\frac{dF_C}{dV} = \frac{k_A}{2} C_{T0}^2 \left(\frac{F_A}{F_T} \right)^2 \quad (\text{E4-7.8})$$

One can skip the combine step when using Polymath because Polymath or similar ODE solvers combine everything for you: mole balance, rate law, and stoichiometry.

5. **Evaluate:**

$$C_{T0} = \frac{P_0}{RT_0} = \frac{(1641 \text{ kPa})}{\left(8.314 \frac{\text{kPa} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}} \right) 698 \text{ K}} = 0.286 \frac{\text{mol}}{\text{dm}^3} = \frac{0.286 \text{ mmol}}{\text{cm}^3}$$

When using Polymath or another ODE solver, one does not have to actually combine the mole balances, rate laws, and stoichiometry as was done in the combine step in previous examples in this chapter. The ODE solver will do that for you. Thanks, ODE solver! The Polymath Program and output are shown in Table E4-7.1 and Figure E4-7.1.

TABLE E4-7.1. POLYMATH PROGRAM

ODE REPORT (RKF45)

Differential equations as entered by the user

- [1] $d(F_A)/d(V) = r_A$
- [2] $d(F_B)/d(V) = r_B$
- [3] $d(F_C)/d(V) = r_C$

Explicit equations as entered by the user

- [1] $T = 698$
- [2] $C_{T0} = 1641/8.314/T$
- [3] $E = 24000$
- [4] $F_T = F_A + F_B + F_C$
- [5] $C_A = C_{T0} \cdot F_A / F_T$
- [6] $k = 0.29 \cdot \exp(E/1.987 \cdot (1/500 - 1/T))$
- [7] $F_{A0} = 0.0000226$
- [8] $v_0 = F_{A0} / C_{T0}$

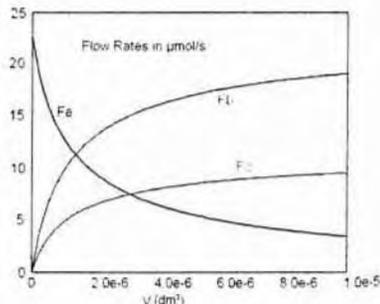


Figure E4-7.1 Profiles of microreactor molar flow rates.

TABLE E4-7.1. POLYMATH PROGRAM (CONTINUED)

