

Figure E4-2.2 CSTRs in parallel.

$$X = \frac{Da}{1 + Da} = \frac{4.34}{1 + 4.34} = 0.81$$

The conversion exiting each of the CSTRs in parallel is 81%.

(c) **CSTRs in series.** If the 800-gal reactors are arranged in series, the conversion in the first reactor [cf. Equation (E4-2.5)] is

$$X_1 = \frac{\tau_1 k}{1 + \tau_1 k} \quad (\text{E4-2.6})$$

where

$$\tau = \frac{V_1}{v_{01}} = \left(800 \text{ gal} \times \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right) \times \frac{1}{15.34 \text{ ft}^3/\text{min}} = 6.97 \text{ min}$$

First CSTR

The Damköhler number is

$$Da_1 = \tau_1 k = 6.97 \text{ min} \times \frac{0.311}{\text{min}} = 2.167$$

$$X_1 = \frac{2.167}{1 + 2.167} = \frac{2.167}{3.167} = 0.684$$

To calculate the conversion exiting the second reactor, we recall that $V_1 = V_2 = V$ and $v_{01} = v_{02} = v_0$; then

$$\tau_1 = \tau_2 = \tau$$

A mole balance on the second reactor is

$$\begin{array}{rcccccc} \text{In} & - & \text{Out} & + & \text{Generation} & = & 0 \\ \underbrace{F_{A1}} & - & \underbrace{F_{A2}} & + & \underbrace{r_{A2}V} & = & 0 \end{array}$$

Basing the conversion on the total number of moles reacted up to a point per mole of A fed to the first reactor,

$$F_{A1} = F_{A0}(1 - X_1) \quad \text{and} \quad F_{A2} = F_{A0}(1 - X_2)$$

Rearranging

$$V = \frac{F_{A1} - F_{A2}}{-r_{A2}} = F_{A0} \frac{X_2 - X_1}{-r_{A2}}$$

$$-r_{A2} = kC_{A2} = k \frac{F_{A2}}{v_0} = \frac{kF_{A0}(1 - X_2)}{v_0} = kC_{A0}(1 - X_2)$$

Combining the mole balance on the second reactor [cf. Equation (2-24)] with the rate law, we obtain

$$V = \frac{F_{A0}(X_2 - X_1)}{-r_{A2}} = \frac{C_{A0}v_0(X_2 - X_1)}{kC_{A0}(1 - X_2)} = \frac{v_0}{k} \left(\frac{X_2 - X_1}{1 - X_2} \right) \quad (\text{E4-2.7})$$

Second CSTR

Solving for the conversion exiting the second reactor yields

$$X_2 = \frac{X_1 + \text{Da}}{1 + \text{Da}} = \frac{X_1 + \tau k}{1 + \tau k} = \frac{0.684 + 2.167}{1 + 2.167} = 0.90$$

The same result could have been obtained from Equation (4-11):

$$X_2 = 1 - \frac{1}{(1 + \tau k)^n} = 1 - \frac{1}{(1 + 2.167)^2} = 0.90$$

Two hundred million pounds of EG per year can be produced using two 800-gal (3.0-m³) reactors in series.

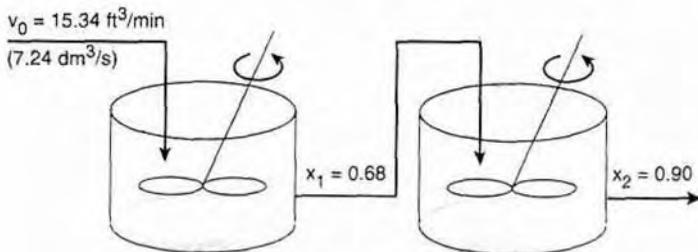


Figure E4-2.3 CSTRs in series.

The two equal-sized CSTRs in series (shown in Figure E4-2.3) will give a higher conversion than two CSTRs in parallel of the same size when the reaction order is greater than zero.

Safety considerations

We can find information about the safety of ethylene glycol and other chemicals from the World Wide Web (WWW) (Table 4-4). One source is the Vermont Safety Information on the Internet (Vermont SIRI). For example, we can learn from the *Control Measures* that we should use neoprene gloves when handling the material, and that we should avoid breathing the vapors. If we click on "Dow Chemical USA" and scroll the *Reactivity Data*, we would find that ethylene glycol will ignite in air at 413°C.

Conversion in the series arrangement is greater than in parallel for CSTRs. From our discussion of reactor staging in Chapter 2, we could have predicted that the series arrangement would have given the higher conversion.

TABLE 4-4. ACCESSING SAFETY INFORMATION

Safety Information MSDS	<ol style="list-style-type: none"> Type in http://www.siri.org/ When the first screen appears, click on "Material Safety Data Sheets." ("MSDS") When the next page appears, type in the chemical you want to find. Example: Find ethylene glycol Then click on Enter. The next page will show a list of a number of companies that provide the data on ethylene glycol. MALLINCKRODT BAKER FISHER DOW CHEMICAL USA etc. Let's click on "Mallinckrodt Baker." The materials safety data sheet provided will appear. Scroll "ethylene glycol" for information you desire. <ol style="list-style-type: none"> Product Identification Composition/Information on Ingredients Hazards Identification First Aid Measures Fire Fighting Measures Accidental Release Measures Handling and Storage Exposure Controls/Personal Protection Physical and Chemical Properties 10-16. Other Information
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4.4 Tubular Reactors

Gas-phase reactions are carried out primarily in tubular reactors where the flow is generally turbulent. By assuming that there is no dispersion and there are no radial gradients in either temperature, velocity, or concentration, we can model the flow in the reactor as plug-flow.

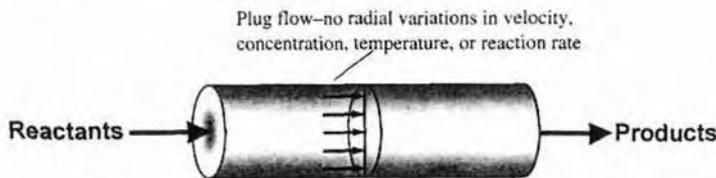


Figure 1-9 (Revisited) Tubular reactor.

Laminar reactors are discussed in Chapter 13 and dispersion effects in Chapter 14. The *differential form* of the PFR design equation

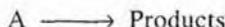
Use this differential form of the PFR/PBR mole balances when there is ΔP .

$$F_{A0} \frac{dX}{dV} = -r_A \quad (2-15)$$

must be used when there is a pressure drop in the reactor or heat exchange between the PFR and the surroundings. In the absence of pressure drop or heat exchange, the integral form of the *plug-flow design* equation is used,

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (2-16)$$

As an example, consider the reaction



for which the rate law is

Rate law
$$-r_A = kC_A^2$$

We shall first consider the reaction to take place as a liquid-phase reaction and then to take place as a gas-phase reaction.

