ChE-403 Problem Set 3.4

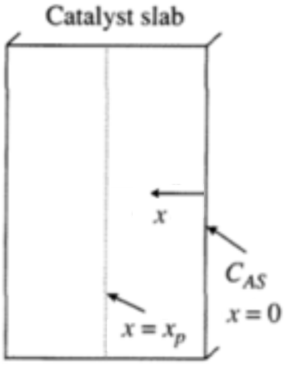
Week 13

Problem 1

Consider a reaction with kinetics:

$r = k$ (zero order)

Occurring in catalyst pellets in the form of slabs:



Assume that we are at low conversion and that there is no external mass transfer limitations so that $C_{A,0} = C_{AS}$.

Equimolar counter-diffusion can also be assumed.

Write the internal mass transfer balance for this reaction, determine the Thiele modulus after putting it in dimensionless form and propose appropriate boundary conditions.

Note: because it's a zero order reaction, you have to assume that in certain conditions, the concentration will be zero before the middle of the particle. You can assume that this occurs at χ_0 where we will have a no flux conditions $\left(\left. \frac{dC_{A'}}{d\chi} \right|_{\chi=\chi_0} = 0 \right)$ instead of at the center. With the two boundary conditions and the property $C_A'(\chi_0) = 0$ you can solve for χ_0 and the integration constants.

Solution:

1-D mass balance:

Acc. = In – Out + Source

$$0 = A\,\dot{n}_A - A\,(\dot{n}_A + d\dot{n}_A) - r\,A\,dx$$

$$\frac{d\dot{n}_A}{dx} = -r$$

$$\frac{d}{dx}\left(-D_{TA}^{e}\frac{dC_A}{dx}\right) = -D_{TA}^{e}\frac{d^2C_A}{dx^2} = -k$$

$$\frac{d^2C_A}{dx^2} = \frac{k}{D_{TA}^{e}}$$

$$C_A' = \frac{C_A}{C_{A,0}}$$

$$\chi = \frac{x}{x_p}$$

$$\frac{d^2 C_A{}'}{d\chi^2} = \frac{x_p^2 k}{D_{TA}^e C_{A,0}} = \phi^2 \quad where \quad \phi = x_p \sqrt{\frac{k}{D_{TA}^e C_{A,0}}}$$

Integrating twice, we get:

$$C_A' = \frac{\phi^2 \chi^2}{2} + cst1\chi + cst2$$

The boundary conditions are:

$$C_A' = 1 \quad @ \ \chi = 0$$

and

$$\frac{dC_A{}'}{d\chi} = 0 \quad @ \ \chi = \chi_0$$

Along with

$$C_A' = 0 \quad @ \ \chi = \chi_0$$

$$1 = cst2$$

$$\phi^2 \chi_0 + cst1 = 0 \rightarrow cst1 = -\phi^2 \chi_0$$

$$C_A' = \frac{\phi^2 \chi^2}{2} - \phi^2 \chi_0 \chi + 1$$

$$C_A' = 0 = \frac{\phi^2 \chi_0^2}{2} - \phi^2 \chi_0^2 + 1 = 1 - \frac{\phi^2 \chi_0^2}{2} \rightarrow \chi_0 = \frac{\sqrt{2}}{\phi}$$

$$C_A' = \frac{\phi^2 \chi^2}{2} - \sqrt{2}\phi\chi + 1$$

Problem 2

Solve the problem of combined internal and external transport we saw in class for a slab for the case where we have a first order RX and an isothermal slab.

The general form of the equation was:

$$\frac{d^2\overline{C_A'}}{d\chi^2} = \phi^2 \exp\left[-\gamma\left(\frac{1}{\overline{T'}} - 1\right)\right]\overline{C_A'}$$

$$\frac{d^2\overline{T'}}{d\chi^2} = -\phi^2\,\beta\,\exp\left[-\gamma\left(\frac{1}{\overline{T'}} - 1\right)\right]\overline{C_A'}$$

