A First Course on Kinetics and Reaction Engineering

Example 12.3

This example is based upon information and examples from Satterfield's books "Mass Transfer in Heterogeneous Catalysis," Krieger Publishing Co., Malabar, FL, 1981, and "Heterogeneous Catalysis," McGraw-Hill, New York, 1980. These are excellent references that examine the topics presented in Unit 12 in much greater depth and detail.

Problem Purpose

This example illustrates the use of computational tests for the presence of internal mass transfer limitations.

Problem Statement

The kinetics of the reaction between thiophene and hydrogen are being studied in a packed bed catalytic reactor. The reactor operates at 650 K and 30 atm, with a feed containing 15% thiophene and flowing with a mass velocity, G, of 0.2 g s^{-1} cm^{-2}. At these conditions the diffusivity of thiophene will be approximately 5.2 x 10^{-3} cm^{2} s^{-1}, the viscosity of the gas will equal 3.8 x 10^{-4} P, its thermal conductivity will be 5.4 x 10^{-4} cal cm^{-1} K^{-1} s^{-1}, its heat capacity will equal 0.9 cal g^{-1} K^{-1} and its density will equal 0.0168 g cm^{-3}. The catalyst bed contains particles with an effective diameter of 0.4 cm that pack giving a bed porosity, ε, of 0.4 and have an estimated thermal conductivity of 0.001 cal s^{-1} cm^{-1} K^{-1}. The effective diffusivity of thiophene in the pores of this catalyst has been estimated to equal 0.0015 cm^{2} s^{-1}. The observed reaction rate is 1 x 10^{-6} mol s^{-1} cm^{-3} and may be assumed to be first order in thiophene with an activation energy of 60 kJ mol^{-1}. The heat of reaction is 2.5 x 10^{4} cal mol^{-1}. At these conditions, are internal concentration or temperature gradients expected to affect the measured kinetics?

Problem Solution

For first order reactions, internal concentration gradients are expected to have a negligible effect upon the kinetics if the criterion given in equation (1) is satisfied.

$$\phi_s = \frac{r_p^2\left(-r\right)}{D_{eff}C} < 1 \tag{1}$$

The rate of reaction, r, and the effective diffusivity of thiophene are given in the problem statement. The particle radius, r_p, is one-half of the particle diameter given in the problem statement. The thiophene concentration can be found using the ideal gas law and the statement that gas contains 15% thiophene:

$$C_{thiophene} = \frac{n_{thiophene}}{V} = \frac{0.15 n_{total}}{V} = 0.15\frac{P}{RT} = 0.15\frac{30\text{ atm}}{\left(82.06\ \frac{\text{cm}^3\text{ atm}}{\text{mol K}}\right)\left(650\text{ K}\right)} \tag{2}$$

$C_{thiophene}$ = 8.44 x 10^{-5} mol cm^{-3} (3)

Substituting these quantities into criterion (1) gives

$$\frac{r_p^2\left(-r\right)}{D_{eff}C} < 1 \tag{4}$$

$$\frac{\left(0.2\ \text{cm}\right)^2\left(10^{-6}\ \frac{\text{mol}}{\text{cm}^3\ \text{s}}\right)}{\left(0.0015\ \frac{\text{cm}^2}{s}\right)\left(8.44\times10^{-5}\ \frac{\text{mol}}{\text{cm}^3}\right)} < 1 \tag{5}$$

0.32 < 1.0 (6)

Therefore, internal concentration gradients are not expected to influence the measured rates.

Internal temperature gradients are expected to have a negligible effect upon the kinetics if the criterion given in equation (7) is satisfied.

$$\frac{r_p^2\left(-r\right)\Delta H}{\lambda T} < 0.75\frac{RT}{E} \tag{7}$$

The new quantities appearing in this criterion are the heat of reaction, activation energy and particle thermal conductivity (given in the problem statement).

Evaluating criterion (7) gives

$$\frac{r_p^2\left(-r\right)\Delta H}{\lambda T} < 0.75\frac{RT}{E} \tag{8}$$

$$\frac{\left(25000\frac{\text{cal}}{\text{mol}}\right)\left(10^{-6}\frac{\text{mol}}{\text{s cm}^3}\right)\left(0.2\ \text{cm}\right)^2}{\left(0.001\frac{\text{cal}}{\text{cm s K}}\right)\left(650\ \text{K}\right)} < 0.75\frac{\left(8.3144\frac{\text{J}}{\text{mol K}}\right)\left(650\ \text{K}\right)}{\left(60000\frac{\text{J}}{\text{mol}}\right)} \tag{9}$$

0.0015 < 0.068

Therefore, internal temperature gradients should not influence the measured rates.