Liquid Phase $v = v_0$

The combined PFR mole balance and rate law is

$$\frac{dX}{dV} = \frac{kC_A^2}{F_{A0}}$$

If the reaction is carried out in the liquid phase, the concentration is

Stoichiometry
(liquid phase)

$$C_A = C_{A0}(1 - X)$$

and for the isothermal operation, we can bring k outside the integral

Combine
$$V = \frac{F_{A0}}{kC_{A0}^2} \int_0^X \frac{dx}{(1 - X)^2} = \frac{v_0}{kC_{A0}} \left(\frac{X}{1 - X} \right)$$

This equation gives the reactor volume to achieve a conversion X . Dividing by v_0 ($\tau = V/v_0$) and solving for conversion, we find

$$X = \frac{\tau k C_{A0}}{1 + \tau k C_{A0}} = \frac{Da_2}{1 + Da_2}$$

where Da_2 is the Damköhler number for a second-order reaction.

Gas Phase

For constant-temperature ($T = T_0$) and constant-pressure ($P = P_0$) *gas-phase reactions*, the concentration is expressed as a function of conversion:

Stoichiometry
(gas phase)

$$C_A = \frac{F_A}{v} = \frac{F_A}{v_0(1 + \epsilon X)} = \frac{F_{A0}(1 - X)}{v_0(1 + \epsilon X)} = C_{A0} \frac{(1 - X)}{(1 + \epsilon X)}$$

and then combining the PFR mole balance, rate law, and stoichiometry

Combine

$$V = F_{A0} \int_0^X \frac{(1 + \varepsilon X)^2}{k C_{A0}^2 (1 - X)^2} dX$$

The entering concentration C_{A0} can be taken outside the integral sign since it is not a function of conversion. Because the reaction is carried out isothermally, the specific reaction rate constant, k , can also be taken outside the integral sign.

For an isothermal reaction, k is constant.

$$V = \frac{F_{A0}}{k C_{A0}^2} \int_0^X \frac{(1 + \varepsilon X)^2}{(1 - X)^2} dX$$

From the integral equations in Appendix A.1, we find that

Reactor volume for a second-order gas-phase reaction

$$V = \frac{v_0}{k C_{A0}} \left[2\varepsilon(1 + \varepsilon) \ln(1 - X) + \varepsilon^2 X + \frac{(1 + \varepsilon)^2 X}{1 - X} \right] \quad (4-17)$$

Using Equation (4-17), a plot of conversion along the length (i.e., volume) of the reactor is shown for four different reactions, and values of ε are given in Figure 4-7 for the same value of $[v_0/kC_{A0}]$ to illustrate the effect of volume change with reaction.

The term $\left[\frac{v_0}{k C_{A0}} \right]$ is the same for each reaction.

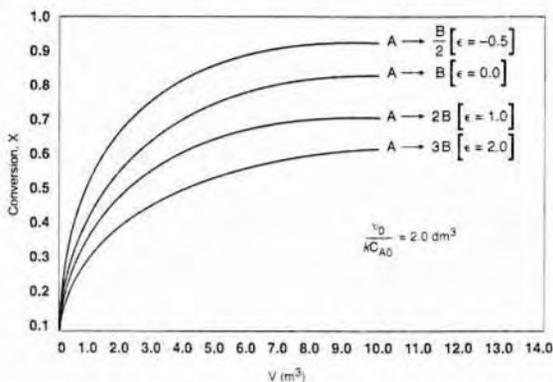


Figure 4-7 Conversion as a function of distance down the reactor.

We now look at the effect of the change in the number of moles in the gas phase on the relationship between conversion and volume. For constant temperature and pressure, Equation (3-45) becomes

$$v = v_0 (1 + \varepsilon X) \quad (3-45)$$

Let's now consider three types of reactions, one in which $\varepsilon = 0$ ($\delta = 0$), one in which $\varepsilon < 0$ ($\delta < 0$), and one in which $\varepsilon > 0$ ($\delta > 0$). When there is no change in the number of moles with reaction, (e.g., $A \rightarrow B$) $\delta = 0$ and $\varepsilon = 0$; then the

fluid moves through the reactor at a constant volumetric flow rate ($v = v_0$) as the conversion increases.

When there is a decrease in the number of moles ($\delta < 0$, $\epsilon < 0$) in the gas phase (e.g., $2A \rightarrow B$), the volumetric gas flow rate decreases as the conversion increases; for example,

$$v = v_0(1 - 0.5X)$$

Consequently, the gas molecules will spend longer in the reactor than they would if the flow rate were constant, $v = v_0$. As a result, this longer residence time would result in a higher conversion than if the flow were constant at v_0 .

On the other hand, if there is an increase in the total number of moles ($\delta > 0$, $\epsilon > 0$) in the gas phase (e.g., $A \rightarrow 2B$), then the volumetric flow rate will increase as the conversion increases; for example,

$$v = v_0(1 + X)$$

and the molecules will spend less time in the reactor than they would if the volumetric flow rate were constant. As a result of this smaller residence time in the reactor the conversion will be less than what would result if the volumetric flow rate were constant at v_0 .

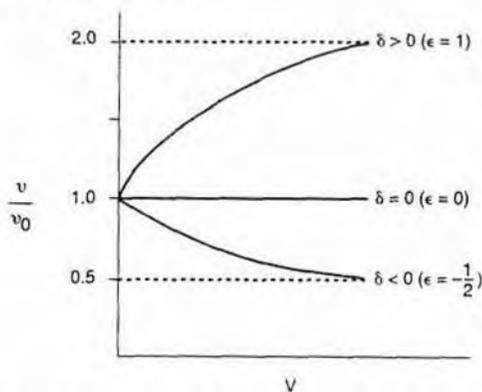


Figure 4-8 Change in gas-phase volumetric flow rate down the length of the reactor.

Figure 4-8 shows the volumetric flow rate profiles for the three cases just discussed. We note that, at the end of the reactor, virtually complete conversion has been achieved.

Example 4-3 *Producing 300 Million Pounds per Year of Ethylene in a Plug-Flow Reactor: Design of a Full-Scale Tubular Reactor*

Ethylene ranks fourth in the United States in total pounds of chemicals produced each year, and it is the number one organic chemical produced each year. Over 50 billion pounds were produced in 2000, and it sold for \$0.27 per pound. Sixty-five percent of the ethylene produced is used in the manufacture of fabricated plastics,

The importance of changes in volumetric flow rate (i.e., $\epsilon \neq 0$) with reaction

The economics

The uses

20% for ethylene oxide, 16% for ethylene dichloride and ethylene glycol, 5% for fibers, and 5% for solvents.

