compared to the diffusion rate, and the pellet concentration becomes nearly uniform. For large values of Thiele modulus, the reaction rate is large compared to the diffusion rate, and the reactant is converted to product before it can penetrate very far into the pellet.

We now calculate the pellet's overall production rate given this concentration profile. We can perform this calculation in two ways. The first and more direct method is to integrate the local production rate over the pellet volume. The second method is to use the fact that, at steady state, the rate of consumption of reactant within the pellet is equal to the rate at which material fluxes through the pellet's exterior surface. The two expressions are

$$R_{Ap} = \frac{1}{V_p}\int_0^R R_A(r)4\pi r^2 dr \qquad \text{volume integral} \tag{7.26}$$

$$R_{Ap} = -\frac{S_p}{V_p}D_A \left.\frac{dc_A}{dr}\right|_{r=R} \qquad \begin{array}{l}\text{surface flux}\\ \text{(assumes steady state)}\end{array} \tag{7.27}$$

in which the local production rate is given by $R_A(r) = -kc_A(r)$. We use the direct method here and leave the other method as an exercise. Substituting the local production rate into Equation 7.26 and converting the integral to dimensionless radius gives

$$R_{Ap} = -\frac{kc_{As}}{9}\int_0^3 \overline{c}(\overline{r})\overline{r}^2 d\overline{r} \tag{7.28}$$

Substituting the concentration profile, Equation 7.25, and changing the variable of integration to $x = \Phi r$ gives

$$R_{Ap} = -\frac{kc_{As}}{3\Phi^2 \sinh 3\Phi}\int_0^{3\Phi} x \sinh x dx \tag{7.29}$$

The integral can be found in a table or derived by integration by parts to yield finally

$$R_{Ap} = -kc_{As}\frac{1}{\Phi}\left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi}\right] \tag{7.30}$$

It is instructive to compare this actual pellet production rate to the rate in the absence of diffusional resistance. If the diffusion were arbitrarily fast, the concentration everywhere in the pellet would be equal to the surface concentration, corresponding to the limit $\Phi = 0$. The pellet rate for this limiting case is simply

$$R_{As} = -kc_{As} \tag{7.31}$$

We define the effectiveness factor, η, to be the ratio of these two rates

$$\boxed{\eta \equiv \frac{R_{Ap}}{R_{As}}, \qquad \text{effectiveness factor}} \tag{7.32}$$

The effectiveness factor is a dimensionless pellet production rate that measures how effectively the catalyst is being used. For η near unity, the entire volume of the pellet is reacting at the same high rate because the reactant is able to diffuse quickly through the pellet. For η near zero, the pellet reacts at a low rate. The reactant is unable to penetrate significantly into the interior of the pellet and the reaction rate is small in a large portion of the pellet volume. The pellet's diffusional resistance is large and this resistance lowers the overall reaction rate. We can substitute Equations 7.30 and 7.31 into the definition of effectiveness factor to obtain for the first-order reaction in the spherical pellet

$$\eta = \frac{1}{\Phi}\left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi}\right] \tag{7.33}$$

Figures 7.5 and 7.6 display the effectiveness factor versus Thiele modulus relationship given in Equation 7.33. The log-log scale in Figure 7.6 is particularly useful, and we see the two asymptotic limits of Equation 7.33. At small Φ, $\eta \approx 1$, and at large Φ, $\eta \approx 1/\Phi$. Figure 7.6 shows that the asymptote $\eta = 1/\Phi$ is an excellent approximation for the spherical pellet for $\Phi \geq 10$. For large values of the Thiele modulus, the rate of reaction is much greater than the rate of diffusion, the effectiveness factor is much less than unity, and we say the pellet is *diffusion limited.* Conversely, when the diffusion rate is much larger than the reaction rate, the effectiveness factor is near unity, and we say the pellet is *reaction limited.*

Example 7.1: Using the Thiele modulus and effectiveness factor

The first-order, irreversible reaction ($A \longrightarrow B$) takes place in a 0.3 cm radius spherical catalyst pellet at $T = 450$ K. At 0.7 atm partial pressure of A, the pellet's production rate is -2.5×10^{-5} mol/(g s). Determine the production rate at the same temperature in a 0.15 cm radius spherical pellet. The pellet density is $\rho_p = 0.85$ g/cm^3. The effective diffusivity of A in the pellet is $D_A = 0.007$ cm^2/s.

