A First Course on Kinetics and Reaction Engineering

Example 12.2

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 external 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 external concentration or temperature gradients expected to affect the measured kinetics?

Problem Solution

You may need values for the heat and mass transfer coefficients to answer this question, in which case you may assume that the following correlation applies.

$$\varepsilon j_D = \frac{0.357}{N_{\text{Re}}^{0.359}} \tag{1}$$

with

$$j_D \equiv \frac{k_c \rho_{fluid}}{G} N_{Sc}^{2/3} \tag{2}$$

$$N_{Sc} = \frac{\mu_{fluid}}{\rho_{fluid} D_{im}} \tag{3}$$

$$N_{\text{Re}} = \frac{d_p G}{\mu_{fluid}} \tag{4}$$

You may also assume that

$$j_H = 1.51 j_D \tag{5}$$

with

$$j_H \equiv \frac{h}{\widehat{C}_{p,m} G} N_{\text{Pr}}^{2/3} \tag{6}$$

$$N_{\text{Pr}} = \frac{\widehat{C}_{p,m} \mu_{fluid}}{k_{fluid}} \tag{7}$$

Solution

External concentration gradients are expected to have a negligible effect upon the kinetics if the criterion given in equation (8) is satisfied.

$$\frac{(-r_i) r_p}{C_i k_c} < \frac{0.15}{n} \tag{8}$$

The rate of reaction, r, and the reaction order, n, 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:

$$C_{thiophene} = \frac{n_{thiophene}}{V} = \frac{0.15 n_{total}}{V} = 0.15 \frac{P}{RT} = 0.15 \frac{30 \text{ atm}}{\left(82.06 \dfrac{\text{cm}^3 \text{ atm}}{\text{mol K}}\right)(650 \text{ K})} \tag{9}$$

$$C_{thiophene} = 8.44 \times 10^{-5} \text{ mol cm}^{-3} \tag{10}$$

The mass transfer coefficient is found using the correlations given in the problem statement. First, the Reynolds number is computed.

$$N_{\text{Re}} = \frac{d_p G}{\mu_{fluid}} = \frac{(0.4 \text{ cm})(0.2 \text{ g s}^{-1} \text{ cm}^{-2})}{(0.00038 \text{ P})(1 \text{ g s}^{-1} \text{ cm}^{-1} \text{ P}^{-1})} \tag{11}$$

$$N_{Re} = 210 \tag{12}$$

Next j_D is found.

$$\varepsilon j_D = \frac{0.357}{N_{\text{Re}}^{0.359}} \tag{13}$$

$$j_D = \frac{0.357\varepsilon}{N_{\text{Re}}^{0.359}} = \frac{(0.357)(0.4)}{(210)^{0.359}} = 0.0209 \tag{14}$$

The Schmidt number will also be needed to find the mass transfer coefficient.

$$N_{Sc} = \frac{\mu_{fluid}}{\rho_{fluid} D_{im}} = \frac{0.00038 \text{ P}\left(1 \text{ g s}^{-1} \text{ cm}^{-1} \text{ P}^{-1}\right)}{\left(0.0168 \text{ g cm}^{-3}\right)\left(0.0052 \text{ cm}^2 \text{ s}^{-1}\right)} \tag{15}$$

$$N_{Sc} = 4.35 \tag{16}$$

Finally, the mass transfer coefficient can be found.

$$j_D \equiv \frac{k_c \rho_{fluid}}{G} N_{Sc}^{2/3} \tag{17}$$

$$k_c = \frac{j_D G}{\rho_{fluid} N_{Sc}^{2/3}} = \frac{(0.0209)\left(0.2 \text{ g s}^{-1} \text{ cm}^{-2}\right)}{\left(0.0168 \text{ g cm}^{-3}\right)(4.35)^{2/3}} = 0.0792 \text{ cm s}^{-1} \tag{18}$$

Substituting all these quantities into criterion (8) gives

$$\frac{(-r_i) r_p}{C_i k_c} < \frac{0.15}{n} \tag{19}$$

$$\frac{\left(10^{-6} \ \frac{\text{mol}}{\text{s cm}^3}\right)(0.2 \text{ cm})}{\left(8.44 \times 10^{-5} \ \frac{\text{mol}}{\text{cm}^3}\right)\left(0.0792 \frac{\text{cm}}{\text{s}}\right)} < \frac{0.15}{1} \tag{20}$$

$$0.03 < 0.15 \tag{21}$$

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

External temperature gradients are expected to have a negligible effect upon the kinetics if the criterion given in equation (22) is satisfied.

$$\frac{(-\Delta H)(-r_i) r_p}{hT} < 0.15 \frac{RT}{E} \tag{22}$$

The new quantities appearing in this criterion are the heat of reaction (given in the problem statement), the activation energy (also given in the problem statement) and the heat transfer coefficient. Having already calculated j_D, j_H can be calculated.

$$j_H = 1.51\, j_D = 1.51(0.0209) = 0.0316 \tag{23}$$

The Prandtl number will also be needed for the calculation of the heat transfer coefficient.

$$N_{\mathrm{Pr}} = \frac{\widehat{C}_{p,m}\mu_{fluid}}{k_{fluid}} \tag{24}$$

$$N_{\mathrm{Pr}} = \frac{\left(0.9\,\frac{\mathrm{cal}}{\mathrm{g\ K}}\right)\left(0.00038\ \mathrm{P}\right)\left(1\ \mathrm{g\ s^{-1}\ cm^{-1}\ P^{-1}}\right)}{\left(5.4\times10^{-4}\,\frac{\mathrm{cal}}{\mathrm{cm\ K\ s}}\right)} \tag{25}$$

N_{Pr} = 0.633 (26)

With these data, the heat transfer coefficient can be computed.

$$j_H \equiv \frac{h}{\widehat{C}_{p,m}G}N_{\mathrm{Pr}}^{2/3} \tag{27}$$

$$h = \frac{j_H\widehat{C}_{p,m}G}{N_{\mathrm{Pr}}^{2/3}} \tag{28}$$

$$h = \frac{\left(0.0316\right)\left(0.9\,\frac{\mathrm{cal}}{\mathrm{g\ K}}\right)\left(0.2\ \mathrm{g\ s^{-1}\ cm^{-2}}\right)}{\left(0.633\right)^{2/3}} \tag{29}$$

h = 0.00772 cal cm^{-2} s^{-1} K^{-1} (30)

Criterion (22) can now be evaluated.

$$\frac{\left(-\Delta H\right)\left(-r_i\right)r_p}{hT} < 0.15\frac{RT}{E} \tag{31}$$

$$\frac{\left(25000\,\frac{\mathrm{cal}}{\mathrm{mol}}\right)\left(10^{-6}\,\frac{\mathrm{mol}}{\mathrm{s\ cm^3}}\right)\left(0.2\ \mathrm{cm}\right)_p}{\left(0.00772\,\frac{\mathrm{cal}}{\mathrm{cm^2\ s\ K}}\right)\left(650\ \mathrm{K}\right)} < 0.15\frac{\left(8.3144\,\frac{\mathrm{J}}{\mathrm{mol\ K}}\right)\left(650\ \mathrm{K}\right)}{\left(60000\,\frac{\mathrm{J}}{\mathrm{mol}}\right)} \tag{32}$$

$9.96 \times 10^{-4} < 1.35 \times 10^{-2}$ (33)

Therefore, external temperature gradients are not expected to influence the measured rates.