Determine the plug-flow reactor volume necessary to produce 300 million pounds of ethylene a year from cracking a feed stream of pure ethane. The reaction is irreversible and follows an elementary rate law. We want to achieve 80% conversion of ethane, operating the reactor isothermally at 1100 K at a pressure of 6 atm.

Solution



Let $A = \text{C}_2\text{H}_6$, $B = \text{C}_2\text{H}_4$, and $C = \text{H}_2$. In symbols,



Because we want the reader to be familiar with both metric units and English units, we will work some of the examples using English units.

The molar flow rate of ethylene exiting the reactor is

$$\begin{aligned} F_B &= 300 \times 10^6 \frac{\text{lb}}{\text{year}} \times \frac{1 \text{ year}}{365 \text{ days}} \times \frac{1 \text{ day}}{24 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{\text{lb mol}}{28 \text{ lb}} \\ &= 0.340 \frac{\text{lb mol}}{\text{s}} \left(154.4 \frac{\text{g mol}}{\text{s}} \right) \end{aligned}$$

Next calculate the molar feed rate of ethane, F_{A0} , to produce 0.34 lb mol/s of ethylene when 80% conversion is achieved,

$$\begin{aligned} F_B &= F_{A0} X \\ F_{A0} &= \frac{0.34}{0.8} = 0.425 \frac{\text{lb mol}}{\text{s}} \quad (402 \times 10^6 \text{ lb/yr}) \end{aligned}$$

1. Plug-flow design equation:

Mole balance

$$F_{A0} \frac{dX}{dV} = -r_A \quad (\text{E-15})$$

Rearranging and integrating for the case of **no pressure drop** and isothermal operation yields

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (\text{E-4-3.1})$$

2. Rate law:³

³ *Ind. Eng. Chem. Process Des. Dev.*, 14, 218 (1975); *Ind. Eng. Chem.*, 59(5), 7 (1967).

Rate law

$$-r_A = kC_A \quad \text{with } k = 0.072 \text{ s}^{-1} \text{ at } 1000 \text{ K} \quad (\text{E4-3.2})$$

The activation energy is 82 kcal/g mol.

3. **Stoichiometry.** For isothermal operation and negligible pressure drop, the concentration of ethane is calculated as follows:

Gas phase, constant T and P :

Stoichiometry

$$v = v_0 \frac{F_T}{F_{T0}} = v_0(1 + \varepsilon X):$$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = C_{A0} \left(\frac{1-X}{1+\varepsilon X} \right) \quad (\text{E4-3.3})$$

$$C_C = \frac{C_{A0}X}{(1+\varepsilon X)} \quad (\text{E4-3.4})$$

4. We now **combine** Equations (E4-3.1) through (E4-3.3) to obtain

Combining the design equation, rate law, and stoichiometry

$$\begin{aligned} V &= F_{A0} \int_0^X \frac{dX}{kC_{A0}(1-X)/(1+\varepsilon X)} = F_{A0} \int_0^X \frac{(1+\varepsilon X)dX}{kC_{A0}(1-X)} \\ &= \frac{F_{A0}}{C_{A0}} \int_0^X \frac{(1+\varepsilon X)dX}{k(1-X)} \end{aligned} \quad (\text{E4-3.5})$$

5. **Evaluate.**

Since the reaction is carried out isothermally, we can take k outside the integral sign and use Appendix A.1 to carry out our integration.

Analytical solution

$$V = \frac{F_{A0}}{kC_{A0}} \int_0^X \frac{(1+\varepsilon X)dX}{1-X} = \frac{F_{A0}}{kC_{A0}} \left[(1+\varepsilon) \ln \frac{1}{1-X} - \varepsilon X \right] \quad (\text{E4-3.6})$$

6. **Parameter evaluation:**

Evaluate

$$\begin{aligned} C_{A0} &= y_{A0} C_{T0} = \frac{y_{A0} P_0}{RT_0} = (1) \left(\frac{6 \text{ atm}}{(0.73 \text{ ft}^3 \cdot \text{atm} / \text{lb mol} \cdot ^\circ\text{R}) \times (1980^\circ\text{R})} \right) \\ &= 0.00415 \frac{\text{lb mol}}{\text{ft}^3} \quad (0.066 \text{ mol} / \text{dm}^3) \end{aligned}$$

$$\varepsilon = y_{A0} \delta = (1)(1 + 1 - 1) = 1$$

Oops! The rate constant k is given at 1000 K, and we need to calculate k at reaction conditions, which is 1100 K.

$$\begin{aligned}
 k(T_2) &= k(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] \\
 &= k(T_1) \exp \left[\frac{E}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \right] \\
 &= \frac{0.072}{\text{s}} \exp \left[\frac{82,000 \text{ cal/g mol} (1100 - 1000) \text{ K}}{1.987 \text{ cal/(g mol} \cdot \text{K)} (1000 \text{ K})(1100 \text{ K})} \right] \\
 &= 3.07 \text{ s}^{-1}
 \end{aligned} \tag{E4-3.7}$$

Substituting into Equation (E4-3.6) yields

$$\begin{aligned}
 V &= \frac{0.425 \text{ lb mol/s}}{(3.07/\text{s})(0.00415 \text{ lb mol/ft}^3)} \left[(1+1) \ln \frac{1}{1-X} - (1)X \right] \\
 &= 33.36 \text{ ft}^3 \left[2 \ln \left(\frac{1}{1-X} \right) - X \right]
 \end{aligned} \tag{E4-3.8}$$

For $X = 0.8$,

$$\begin{aligned}
 V &= 33.36 \text{ ft}^3 \left[2 \ln \left(\frac{1}{1-0.8} \right) - 0.8 \right] \\
 &= 80.7 \text{ ft}^3 = (2280 \text{ dm}^3 = 2.28 \text{ m}^3)
 \end{aligned}$$

It was decided to use a bank of 2-in. schedule 80 pipes in parallel that are 40 ft in length. For pipe schedule 80, the cross-sectional area, A_C , is 0.0205 ft². The number of pipes necessary is

The number of PFRs
in parallel

$$n = \frac{80.7 \text{ ft}^3}{(0.0205 \text{ ft}^2)(40 \text{ ft})} = 98.4 \tag{E4-3.9}$$

To determine the concentrations and conversion profiles down the length of the reactor, z , we divide the volume Equation (E4-3.8) by the cross-sectional area, A_C ,

$$z = \frac{V}{A_C} \tag{E4-3.10}$$

Equation (E4-3.9) was used along with $A_C = 0.0205 \text{ ft}^2$, and Equations (E4-3.8) and (E4-3.3) were used to obtain Figure E4-3.1. Using a bank of 100 pipes will give us the reactor volume necessary to make 300 million pounds per year of ethylene from ethane. The concentration and conversion profiles down any one of the pipes are shown in Figure E4-3.1.

