Homework 6:

5. The irreversible, first-order reaction of gaseous A to B occurs in spherical catalyst pellets with a radius of 2 mm. For this problem, the molecular diffusivity of A is 1.2×10^{-1} cm^2 s^{-1} and the Knudsen diffusivity is 9×10^{-3} cm^2 s^{-1}. The intrinsic first-order rate constant determined from detailed laboratory measurements was found to be 5.0 s^{-1}. The concentration of A in the surrounding gas is 0.01 mol L^{-1}. Assume the porosity and the tortuosity of the pellets are 0.5 and 4, respectively.
   (a) Determine the Thiele modulus for the catalyst pellets.
   (b) Find a value for the internal effectiveness factor.
   (c) For an external mass-transfer coefficient of 32 s^{-1} (based on the external area of the pellets), determine the concentration of A at the surface of the catalyst pellets.
   (d) Find a value for the overall effectiveness factor.

Exercise 5:

part a)

For a first order reaction in a spherical catalyst pellet the Thiele modulus is (Equation (6.3.29)) the following:

$$\phi = R_p \sqrt{\frac{k}{D_{TA}^e}} \qquad (1)$$

Therefore, in order to find the Thiele modulus, the effective diffusivity must be known.

The Bosanquet equation (Equation (6.3.2)) can be used to find D_{TA} since the Knudsen and molecular diffusion coefficients are known:

$$\frac{1}{D_{TA}} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}} \qquad (2)$$

$$D_{TA} = 8.37 \times 10^{-3} \ \tfrac{cm^2}{s}$$

The effective diffusivity is then calculated with the following equation:

$$D_{TA}^{e} = \frac{\bar{\varepsilon}_P D_{TA}}{\bar{\tau}} \qquad (3)$$

Therefore, $D_{TA}^{e} = \dfrac{(0.5)(8.37 \times 10^{-3})}{4} = 1.05 \times 10^{-3} \ \tfrac{\text{cm}^2}{\text{s}}$

After substituting the effective diffusivity into equation (1),

$$\phi = 2 \times 10^{-3} \,\text{m} \sqrt{\frac{5.0 s^{-1}}{(1.05 \times 10^{-3} \ \frac{\text{cm}^2}{\text{s}})(\frac{1^2\,\text{m}^2}{100^2\,\text{cm}^2})}} = 13.8$$

part b)

For a first-order reaction in a spherical catalyst pellet (Equation 6.3.39), the effectiveness factor is

$$\eta = \frac{3}{\phi}\left[\frac{1}{\tanh\phi} - \frac{1}{\phi}\right] \qquad (4)$$

Since the Thiele modulus was found in part (a), the effectiveness factor is found from equation (4).

$$\eta = 0.202$$

part c)

At steady state, the rate of mass transfer = rate of reaction. Therefore,

$$\overline{k_c}(C_{AB} - C_{AS}) = \eta k C_{AS} \tag{5}$$

After solving for C_{AS} and substituting for known values,

$$C_{AS} = \frac{\overline{k_c} C_{AB}}{\overline{k_c} + \eta k} = \frac{(32\text{s}^{-1})(0.01\,\frac{\text{mol}}{\text{L}})}{32\text{s}^{-1} + (0.202)(5\text{s}^{-1})} = 0.0097\,\frac{\text{mol}}{\text{L}}$$

part d)

The overall effectiveness factor, η_o, is the following:

$$\eta_o = \frac{\text{observed rate}}{\text{max rate}} = \frac{\eta k C_{AS}}{k C_{AB}} = \frac{(0.202)(0.0097\,\frac{mol}{L})}{0.01\,\frac{mol}{L}} = 0.196$$

7. The importance of diffusion in catalyst pellets can often be determined by measuring the effect of pellet size on the observed reaction rate. In this exercise, consider an irreversible first-order reaction occurring in catalyst pellets where the surface concentration of reactant A is $C_{AS} = 0.15$ M.

Data:

Diameter of sphere (cm)	0.2	0.06	0.02	0.006
r_{obs} (mol/h/cm^3)	0.25	0.80	1.8	2.5

(a) Calculate the intrinsic rate constant and the effective diffusivity.

(b) Estimate the effectiveness factor and the anticipated rate of reaction (r_{obs}) for a finite cylindrical catalyst pellet of dimensions 0.6 cm × 0.6 cm (diameter = length).

part a)

For a first-order reaction in a spherical catalyst pellet, the Thiele modulus is the following:

$$\phi = R_p \sqrt{\frac{k}{D_{TA}^e}} \quad (1)$$

In addition, the observed rate can be written in terms of the effectiveness factor:

$$r_{obs} = \eta k C_{AS} \quad (3)$$

Again, the ratio of the rate of reaction at two different pellet sizes can be determined, noting that the surface concentration and the intrinsic rate constant, k, do not change.

$$\frac{r_{obs,1}}{r_{obs,2}} = \frac{\eta_1}{\eta_2} \quad (4)$$

A comparison of two large spheres yields,

$$\frac{\phi_1}{\phi_2} = \frac{0.03\text{ cm}}{0.1\text{ cm}} = 0.3 \quad (5)$$

$$\frac{\eta_1}{\eta_2} = \frac{0.8}{0.25} = 3.2 \quad (6)$$

For strong diffusional limitations, the effectiveness factor is $1/\phi$. Notice that the ratio of the two Thiele moduli in equation (5) is approximately 1/0.3. Therefore we can estimate that the large particles are in the strong diffusion control regime.

