

Figure 7.26: Molar flow of A versus reactor volume for second-order, isothermal reaction in a fixed-bed reactor.

to obtain a closed-form solution. If we substitute this approximation for  $\eta$ , and Equation 7.100 into Equation 7.98 and rearrange we obtain

$$\frac{dN_A}{dV} = \frac{-(1 - \epsilon_B) \sqrt{k} (P/RT)^{3/2}}{(R/3) \sqrt{3/D_A} (2N_{Af})^{3/2}} N_A^{3/2}$$

Separating and integrating this differential equation gives

$$V_R = \frac{4[(1 - x_A)^{-1/2} - 1] N_{Af} (R/3) \sqrt{3/D_A}}{(1 - \epsilon_B) \sqrt{k} (P/RT)^{3/2}} \quad (7.104)$$

Large  $\Phi$  approximation

The results for the large  $\Phi$  approximation also are shown in Figure 7.26. Notice from Figure 7.9 that we are slightly overestimating the value of  $\eta$  using Equation 7.103, so we underestimate the required reactor volume. The reactor size and the percent change in reactor size are

$$V_R = 333 \text{ L}, \quad \Delta = -7.7\%$$

Given that we have a result valid for all  $\Phi$  that requires solving only a single differential equation, one might question the value of this closed-

form solution. One advantage is purely practical. We may not have a computer available. Instructors are usually thinking about in-class examination problems at this juncture. The other important advantage is insight. It is not readily apparent from the differential equation what would happen to the reactor size if we double the pellet size, or halve the rate constant, for example. Equation 7.104, on the other hand, provides the solution's dependence on all parameters. As shown in Figure 7.26 the approximation error is small. Remember to check that the Thiele modulus is large for the entire tube length, however, before using Equation 7.104.  $\square$

### Example 7.6: Hougen-Watson kinetics in a fixed-bed reactor

The following reaction converting CO to CO<sub>2</sub> takes place in a catalytic, fixed-bed reactor operating isothermally at 838 K and 1.0 atm



The following rate expression and parameters are adapted from a different model given by Oh et al. [16]. The rate expression is assumed to be of the Hougen-Watson form

$$r = \frac{k c_{\text{CO}} c_{\text{O}_2}}{1 + K c_{\text{CO}}} \quad \text{mol/s cm}^3 \text{ pellet}$$

The constants are provided below

$$k = 8.73 \times 10^{12} \exp(-13,500/T) \text{ cm}^3/\text{mol s}$$

$$K = 8.099 \times 10^6 \exp(409/T) \text{ cm}^3/\text{mol}$$

$$D_{\text{CO}} = 0.0487 \text{ cm}^2/\text{s}$$

in which  $T$  is in Kelvin. The catalyst pellet radius is 0.1 cm. The feed to the reactor consists of 2 mol% CO, 10 mol% O<sub>2</sub>, zero CO<sub>2</sub> and the remainder inerts. Find the reactor volume required to achieve 95% conversion of the CO.

### Solution

Given the reaction stoichiometry and the excess of O<sub>2</sub>, we can neglect the change in  $c_{\text{O}_2}$  and approximate the reaction as pseudo-first order

in CO

$$r = \frac{k' c_{\text{CO}}}{1 + K c_{\text{CO}}} \quad \text{mol/s cm}^3 \text{ pellet}$$

$$k' = k c_{\text{O}_2 f}$$

which is of the form analyzed in Section 7.4.4. We can write the mass balance for the molar flow of CO,

$$\frac{dN_{\text{CO}}}{dV} = -(1 - \epsilon_B) \eta r(c_{\text{CO}})$$

in which  $c_{\text{CO}}$  is the fluid CO concentration. From the reaction stoichiometry, we can express the remaining molar flows in terms of  $N_{\text{CO}}$

$$N_{\text{O}_2} = N_{\text{O}_2 f} + 1/2(N_{\text{CO}} - N_{\text{CO}f})$$

$$N_{\text{CO}_2} = N_{\text{CO}f} - N_{\text{CO}}$$

$$N = N_{\text{O}_2 f} + 1/2(N_{\text{CO}} + N_{\text{CO}f})$$

The concentrations follow from the molar flows assuming an ideal-gas mixture

$$c_j = \frac{P}{RT} \frac{N_j}{N}$$

To decide how to approximate the effectiveness factor shown in Figure 7.14, we evaluate  $\phi = K_{\text{CO}} c_{\text{CO}}$ , at the entrance and exit of the fixed-bed reactor. With  $\phi$  evaluated, we compute the Thiele modulus given in Equation 7.58 and obtain

$$\begin{array}{lll} \phi = 32.0 & \Phi = 79.8, & \text{entrance} \\ \phi = 1.74 & \Phi = 326, & \text{exit} \end{array}$$