Solution

We can use the production rate and pellet parameters for the 0.3 cm pellet to find the value for the rate constant k, and then compute the Thiele

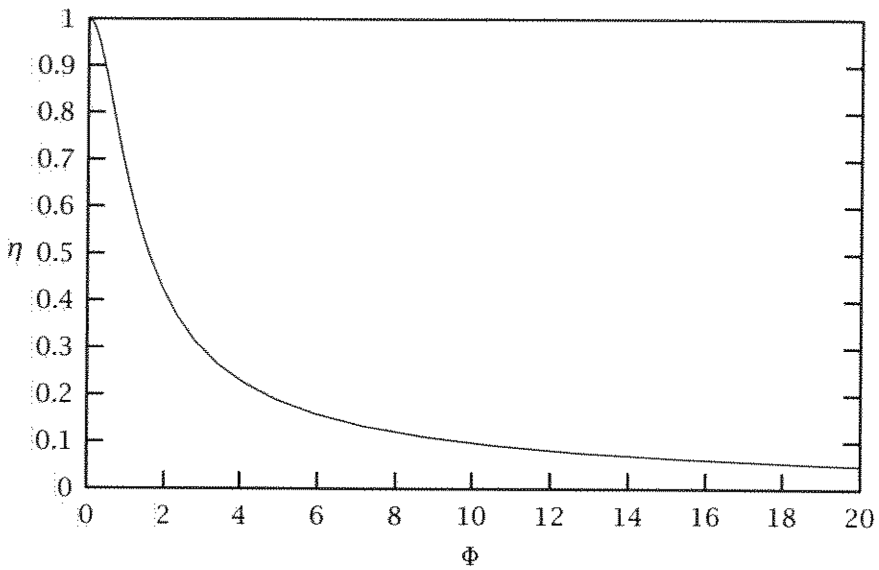

Figure 7.5: Effectiveness factor versus Thiele modulus for a first-order reaction in a sphere.

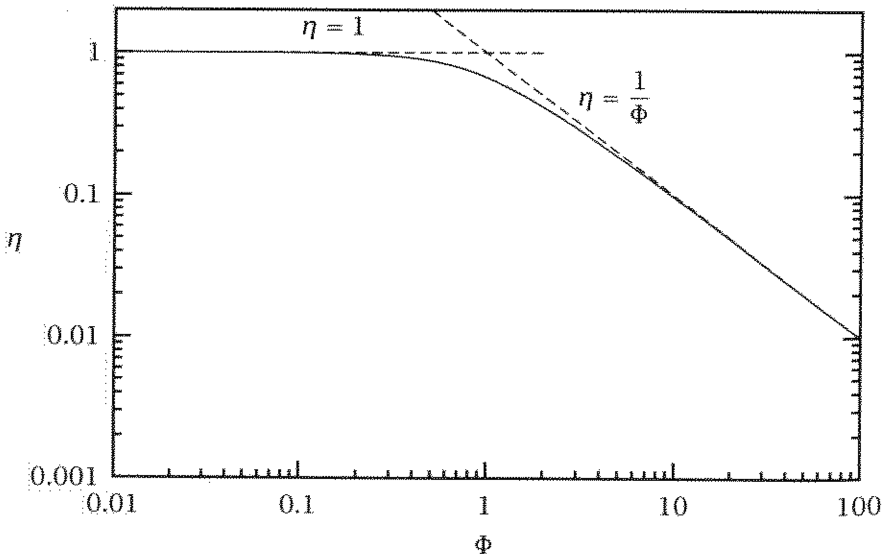

Figure 7.6: Effectiveness factor versus Thiele modulus for a first-order reaction in a sphere (log-log scale).

modulus, effectiveness factor and production rate for the smaller pellet.

We have three unknowns, k, Φ, η, and the following three equations

$$R_{Ap} = -\eta k c_{As} \tag{7.34}$$

$$\Phi = \sqrt{\frac{ka^2}{D_A}} \tag{7.35}$$

$$\eta = \frac{1}{\Phi}\left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi}\right] \tag{7.36}$$

The production rate is given in the problem statement. Solving Equation 7.35 for k, and substituting that result and Equation 7.36 into 7.34, give one equation in the unknown Φ

$$\Phi\left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi}\right] = -\frac{R_{Ap}a^2}{D_A c_{As}} \tag{7.37}$$

The surface concentration and pellet production rates are given by

$$c_{As} = \frac{0.7 \text{ atm}}{\left(82.06 \frac{\text{cm}^3 \text{ atm}}{\text{mol K}}\right)(450 \text{ K})} = 1.90 \times 10^{-5} \text{mol/cm}^3$$

$$R_{Ap} = \left(-2.5 \times 10^{-5} \frac{\text{mol}}{\text{g s}}\right)\left(0.85 \frac{\text{g}}{\text{cm}^3}\right) = -2.125 \frac{\text{mol}}{\text{cm}^3 \text{ s}}$$

Substituting these values into Equation 7.37 gives

$$\Phi\left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi}\right] = 1.60$$

This equation can be solved numerically yielding the Thiele modulus

$$\Phi = 1.93$$

Using this result, Equation 7.35 gives the rate constant

$$k = 2.61 \text{ s}^{-1}$$

The smaller pellet is half the radius of the larger pellet, so the Thiele modulus is half as large or $\Phi = 0.964$, which gives $\eta = 0.685$. The production rate is therefore

$$R_{Ap} = -0.685\left(2.6\text{s}^{-1}\right)\left(1.90 \times 10^{-5} \text{mol/cm}^3\right) = -3.38 \times 10^{-5} \frac{\text{mol}}{\text{cm}^3 \text{ s}}$$

We see that decreasing the pellet size increases the production rate by almost 60%. Notice that this type of increase is possible only when the pellet is in the diffusion-limited regime. □