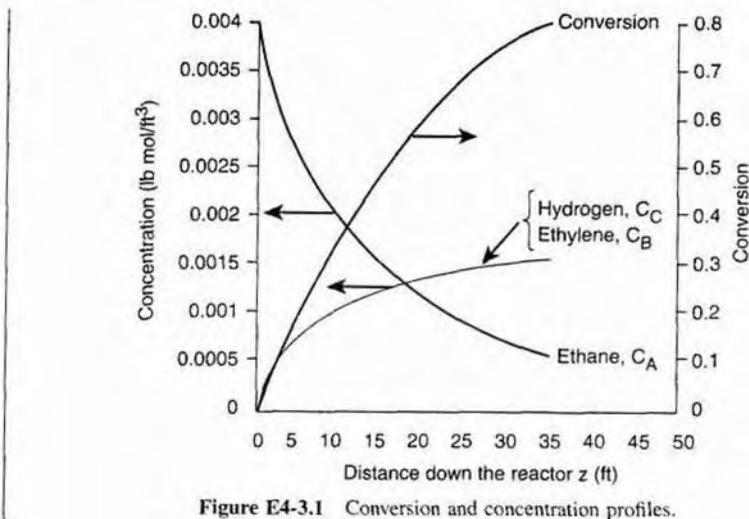


Figure E4-3.1 Conversion and concentration profiles.

4.5 Pressure Drop in Reactors

Pressure drop is ignored for liquid-phase kinetics calculations

In liquid-phase reactions, the concentration of reactants is insignificantly affected by even relatively large changes in the total pressure. Consequently, we can totally ignore the effect of pressure drop on the rate of reaction when sizing liquid-phase chemical reactors. However, in gas-phase reactions, the concentration of the reacting species is proportional to the total pressure; consequently, proper accounting for the effects of pressure drop on the reaction system can, in many instances, be a key factor in the success or failure of the reactor operation. This fact is especially true in microreactors packed with solid catalyst. Here the channels are so small (see Section 4.8) that pressure drop can limit the throughput and conversion for gas-phase reactions.

4.5.1 Pressure Drop and the Rate Law

For gas-phase reactions, pressure drop may be very important.

We now focus our attention on accounting for the pressure drop in the rate law. For an ideal gas, we recall Equation (3-46) to write the concentration of reacting species i as

$$C_i = C_{A0} \left(\frac{\Theta_i + v_i X}{1 + \epsilon X} \right) \frac{P T_0}{P_0 T} \quad (4-18)$$

where $\Theta_i = \frac{F_{i0}}{F_{A0}}$, $\varepsilon = y_{A0}\delta$ and ν is the stoichiometric coefficient (e.g., $\nu_A = -1$

$\nu_B = -b/a$). We now must determine the ratio P/P_0 as a function of the volume, V , or the catalyst weight, W , to account for pressure drop. We then combine the concentration, rate law, and design equation. However, whenever accounting for the effects of pressure drop, *the differential form of the mole balance (design equation) must be used.*

If, for example, the second-order isomerization reaction



When $P \neq P_0$ one must use the differential forms of the PFR/PBR design equations.

is being carried out in a packed-bed reactor, the **differential form of the mole balance** equation in terms of catalyst weight is

$$F_{A0} \frac{dX}{dW} = -r'_A \left(\frac{\text{gram moles}}{\text{gram catalyst} \cdot \text{min}} \right) \quad (2-17)$$

The **rate law** is

$$-r'_A = kC_A^2 \quad (4-19)$$

From **stoichiometry** for gas-phase reactions (Table 3-5),

$$C_A = \frac{C_{A0}(1-X)}{1+\varepsilon X} \frac{P}{P_0} \frac{T_0}{T}$$

and the rate law can be written as

$$-r'_A = k \left[\frac{C_{A0}(1-X)}{1+\varepsilon X} \frac{P}{P_0} \frac{T_0}{T} \right]^2 \quad (4-20)$$

Note from Equation (4-20) that the larger the pressure drop (i.e., the smaller P from frictional losses, the smaller the reaction rate!

Combining Equation (4-20) with the mole balance (2-17) and assuming isothermal operation ($T = T_0$) gives

$$F_{A0} \frac{dX}{dW} = k \left[\frac{C_{A0}(1-X)}{1+\varepsilon X} \right]^2 \left(\frac{P}{P_0} \right)^2$$

Dividing by F_{A0} (i.e., $v_0 C_{A0}$) yields

$$\frac{dX}{dW} = \frac{kC_{A0}}{v_0} \left(\frac{1-X}{1+\varepsilon X} \right)^2 \left(\frac{P}{P_0} \right)^2$$

For isothermal operation ($T = T_0$), the right-hand side is a function of only conversion and pressure: -

Another equation
is needed
(e.g., $P = f(W)$).

$$\frac{dX}{dW} = F_1(X, P) \quad (4-21)$$

We now need to relate the pressure drop to the catalyst weight in order to determine the conversion as a function of catalyst weight.

4.5.2 Flow Through a Packed Bed

The majority of gas-phase reactions are catalyzed by passing the reactant through a packed bed of catalyst particles.



The equation used most to calculate pressure drop in a packed porous bed is the **Ergun equation**:⁴

$$\text{Ergun equation} \quad \frac{dP}{dz} = -\frac{G}{\rho g_c D_p} \left(\frac{1-\phi}{\phi^3} \right) \left[\overbrace{\frac{150(1-\phi)\mu}{D_p}}^{\text{Term 1}} + \overbrace{1.75G}^{\text{Term 2}} \right] \quad (4-22)$$

Term 1 is dominant for laminar flow, and Term 2 is dominant for turbulent flow.

⁴ R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, 2nd ed. (New York: Wiley, 2001), p. 200.

where $P =$ pressure, lb_f/ft^2 (kPa)

$$\phi = \text{porosity} = \frac{\text{volume of void}}{\text{total bed volume}} = \text{void fraction}$$

$$1 - \phi = \frac{\text{volume of solid}}{\text{total bed volume}}$$

$$g_c = 32.174 \text{ lb}_m \cdot \text{ft}/\text{s}^2 \cdot \text{lb}_f (\text{conversion factor})$$

$$= 4.17 \times 10^8 \text{ lb}_m \cdot \text{ft}/\text{h}^2 \cdot \text{lb}_f$$

(recall that for the metric system $g_c = 1.0$)

$D_p =$ diameter of particle in the bed, ft (m)

$\mu =$ viscosity of gas passing through the bed, $\text{lb}_m/\text{ft} \cdot \text{h} (\text{kg}/\text{m} \cdot \text{s})$

$z =$ length down the packed bed of pipe, ft (m)

$u =$ superficial velocity = volumetric flow \div cross-sectional area of pipe, $\text{ft}/\text{h} (\text{m}/\text{s})$

$\rho =$ gas density, $\text{lb}/\text{ft}^3 (\text{kg}/\text{m}^3)$

$G = \rho u =$ superficial mass velocity, $\text{lb}_m/\text{ft}^2 \cdot \text{h} (\text{kg}/\text{m}^2 \cdot \text{s})$

In calculating the pressure drop using the Ergun equation, the only parameter that varies with pressure on the right-hand side of Equation (4-22) is the gas density, ρ . We are now going to calculate the pressure drop through the bed.