Now for the smallest two pellets,

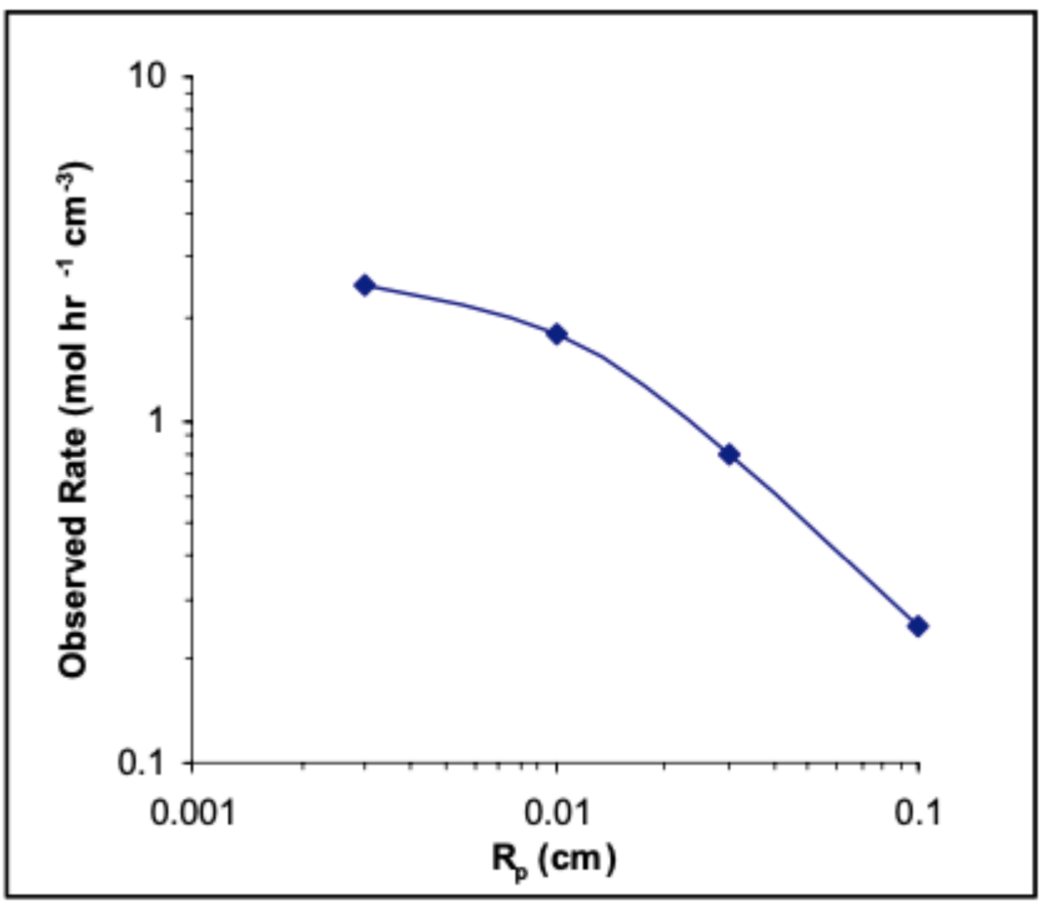
$$\frac{\phi_1}{\phi_2} = \frac{0.003\,\text{cm}}{0.01\,\text{cm}} = 0.3 \qquad (7)$$

while

$$\frac{\eta_1}{\eta_2} = \frac{2.5}{1.8} = 1.39 \qquad (8)$$

Therefore we can estimate that the small pellets are not in the strong diffusion control regime.

From a plot of the observe rate vs. the radius of the particle on a log scale, we can estimate the Thiele modulus.



After all of this exposition, the easiest way to get an answer is to see that for the smallest particle φ is small, probably close to 0.1 and thus η= 1.

This gives:

k= 4.6/s and D_{TA} = 4.2 X 10^{-3} cm ^{2}/s.

For a cylinder, the characteristic length parameter is the following (equation 6.3.48):

$$L_p = \frac{V_p}{S_p} = \frac{R_p}{\frac{R_p}{x_p} + 2} \qquad (1)$$

where x_p is half of the length of the cylinder.

Therefore, in this case $L_p = 0.1$ cm.

The Thiele modulus defined in terms of the length parameter is

$$\phi_o = L_p \sqrt{\frac{k}{D^e_{TA}}} \qquad (2)$$

and the effectiveness factor is

$$\eta = \frac{\tanh(\phi_o)}{\phi_o} \qquad (3)$$

Therefore, $\phi_o = 10$ and $\eta = 0.1$

The observed rate can then be calculated from equation (3).

$r_{obs} = 0.00069$ mol cm^{-3} s^{-1}