With boundary conditions:

$$\left.\frac{d\overline{C_A'}}{d\chi}\right|_{\chi=1} = Bi_m\left[1 - \overline{C_A'}\right] \qquad @\chi = 1$$

$$\left.\frac{d\overline{T'}}{d\chi}\right|_{\chi=1} = Bi_h\left[1 - \overline{T'}\right] \qquad @\chi = 1$$

$$\frac{d\overline{C_A'}}{d\chi} = \frac{d\overline{T'}}{d\chi} = 0 \qquad @\ \ \chi = 0\ \ No\,flux\,through\,the\,center$$

Solution:

Because it's isothermal, we can ignore the change in temperature, therefore, the equation reduces to:

$$\frac{d^2\overline{C_A'}}{d\chi^2} = \phi^2\overline{C_A'}$$

With boundary conditions:

$$\left.\frac{d\overline{C_A'}}{d\chi}\right|_{\chi=1} = Bi_m\left[1 - \overline{C_A'}\right] \qquad @\chi = 1$$

$$\frac{d\overline{C_A'}}{d\chi} = 0 \qquad @\ \ \chi = 0$$

As we have seen before, the general solution to such an equation is:

$$\overline{C_A'} = cst1\exp(\phi\chi) + cst2\exp(-\phi\chi)$$

Let’s apply the boundary conditions:

$$\frac{d\overline{C_A'}}{d\chi} = cst1\,\phi\exp(\phi 0) - cst2\,\phi\exp(-\phi 0) = 0$$

$$\rightarrow cst1 = cst2$$

$$\frac{d\overline{C_A'}}{d\chi} = cst1\,\phi\exp(\phi) - cst1\,\phi\exp(-\phi) = Bi_m\left[1 - \overline{C_A'}(1)\right]$$
$$= Bi_m[1 - cst1\exp(\phi) - cst1\exp(-\phi)]$$

$$cst1\,[\phi(\exp(\phi) - \exp(-\phi)) + Bi_m(\exp(\phi) + \exp(-\phi))] = Bi_m$$

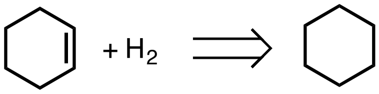
$$cst1 = \frac{Bi_m}{2[\phi\sinh(\phi) + Bi_m\cosh(\phi)]}$$

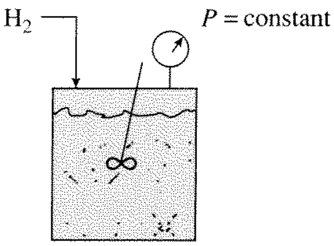
$$\overline{C_A'} = \frac{Bi_m}{2[\phi\sinh(\phi) + Bi_m\cosh(\phi)]}[\exp(\phi\chi) + \exp(-\phi\chi)]$$
$$= \frac{Bi_m}{2[\phi\sinh(\phi) + Bi_m\cosh(\phi)]}2\cosh(\phi\chi)$$

$$\overline{C_A'} = \frac{Bi_m\;\cosh(\phi\chi)}{\phi\sinh(\phi) + Bi_m\cosh(\phi)}$$

Problem 3

Consider the liquid phase hydrogenation of cyclohexene to cyclohexane (in an inert solvent) that happens in the presence of a solid catalyst dispersed in the liquid. The reaction is semi-batch in hydrogen (i.e. hydrogen pressure is kept constant during the entire reaction).





These are the data we measure for this reaction. Can you interpret each of the figures?

Figure 1: We observe a linear relationship between the time and the cyclohexene concentration given below. This relationship is also present for the data collected in Figures 2 and 3.

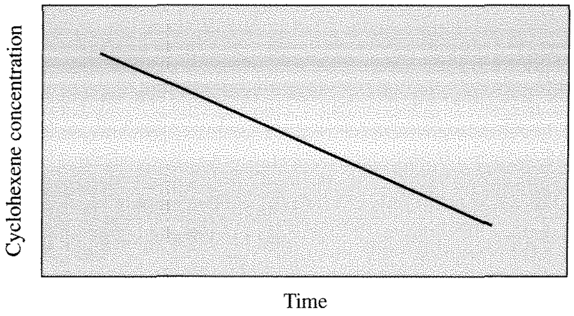


Figure 2: Effect of the catalyst weight (total catalyst added to the solution at a single metal loading) on the reaction rate.