Because the reactor is operated at steady state, the mass flow rate at any point down the reactor, \dot{m} (kg/s), is equal to the entering mass flow rate, \dot{m}_0 (i.e., equation of continuity),

$$\dot{m}_0 = \dot{m}$$

$$\rho_0 v_0 = \rho v$$

Recalling Equation (3-41), we have

$$v = v_0 \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}} \quad (3-41)$$

$$\rho = \rho_0 \frac{v_0}{v} = \rho_0 \frac{P}{P_0} \left(\frac{T_0}{T} \right) \frac{F_{T0}}{F_T} \quad (4-23)$$

Combining Equations (4-22) and (4-23) gives

$$\frac{dP}{dz} = - \frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}}$$

Simplifying yields

$$\boxed{\frac{dP}{dz} = -\beta_0 \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}}} \quad (4-24)$$

where β_0 is a constant down the reactor that depends only on the properties of the packed bed and the entrance conditions.

$$\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \quad (4-25)$$

For tubular packed-bed reactors, we are more interested in catalyst weight rather than the distance z down the reactor. The catalyst weight up to a distance of z down the reactor is

$$\underbrace{W}_{\left[\begin{array}{c} \text{Weight of} \\ \text{catalyst} \end{array} \right]} = \underbrace{(1-\phi)A_c z}_{\left[\begin{array}{c} \text{Volume of} \\ \text{solids} \end{array} \right]} \times \underbrace{\rho_c}_{\left[\begin{array}{c} \text{Density of} \\ \text{solid catalyst} \end{array} \right]} \quad (4-26)$$

where A_c is the cross-sectional area. The bulk density of the catalyst, ρ_b (mass of catalyst per volume of reactor bed), is just the product of the density of the solid catalyst particles, ρ_c , and the fraction of solids, $(1-\phi)$:

Bulk density

$$\rho_b = \rho_c (1-\phi)$$

Using the relationship between z and W [Equation (4-26)] we can change our variables to express the Ergun equation in terms of catalyst weight:

$$\frac{dP}{dW} = -\frac{\beta_0}{A_c(1-\phi)\rho_c} \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}}$$

Use this form for multiple reactions and membrane reactors.

Further simplification yields

$$\frac{dP}{dW} = -\frac{\alpha}{2} \frac{T}{T_0} \frac{P_0}{P/P_0} \left(\frac{F_T}{F_{T0}} \right) \quad (4-27)$$

Let $y = P / P_0$, then

$$\boxed{\frac{dy}{dW} = -\frac{\alpha}{2y} \frac{T}{T_0} \frac{F_T}{F_{T0}}} \quad (4-28)$$

where

$$\alpha = \frac{2\beta_0}{A_c \rho_c (1 - \phi) P_0} \quad (4-29)$$

We will use Equation (4-28) when multiple reactions are occurring or when there is pressure drop in a membrane reactor. However, for single reactions in packed-bed reactors, it is more convenient to express the Ergun equation in terms of the conversion X . Recalling Equation (3-43) for F_T ,

$$F_T = F_{T0} + F_{A0} \delta X = F_{T0} \left(1 + \frac{F_{A0}}{F_{T0}} \delta X \right) \quad (3-43)$$

and dividing by F_{T0}

$$\frac{F_T}{F_{T0}} = 1 + \varepsilon X$$

where, as before,

$$\varepsilon = y_{A0} \delta = \frac{F_{A0}}{F_{T0}} \delta \quad (3-35)$$

Differential form of Ergun equation for the pressure drop in packed beds.

Substituting for the ratio (F_T/F_{T0}), Equation (4-28) can now be written as

$$\frac{dy}{dW} = -\frac{\alpha}{2y} (1 + \varepsilon X) \frac{T}{T_0} \quad (4-30)$$

We note that when ε is negative, the pressure drop ΔP will be less (i.e. higher pressure) than that for $\varepsilon = 0$. When ε is positive, the pressure drop ΔP will be greater than when $\varepsilon = 0$.

For isothermal operation, Equation (4-30) is only a function of conversion and pressure:

$$\frac{dP}{dW} = F_2(X, P) \quad (4-31)$$

Two coupled equations to be solved numerically

Recalling Equation (4-21), for the combined mole balance, rate law, and stoichiometry,

$$\frac{dX}{dW} = F_1(X, P) \quad (4-21)$$

we see that we have two coupled first-order differential equations, (4-31) and (4-21), that must be solved simultaneously. A variety of software packages and numerical integration schemes are available for this purpose.

Analytical Solution. If $\varepsilon = 0$, or if we can neglect (εX) with respect to 1.0 (i.e., $1 \gg \varepsilon X$), we can obtain an analytical solution to Equation (4-30) for isothermal operation (i.e., $T = T_0$). For isothermal operation with $\varepsilon = 0$, Equation (4-30) becomes

Isothermal with
 $\varepsilon = 0$

$$\frac{dy}{dW} = \frac{-\alpha}{2y} \quad (4-32)$$

Rearranging gives us

$$2y \frac{dy}{dW} = -\alpha$$

Taking y inside the derivative, we have

$$\frac{dy^2}{dW} = -\alpha$$

Integrating with $y = 1$ ($P = P_0$) at $W = 0$ yields

$$(y)^2 = 1 - \alpha W$$

Taking the square root of both sides gives

Pressure ratio
only for $\varepsilon = 0$

$$y = \frac{P}{P_0} = (1 - \alpha W)^{1/2} \quad (4-33)$$

Be sure *not* to use this equation if $\varepsilon \neq 0$ or the reaction is not carried out isothermally, where again

$$\alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_c P_0} \quad (4-29)$$

Equation (4-33) can be used to substitute for the pressure in the rate law, in which case the mole balance can be written solely as a function of conversion and catalyst weight. The resulting equation can readily be solved either analytically or numerically.