ODE REPORT (RKF45) (Continued)

```

[9] Tau = V/v0
[10] ra = -k*Ca^2
[11] X = 1-Fa/Fao
[12] rb = -ra
[13] rc = -ra/2
[14] rateA = -ra

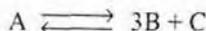
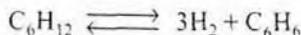
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4.9 Membrane Reactors

Membrane reactors can be used to increase conversion when the reaction is thermodynamically limited as well as to increase the selectivity when multiple reactions are occurring. Thermodynamically limited reactions are reactions where the equilibrium lies far to the left (i.e., reactant side) and there is little conversion. If the reaction is exothermic, increasing the temperature will only drive the reaction further to the left, and decreasing the temperature will result in a reaction rate so slow that there is very little conversion. If the reaction is endothermic, increasing the temperature will move the reaction to the right to favor a higher conversion; however, for many reactions these higher temperatures cause the catalyst to become deactivated.

The term *membrane reactor* describes a number of different types of reactor configurations that contain a membrane. The membrane can either provide a barrier to certain components while being permeable to others, prevent certain components such as particulates from contacting the catalyst, or contain reactive sites and be a catalyst in itself. Like reactive distillation, the membrane reactor is another technique for driving reversible reactions to the right toward completion in order to achieve very high conversions. These high conversions can be achieved by having one of the reaction products diffuse out of a semipermeable membrane surrounding the reacting mixture. As a result, the reverse reaction will not be able to take place, and the reaction will continue to proceed to the right toward completion.

Two of the main types of catalytic membrane reactors are shown in Figure 4-13. The reactor in Figure 4-13(b) is called an *inert membrane reactor with catalyst pellets on the feed side* (IMRCF). Here the membrane is inert and serves as a barrier to the reactants and some of the products. The reactor in Figure 4-13(c) is a *catalytic membrane reactor* (CMR). The catalyst is deposited directly on the membrane, and only specific reaction products are able to exit the permeate side. For example, in the reversible reaction



By having one of the products pass throughout the membrane, we drive the reaction toward completion.

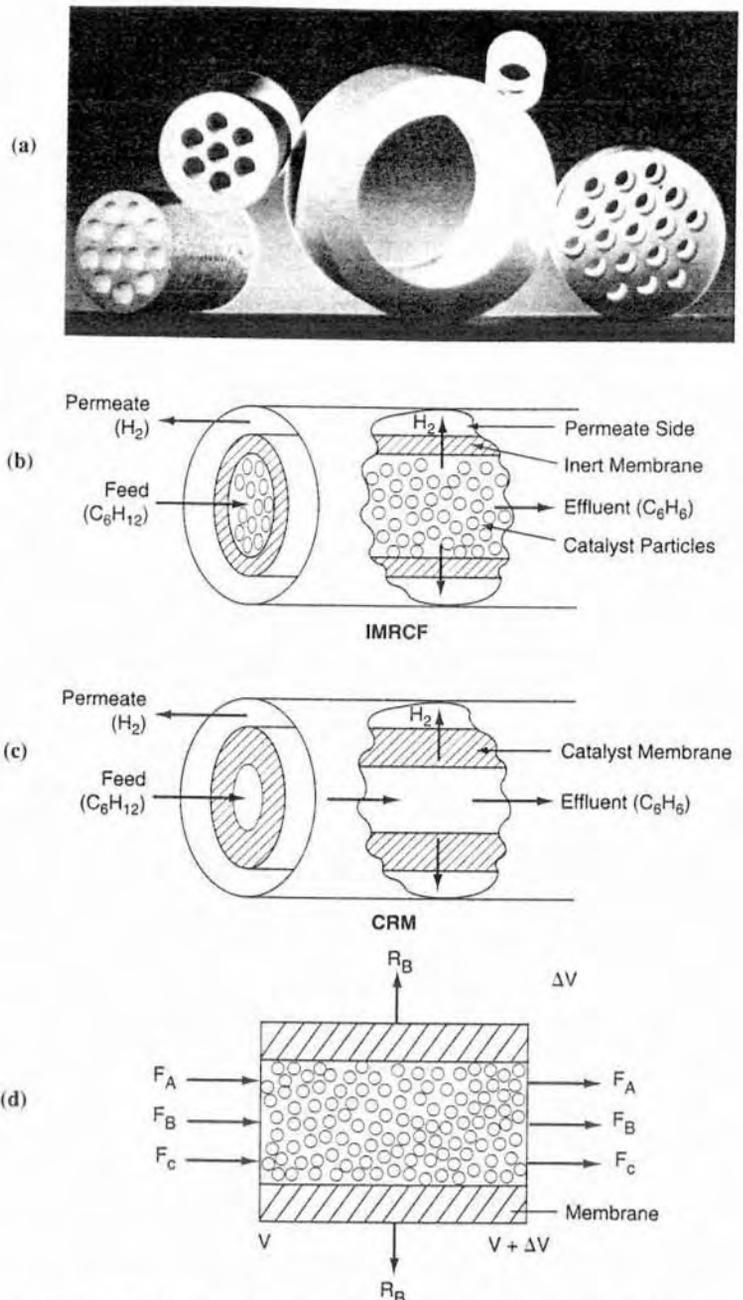
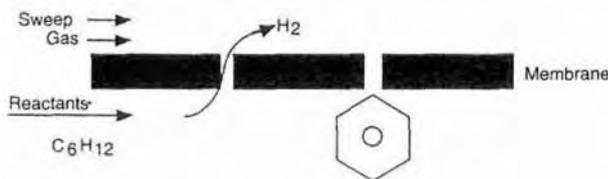


Figure 4-13 Membrane reactors. (Photo courtesy of Coors Ceramics, Golden, Colorado.) (a) Photo of ceramic reactors, (b) cross section of IMRCF, (c) cross section of CRM, (d) schematic of IMRCF for mole balance.

H_2 diffuses through the membrane while C_6H_6 does not.

the hydrogen molecule is small enough to diffuse through the small pores of the membrane while C_6H_{12} and C_6H_6 cannot. Consequently, the reaction continues to proceed to the right even for a small value of the equilibrium constant.



Hydrogen, species B, flows out through the sides of the reactor as it flows down the reactor with the other products, which cannot leave until they exit the reactor.

In analyzing membrane reactors, we only need to make a small change to the algorithm shown in Figure 4-11. We shall choose the reactor volume rather than catalyst weight as our independent variable for this example. The catalyst weight, W , and reactor volume, V , are easily related through the bulk catalyst density, ρ_b (i.e., $W = \rho_b V$). The mole balances on the chemical species that stay *within* the reactor, namely A and C, are shown in Figure 4-11 and also in Table 4-6.