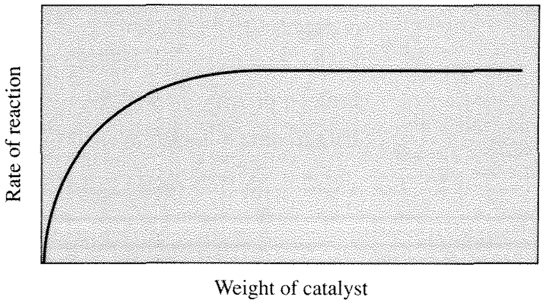
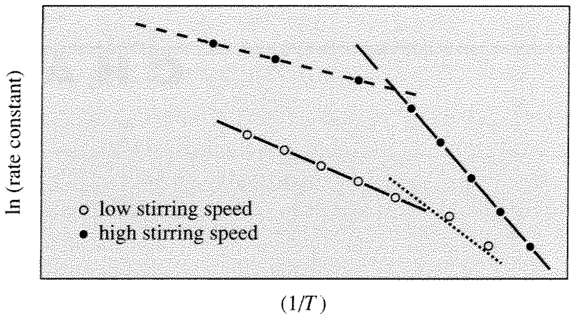


Figure 3: Evaluation of temperature effects and stirring speed on the reaction rate.



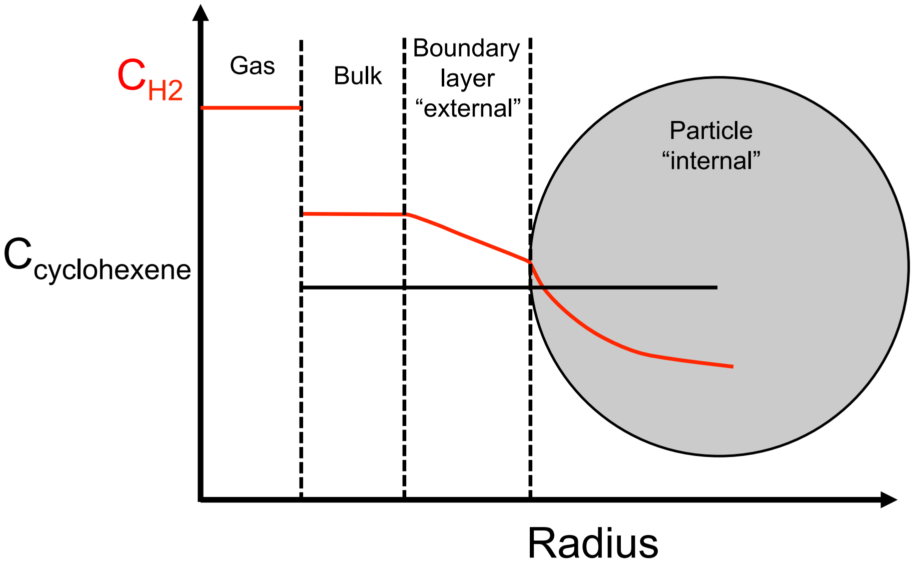
Solution:

In Figure 1 we observe a linear relationship between time and the concentration of cyclohexene. This means that the reaction is zero order in cyclohexene. Of course this is not physically possible. In all likelihood the rate is dependent on cyclohexene but only at more advanced times. At these conversions, it is likely that we have the following rate expression:

$$r \sim \frac{k C_{cyclo} C_{H_2}}{1 + K C_{cyclo} + \cdots} \approx \frac{k}{K} C_{H_2}$$

Which indicates that cyclohexene is saturating the surface of the catalyst.

Therefore, there can be no mass transfer dependence on cyclohexene, only on H_2. We can draw the system as:



In Figure 2, we see that at low loadings, the rate is proportional to catalyst mass, which is consistent with intrinsic kinetics (no mass transfer). As the dependence slows, it is possible mass transfer plays a role but once the rate stays constant with increased catalyst mass, it cannot be dependent on either external or internal mass transfer. In this case, the rate must be dependent on the mass transfer of H_2 between the gas and the liquid, which is independent of the amount of catalyst that is added.

Figure 3 shows that at low stirring speed, there are mass transfer limitations at all temperatures. The fact that we always see a smaller slope than at high stirring speed (even at low T°) indicates this. At high stirring speed, there is definitely mass transfer limitations at high T° but we could be measuring the actual E_a at low T°.