It is clear from these values and Figure 7.14 that  $\eta = 1/\Phi$  is an excellent approximation for this reactor. Substituting this equation for  $\eta$  into the mass balance and solving the differential equation produces the results shown in Figure 7.27. The concentration of  $\text{O}_2$  is nearly constant, which justifies the pseudo-first-order rate expression. Reactor volume

$$V_R = 233 \text{ L}$$

is required to achieve 95% conversion of the CO. Recall that the volumetric flowrate varies in this reactor so conversion is based on molar flow, not molar concentration. Figure 7.28 shows how  $\Phi$  and  $\phi$  vary with position in the reactor. □

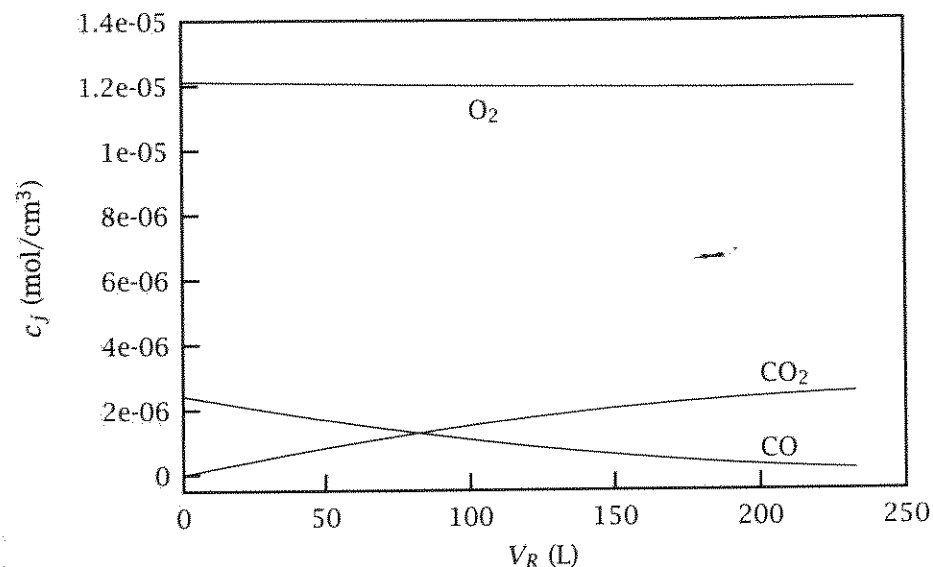


Figure 7.27: Molar concentrations versus reactor volume.

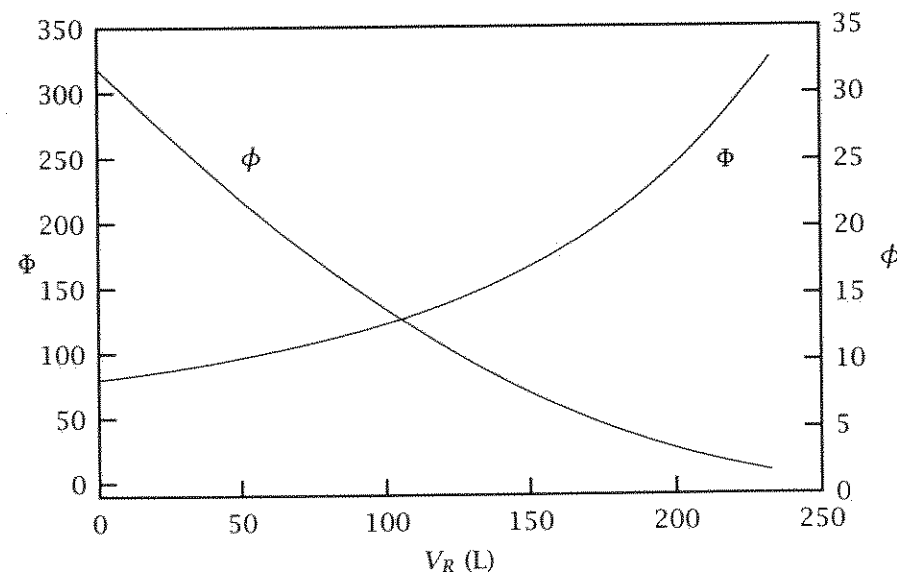


Figure 7.28: Dimensionless equilibrium constant and Thiele modulus versus reactor volume. Values indicate  $\eta = 1/\Phi$  is a good approximation for entire reactor.