If we wish to express the pressure in terms of reactor length z , we can use Equation (4-26) to substitute for W in Equation (4-33). Then

$$y = \frac{P}{P_0} = \left(1 - \frac{2\beta_0 z}{P_0}\right)^{1/2} \quad (4-34)$$

4.5.3 Pressure Drop in Pipes

Normally, the pressure drop for gases flowing through pipes without packing can be neglected. For flow in pipes, the pressure drop along the length of the pipe is given by

$$\frac{dP}{dL} = -G \frac{du}{dL} - \frac{2fG^2}{\rho D} \quad (4-35)$$

where D = pipe diameter, cm

u = average velocity of gas, cm/s

f = Fanning friction factor

$G = \rho u$, g/cm²·s

The friction factor is a function of the Reynolds number and pipe roughness. The mass velocity, G , is constant along the length of the pipe. Replacing u with G/ρ , and combining with Equation (4-23) for the case of constant temperature, T , and total molar flow rate, F_T , Equation (4-35) becomes

$$\rho_0 \frac{P}{P_0} \frac{dP}{dL} - G^2 \frac{dP}{P dL} + \frac{2fG^2}{D} = 0$$

Integrating with limits $P = P_0$ when $L = 0$, and assuming that f does not vary, we have

$$\frac{P_0^2 - P^2}{2} = G^2 \frac{P_0}{\rho_0} \left(2f \frac{L}{D} + \ln \frac{P_0}{P} \right)$$

Neglecting the second term on the right-hand side gives upon rearrangement

$$\frac{P}{P_0} = \left[1 - \frac{4fG^2V}{\rho_0 P_0 A_c D} \right]^{1/2} = (1 - \alpha_p V)^{1/2} \quad (4-36)$$

where

$$\alpha_p = \frac{4fG^2}{A_c \rho_0 P_0 D}$$

For the flow conditions given in Example 4-4 in a 1000-ft length of 1½-in. schedule 40 pipe ($\alpha_p = 0.0118$), the pressure drop is less than 10%. However, for high volumetric flow rates through microreactors, the pressure drop may be significant.

Example 4-4 Calculating Pressure Drop in a Packed Bed

Plot the pressure drop in a 60 ft length of $1\frac{1}{2}$ -in. schedule 40 pipe packed with catalyst pellets $\frac{1}{4}$ -in. in diameter. There is 104.4 lb/h of gas passing through the bed. The temperature is constant along the length of pipe at 260°C. The void fraction is 45% and the properties of the gas are similar to those of air at this temperature. The entering pressure is 10 atm.

Solution

At the end of the reactor, $z = L$ and Equation (4-34) becomes

$$\frac{P}{P_0} = \left(1 - \frac{2\beta_0 L}{P_0}\right)^{1/2} \quad (\text{E4-4.1})$$

$$\beta_0 = \frac{G(1-\phi)}{g_c \rho_0 D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \quad (4-25)$$

$$G = \frac{\dot{m}}{A_c} \quad (\text{E4-4.2})$$

Evaluating
the pressure drop
parameters

For $1\frac{1}{2}$ -in. schedule 40 pipe, $A_c = 0.01414 \text{ ft}^2$:

$$G = \frac{104.4 \text{ lb}_m/\text{h}}{0.01414 \text{ ft}^2} = 7383.3 \frac{\text{lb}_m}{\text{h} \cdot \text{ft}^2}$$

For air at 260°C and 10 atm.

$$\mu = 0.0673 \text{ lb}_m/\text{ft} \cdot \text{h}$$

$$\rho_0 = 0.413 \text{ lb}_m/\text{ft}^3$$

$$v_0 = \frac{\dot{m}}{\rho_0} = \frac{104.4 \text{ lb}_m/\text{h}}{0.413 \text{ lb}_m/\text{ft}^3} = 252.8 \text{ ft}^3/\text{h} \quad (7.16 \text{ m}^3/\text{h})$$

From the problem statement,

$$D_p = \frac{1}{4} \text{ in.} = 0.0208 \text{ ft}, \quad \phi = 0.45$$

$$g_c = 4.17 \times 10^8 \frac{\text{lb}_m \cdot \text{ft}}{\text{lb}_f \cdot \text{h}^2}$$

Substituting these values into Equation (4-25) gives

$$\beta_0 = \left[\frac{7383.3 \text{ lb}_m/\text{ft}^2 \cdot \text{h}(1 - 0.45)}{(4.17 \times 10^8 \text{ lb}_m \cdot \text{ft}/\text{lb}_f \cdot \text{h}^2)(0.413 \text{ lb}_m/\text{ft}^3)(0.0208 \text{ ft})(0.45)^3} \right] \quad (\text{E4-4.3})$$

$$\times \left[\frac{150(1 - 0.45)(0.0673 \text{ lb}_m/\text{ft} \cdot \text{h})}{0.0208 \text{ ft}} + 1.75(7383.3) \frac{\text{lb}_m}{\text{ft}^2 \cdot \text{h}} \right]$$

$$\beta_0 = 0.01244 \frac{\text{lb}_f \cdot \text{h}}{\text{ft} \cdot \text{lb}_m} \left[\overbrace{(266.9)}^{\text{Term 1}} + \overbrace{(12,920.8)}^{\text{Term 2}} \right] \frac{\text{lb}_m}{\text{ft}^2 \cdot \text{h}} = 164.1 \frac{\text{lb}_f}{\text{ft}^3} \quad (\text{E4-4.4})$$

We note that the turbulent flow term, Term 2, is dominant.

$$\beta_0 = 164.1 \frac{\text{lb}_f}{\text{ft}^3} \times \frac{1 \text{ ft}^2}{144 \text{ in.}^2} \times \frac{1 \text{ atm}}{14.7 \text{ lb}_f/\text{in.}^2} \quad (\text{E4-4.5})$$

Unit Conversion
for β_0

$$\frac{1 \text{ atm}}{\text{ft}} = 333 \frac{\text{kPa}}{\text{m}}$$

$$\beta_0 = 0.0775 \frac{\text{atm}}{\text{ft}} = 25.8 \frac{\text{kPa}}{\text{m}}$$

$$y = \frac{P}{P_0} = \left(1 - \frac{2\beta_0 L}{P_0} \right)^{1/2} = \left(1 - \frac{2 \times \overbrace{0.0775}^{0.155} \text{ atm/ft} \times 60 \text{ ft}}{10 \text{ atm}} \right)^{1/2} \quad (\text{E4-4.6})$$

$$P = 0.265P_0 = 2.65 \text{ atm} \quad (268 \text{ kPa}) \quad (\text{E4-4.7})$$

$$\Delta P = P_0 - P = 10 - 2.65 = 7.35 \text{ atm} \quad (744 \text{ kPa})$$

Now let's use the data to plot the pressure and the volumetric flow rate profiles. Recalling Equation (4-34) for the case $\varepsilon = 0$ and $T = T_0$

$$v = v_0 \frac{P_0}{P} = \frac{v_0}{y} \quad (\text{E4-4.8})$$

Equations (4-34) and (E4-4.8) were used in the construction of Table E4-4.1.