$$V = \frac{W}{\rho_b}$$

$$\frac{dF_A}{dV} = r_A \quad (1-11)$$

The mole balance on C is carried out in an identical manner to A, and the resulting equation is

$$\frac{dF_C}{dV} = r_C \quad (4-40)$$

However, the mole balance on B (H_2) must be modified because hydrogen leaves through both the sides of the reactor and at the end of the reactor.

First we shall perform mole balances on the volume element ΔV shown in Figure 4-12(c). The mole balance on hydrogen (B) is over a differential volume ΔV shown in Figure 4-12(d) and it yields

Balance on B in the catalytic bed:

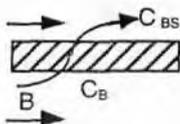
$$\left[\begin{array}{c} \text{In} \\ \text{by flow} \end{array} \right] - \left[\begin{array}{c} \text{Out} \\ \text{by flow} \end{array} \right] - \left[\begin{array}{c} \text{Out} \\ \text{by diffusion} \end{array} \right] + [\text{Generation}] = [\text{Accumulation}]$$

$$\underbrace{F_{B|V}} - \underbrace{F_{B|V+\Delta V}} - \underbrace{R_B \Delta V} + \underbrace{r_B \Delta V} = 0$$

Now there are two "OUT" terms for species B.

where R_B is the molar rate of B leaving through the sides the reactor per unit volume of reactor ($\text{mol}/\text{dm}^3 \cdot \text{s}$). Dividing by ΔV and taking the limit as $\Delta V \rightarrow 0$ gives

$$\frac{dF_B}{dV} = r_B - R_B \quad (4-41)$$



The rate of transport B out through the membrane R_B is the product of the molar flux of B, W_B , and a , the surface area, per unit volume of reactor. The molar flux of B, W_B in ($\text{mol}/\text{m}^2 \cdot \text{s}$) out of the reactor is a mass transfer coefficient times the concentration driving force across the membrane.

$$W_B = k'_C (C_B - C_{BS}) \quad (4-42)$$

Where k'_C is the overall mass transfer coefficient in m/s and C_{BS} is the concentration of B in the sweep gas channel (mol/dm^3). The overall mass transfer coefficient accounts for all resistances to transport: the tube side resistance of the membrane, the membrane itself, and on the shell (sweep gas) side resistance. Further elaboration of the mass transfer coefficient and its correlations can be found in the literature and in Chapter 11. In general, this coefficient can be a function of the membrane and fluid properties, the fluid velocity, and the tube diameters.

To obtain the rate of removal of B, we need to multiply the flux through the membrane by the surface area of membrane in the reactor. The rate at which B is removed per unit volume of reactor, R_B , is just the flux W_B times the surface area membrane per volume of reactor, a (m^2/m^3); that is,

$$R_B = W_B a = k'_C a (C_B - C_{BS}) \quad (4-43)$$

The membrane surface area per unit volume of reactor is

$$a = \frac{\text{Area}}{\text{Volume}} = \frac{\pi D L}{\frac{\pi D^2 L}{4}} = \frac{4}{D}$$

Letting $k_C = k'_C a$ and assuming the concentration in the sweep gas is essentially zero (i.e., $C_{BS} \approx 0$), we obtain

$$R_B = k_C C_B$$

where the units of k_C are s^{-1} .

More detailed modeling of the transport and reaction steps in membrane reactors is beyond the scope of this text but can be found in *Membrane Reactor Technology*.⁹ The salient features, however, can be illustrated by the following example. When analyzing membrane reactors, it is much more convenient to use molar flow rates than conversion.

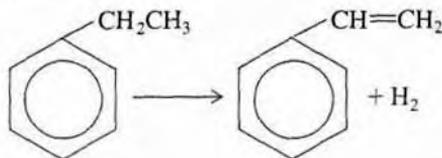
Rate of B out through the sides.

⁹ R. Govind, and N. Itoh, eds., *Membrane Reactor Technology*, AIChE Symposium Series No. 268, Vol. 85 (1989). T. Sun and S. Khang, *Ind. Eng. Chem. Res.*, 27, 1136 (1988).

According to the DOE, 10 trillion BTU/yr could be saved by using membrane reactors.

Example 4-8 Membrane Reactor