TABLE E4-4.1. P AND v PROFILES

z (ft)	0	10	20	30	40	50	60
P (atm)	10	9.2	8.3	7.3	6.2	4.7	2.65
v (ft ³ /h)	253	275	305	347	408	538	955

For $\rho_c = 120 \text{ lb}/\text{ft}^3$

$$\alpha = \frac{2\beta_0}{\rho_c(1-\phi)A_c P_0} = \frac{2(0.0775)\text{atm/ft}}{120\text{ lb/ft}^3(1-0.45)(0.1414\text{ ft}^2)10\text{ atm}}$$

$$\alpha = 0.00165\text{ lb}^{-1} = 0.037\text{ kg}^{-1}$$

The values in Table E4-4.1 were used to obtain Figure E4-4.1.

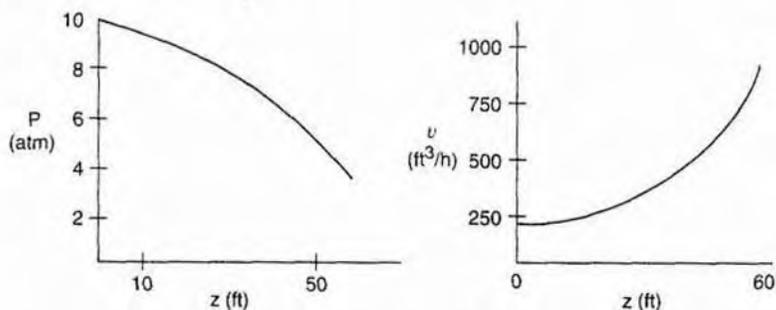


Figure E4-4.1 P and v profiles.

4.5.4 Analytical Solution for Reaction with Pressure Drop

We will first describe how pressure drop affects our CRE algorithm. Figure 4-9 shows qualitatively the effects of pressure drop or reactor design.

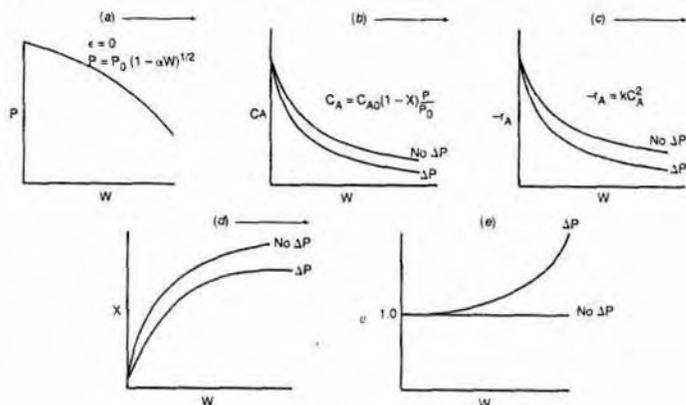


Figure 4-9 Effect of pressure drop on P (a), C_A (b), $-r_A$ (c), X (d), and v (e).

These graphs compare the concentrations, reaction rates, and conversion profiles for the cases of pressure drop and no pressure drop. We see that when there is pressure drop in the reactor, the reactant concentrations and thus reaction rate for reaction (for reaction orders greater than 0 order) will always be

smaller than the case with no pressure drop. As a result of this smaller reaction rate, the conversion will be less with pressure drop than without pressure drop.

Now that we have expressed pressure as a function of catalyst weight [Equation (4-33)], we can return to the second-order isothermal reaction,



to relate conversion and catalyst weight. Recall our mole balance, rate law, and stoichiometry.

$$1. \text{ Mole balance: } F_{A0} \frac{dX}{dW} = -r'_A \quad (2-17)$$

$$2. \text{ Rate law: } -r'_A = kC_A^2 \quad (4-19)$$

3. **Stoichiometry.** Gas-phase isothermal reaction ($T = T_0$) with $\varepsilon = 0$. From Equation (3-45), $v = v_0/y$

$$C_A = \frac{F_A}{v} = C_{A0}(1-X)y \quad (4-37)$$

Only
for
 $\varepsilon = 0$

$$y = (1 - \alpha W)^{1/2} \quad (4-33)$$

Using Equation (4-33) to substitute for y in terms of the catalyst weight, we obtain

$$C_A = C_{A0}(1-X)(1-\alpha W)^{1/2}$$

$$4. \text{ Combining: } \frac{dX}{dW} = \frac{kC_{A0}^2}{F_{A0}} (1-X)^2 [(1-\alpha W)^{1/2}]^2$$

$$5. \text{ Separating variables: } \frac{F_{A0}}{kC_{A0}^2} \frac{dX}{(1-X)^2} = (1-\alpha W) dW$$

Integrating with limits $X = 0$ when $W = 0$ and substituting for $F_{A0} = C_{A0}v_0$ yields

$$\frac{v_0}{kC_{A0}} \left(\frac{X}{1-X} \right) = W \left(1 - \frac{\alpha W}{2} \right)$$

Solving for conversion gives

$$X = \frac{\frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2}\right)}{1 + \frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2}\right)} \quad (4-38)$$

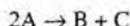
Solving for the catalyst weight, we have

Catalyst weight
for
second-order
reaction in PFR
with ΔP

$$W = \frac{1 - \{1 - [(2v_0\alpha)/kC_{A0}][X/(1-X)]\}^{1/2}}{\alpha} \quad (4-39)$$

Example 4-5 Effect of Pressure Drop on the Conversion Profile

Reconsider the packed bed in Example 4-4 for the case where a second-order reaction



is taking place in 20 meters of a 1½ schedule 40 pipe packed with catalyst. The flow and packed-bed conditions in the example remain the same except that they are converted to SI units; that is, $P_0 = 10 \text{ atm} = 1013 \text{ kPa}$, and

Entering volumetric flow rate: $v_0 = 7.15 \text{ m}^3/\text{h}$ (252 ft³/h)

Catalyst pellet size: $D_p = 0.006 \text{ m}$ (ca. ¼-inch)

Solid catalyst density: $\rho_c = 1923 \text{ kg/m}^3$ (120 lb/ft³)

Cross-sectional area of 1½-in. schedule 40 pipe: $A_c = 0.0013 \text{ m}^2$

Pressure drop parameter: $\beta_0 = 25.8 \text{ kPa/m}$

Reactor length: $L = 20 \text{ m}$

We will change the particle size to learn its effect on the conversion profile. However, we will assume that the specific reaction rate, k , is unaffected by particle size, an assumption we know from Chapter 12 is valid only for small particles.

- First, calculate the conversion in the absence of pressure drop.
- Next, calculate the conversion accounting for pressure drop.
- Finally, determine how your answer to (b) would change if the catalyst particle diameter were doubled.

The entering concentration of A is 0.1 kmol/m^3 and the specific reaction rate is

$$k = \frac{12 \text{ m}^6}{\text{kmol} \cdot \text{kg cat} \cdot \text{h}}$$

We need to be able
to work either
metric, S.I., or
English units.

Solution

Using Equation (4-38)

$$X = \frac{\frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2}\right)}{1 + \frac{kC_{A0}W}{v_0} (1 - \alpha W)} \quad (4-3)$$

For the bulk catalyst density,

$$\rho_b = \rho_c(1 - \phi) = (1923)(1 - 0.45) = 1058 \text{ kg/m}^3$$

The weight of catalyst in the 20 m of 1½-in. schedule 40 pipe is

$$W = A_c \rho_b L = (0.0013 \text{ m}^2) \left(1058 \frac{\text{kg}}{\text{m}^3}\right) (20 \text{ m})$$

$$W = 27.5 \text{ kg}$$

$$\frac{kC_{A0}W}{v_0} = \frac{12\text{m}^6}{\text{kmol} \cdot \text{kg cat} \cdot \text{h}} \cdot 0.1 \frac{\text{kmol}}{\text{m}^3} \cdot \frac{27.5 \text{ kg}}{7.15 \text{ m}^3/\text{h}} = 4.6$$

(a) First calculate the conversion for $\Delta P = 0$ (i.e., $\alpha = 0$)

$$X = \frac{\frac{kC_{A0}W}{v_0}}{1 + \frac{kC_{A0}W}{v_0}} = \frac{4.6}{1 + 4.6} = 0.82 \quad (E4-5)$$

$$\boxed{X = 0.82}$$

(b) Next, we calculate the conversion with pressure drop. Recalling Equation (4-29) and substituting the bulk density $\rho_b = (1 - \phi) \rho_c = 1058 \text{ kg/m}^3$

$$\alpha = \frac{2\beta_0}{P_0 A_c \rho_b} = \frac{2 \left(25.8 \frac{\text{kPa}}{\text{m}}\right)}{(1013 \text{ kPa})(0.0013 \text{ m}^2) \left(1058 \frac{\text{kg}}{\text{m}^3}\right)} \quad (E4-5)$$

$$= 0.037 \text{ kg}^{-1}$$

then

$$\left(1 - \frac{\alpha W}{2}\right) = 1 - \frac{(0.037)(27.5)}{2} = 0.49 \quad (E4-5)$$

$$X = \frac{\frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2}\right)}{1 + \frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2}\right)} = \frac{(4.6)(0.49)}{1 + (4.6)(0.49)} = \frac{2.36}{3.26} \quad (\text{E4-5.4})$$

$$X = 0.693$$

We see the predicted conversion dropped from 82.2% to 69.3% because of pressure drop. It would be not only embarrassing but also an economic disaster if we had neglected pressure drop and the actual conversion had turned out to be significantly smaller.

- (c) *Robert the Worrier* wonders: What if we increase the catalyst size by a factor of 2? We see from Equation (E4-4.5) that the second term in the Ergun equation is dominant; that is,

$$1.75G \gg \frac{150(1-\phi)\mu}{D_p} \quad (\text{E4-5.5})$$

Therefore from Equation (4-25)

$$\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right]$$

we have

$$\beta_0 = \frac{1.75G^2(1-\phi)}{\rho_0 g_c D_p \phi^3} \quad (\text{E4-5.6})$$

We see for the conditions given by Equation (E4-4.4) that the pressure drop parameter varies inversely with the particle diameter

$$\beta_0 \sim \frac{1}{D_p}$$

and thus

$$\alpha \sim \frac{1}{D_p}$$

For Case 2, $D_{p_2} = 2D_{p_1}$

$$\begin{aligned} \alpha_2 &= \alpha_1 \frac{D_{p_1}}{D_{p_2}} = (0.037 \text{ kg}^{-1}) \frac{1}{2} \\ &= 0.0185 \text{ kg}^{-1} \end{aligned} \quad (\text{E4-5.7})$$



We will learn more about *Robert the Worrier* in Chapter 11.

Substituting this new value of α in Equation (E4-5.4)

$$X_2 = \frac{(4.6) \left(1 - \frac{0.0185(27.5)}{2} \right)}{1 + (4.6) \left(1 - \frac{0.0185(27.5)}{2} \right)} = \frac{3.43}{4.43}$$

$$X = 0.774$$

By increasing the particle diameter we decrease the pressure drop parameter and thus increase the reaction rate and the conversion. However, Chapters 10 and 12 explain that when interparticle diffusion effects are important in the catalyst pellet, this increase in conversion with increasing particle size will not always be the case. For larger particles, it takes a longer time for a given number of reactant and product molecules to diffuse in and out of the catalyst particle where they undergo reaction (see Figure 10-6). Consequently, the specific reaction rate decreases with increasing particle size $k \sim 1/D_p$ [see Equation (12-35)], which in turn decreases the conversion. At small particle diameters, the rate constant, k , is large, and at its maximum value, but the pressure drop is also large, resulting in a low rate of reaction. At large particle diameters, the pressure drop is small, but so is the rate constant, k , and the rate of reaction, resulting in low conversion. Thus, we see how a low conversion at both large and small particle diameters with an optimum in between. This optimum is shown in Figure E4-5.1. See Problem P4-23.

The variation
 $k \sim \frac{1}{D_p}$
 is discussed in
 detail in Chapter 12.

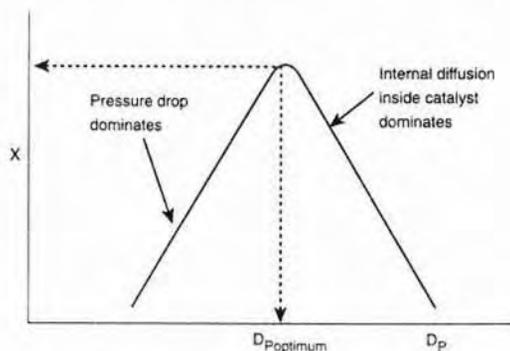


Figure E4-5.1 Finding the optimum particle diameter.

Problems with large diameter tubes

- (1) Bypassing of catalyst
- (2) Smaller heat transfer area

If pressure drop is to be minimized, *why not pack the catalyst into a larger diameter tube* to decrease the superficial velocity, G , thereby reducing ΔP ? There are two reasons for *not* increasing the tube diameter: (1) There is an increased chance the gas could channel and bypass most of the catalyst, resulting in little conversion (see Figures 13-2 and 13-10); (2) the ratio of the heat-transfer surface area to reactor volume (catalyst weight) will be decreased, thereby making heat transfer more difficult for highly exothermic and endothermic reactions. We now proceed (Example 4-6) to combine pressure drop with reaction in a packed bed when we have volume change with reaction and therefore cannot obtain an analytical solution.