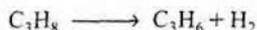
According to The Department of Energy (DOE), an energy saving of 10 trillion BTU per year could result from the use of catalytic membrane reactors as replacements for conventional reactors for dehydrogenation reactions such as the dehydrogenation of ethylbenzene to styrene:



and of butane to butene:



The dehydrogenation of propane is another reaction that has proven successful with a membrane reactor.¹⁰



All the preceding dehydrogenation reactions above can be represented symbolically as



and will take place on the catalyst side of an IMRCF. The equilibrium constant for this reaction is quite small at 227°C (e.g., $K_C = 0.05 \text{ mol/dm}^3$). The membrane is permeable to B (e.g., H_2) but not to A and C. Pure gaseous A enters the reactor at 8.2 atm and 227°C at a rate of 10 mol/min.

We will take the rate of diffusion of B out of the reactor per unit volume of reactor, R_B , to be proportional to the concentration of B (i.e., $R_B = k_C C_B$).

- Perform differential mole balances on A, B, and C to arrive at a set of coupled differential equations to solve.
- Plot the molar flow rates of each species as a function of space time.
- Calculate the conversion.

Additional information: Even though this reaction is a gas–solid catalytic reaction, we will use the bulk catalyst density in order to write our balances in terms of reactor volume rather than catalyst weight (recall $-r_A = -r'_A \rho_b$). For the bulk catalyst density of $\rho_b = 1.5 \text{ g/cm}^3$ and a 2-cm inside diameter of the tube containing the catalyst pellets, the specific reaction rate, k , and the transport coefficient, k_C , are $k = 0.7 \text{ min}^{-1}$ and $k_C = 0.2 \text{ min}^{-1}$, respectively.

Solution

We shall choose reactor volume rather than catalyst weight as our independent variable for this example. The catalyst weight, W , and reactor volume, V , are easily

¹⁰ *J. Membrane Sci.*, 77, 221 (1993).

related through the bulk catalyst density, ρ_b , (i.e., $W = \rho_b V$). First, we shall perform mole balances on the volume element ΔV shown in Figure 4-13(d).

1. Mole balances:

Balance on A in the catalytic bed:

$$\left[\begin{array}{c} \text{In} \\ \text{by flow} \end{array} \right] - \left[\begin{array}{c} \text{Out} \\ \text{by flow} \end{array} \right] + \left[\begin{array}{c} \text{Generation} \end{array} \right] = \left[\begin{array}{c} \text{Accumulation} \end{array} \right]$$

$$\underbrace{F_{A|V}} - \underbrace{F_{A|V+\Delta V}} + \underbrace{r_A \Delta V} = 0$$

Dividing by ΔV and taking the limit as $\Delta V \rightarrow 0$ gives

$$\boxed{\frac{dF_A}{dV} = r_A} \quad (\text{E4-8.})$$

Balance on B in the catalytic bed:

The balance on B is given by Equation (4-41).

$$\boxed{\frac{dF_B}{dV} = r_B - R_B} \quad (\text{E4-8.})$$

where R_B is the molar flow of B out through the membrane per unit volume of reactor.

The mole balance on C is carried out in an identical manner to A and the resulting equation is

$$\boxed{\frac{dF_C}{dV} = r_C} \quad (\text{E4-8.})$$

2. Rate law:

$$\boxed{-r_A = k \left(C_A - \frac{C_B C_C}{K_C} \right)} \quad (\text{E4-8.})$$

3. **Transport out of the reactor.** We apply Equation (4-42) for the case in which the concentration of B of the sweep side is zero, $C_{BS} = 0$, to obtain

$$\boxed{R_B = k_C C_B} \quad (\text{E4-8.})$$

where k_C is a transport coefficient. In this example, we shall assume that the resistance to species B out of the membrane is a constant and, consequently, k_C is a constant.

4. **Stoichiometry.** Recalling Equation (3-42) for the case of constant temperature and pressure, we have for isothermal operation and no pressure drop ($T = T_0$, $P = P_0$),