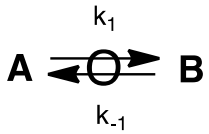
ChE-403 Problem Set 3.3

Week 12

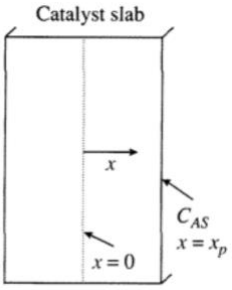
Problem 1

Consider the following first order reversible reaction in a continuous reactor.



With $K = \frac{k_1}{k_{-1}}$ and $C_A(initial) = C_{A,0}$ and $C_B(initial) = 0$

The catalyst pellets are the form of slabs:



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

a) Write the internal mass transfer balance for this reaction, determine the Thiele modulus after making putting it in dimensionless form and propose appropriate boundary conditions.
*Hint: Here you want to write the rate as the simplest possible way in the form of r=cst*f(C_A). Choose C_A' according to the form of f(C_A).*

b) Solve this differential equation and give an expression for C_A.

Solution:

a)
1-D mass balance:
Acc. = In – Out + Source

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

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

$$\frac{d}{dx}\left(-D_{TA}^{e}\frac{dC_A}{dx}\right) = -D_{TA}^{e}\frac{d^2C_A}{dx^2} = -r = -k_1C_A + k_{-1}C_B = -k_1C_A + k_{-1}(C_{A,0} - C_A)$$

$$= -k_1\left(1 + \frac{k_{-1}}{k_1}\right)C_A + k_{-1}C_{A,0} = -k_1\left[\frac{K+1}{K}C_A - \frac{1}{K}C_{A,0}\right]$$

$$= -k_1\left[\frac{K+1}{K}\right]\left(C_A - \frac{C_{A,0}}{K+1}\right) = cst\ f(C_A)$$

$$D_{TA}^{e}\frac{d^2C_A}{dx^2}=k_1\left[\frac{K+1}{K}\right]\left(C_A-\frac{C_{A,0}}{K+1}\right)$$

Let's use:

$$C_A'=\frac{C_A-\frac{C_{A,0}}{K+1}}{C_{A,0}}$$

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

$$\frac{C_{A,0}D_{TA}^{e}}{x_p^2}\frac{d^2C_A{}'}{d\chi^2}=k_1\left[\frac{K+1}{K}\right]C_{A,0}C_A'$$

Rearranging, we have:

$$\frac{d^2C_A{}'}{d\chi^2}=x_p^2\,\frac{k_1\left[\frac{K+1}{K}\right]}{D_{TA}^{e}}C_A'=\phi^2C_A'$$

$$\phi=x_p\sqrt{\frac{k_1\left[\frac{K+1}{K}\right]}{D_{TA}^{e}}}$$

The boundary conditions are:

$$C_A'=1-\frac{1}{K+1}\quad @\chi=1$$

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

b) The general solution to this type of equation is:

$$C_A{}'=cst1\;e^{+\phi\chi}+cst2\;e^{-\phi\chi}$$

$$@\,\chi=0\qquad \frac{dC_A{}'}{d\chi}=\phi cst1\;e^{\phi0}-\phi cst2\;e^{-\phi0}=0\qquad\rightarrow cst1=cst2$$

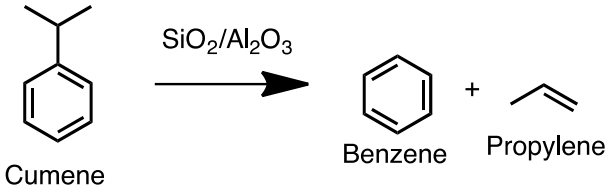
$$@\,\chi=1\qquad C_A'=cst1\;e^{\phi}+cst1\;e^{-\phi}=1-\frac{1}{K+1}\qquad\rightarrow cst1=\frac{\left(1-\frac{1}{K+1}\right)}{e^{\phi}+\;e^{-\phi}}$$

$$C_A'=\frac{\left(1-\frac{1}{K+1}\right)}{e^{\phi}+\;e^{-\phi}}\left(e^{+\phi\chi}+\;e^{-\phi\chi}\right)=\left(1-\frac{1}{K+1}\right)\frac{\cosh(\phi\chi)}{\cosh(\phi)}$$

$$C_A=C_{A,0}\left[C_A'+\frac{1}{K+1}\right]=C_{A,0}\left[\left(1-\frac{1}{K+1}\right)\frac{\cosh(\phi\chi)}{\cosh(\phi)}+\frac{1}{K+1}\right]$$

Problem 2

Cumene cracking on silica-alumina is a pseudo-first order reaction:



The observed first order rate constant was measured to be 0.80 $cm^3/(s\ g_{cat})$. Is this value the true rate constant (or close to it) or is there significant effects of pore diffusion?

We have determined that external mass transfer can be ignored.

We have this additional data:

$R_p = 0.25\ cm$

$\rho = 1.2\ g_{cat}\ cm^{-3}$

$D_{TA}^e = 1\ 10^{-3} cm^2 s^{-1}$

Solution:

For spheres, there are two options. We can use this relation:

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

with: $\phi = R_p\sqrt{\frac{k}{D_{TA}^e}}$

Or the relations based on generalized geometries:

$$\eta = \frac{\tanh(\phi_0)}{\phi_0}$$

with:

$$\phi_0 = L_p\sqrt{\frac{k}{D_{TA}^e}}$$

and: $L_p = \frac{R_p}{3}$ for a sphere

Let's use the latter (it's simpler):

$$\eta = \frac{\tanh(\phi_0)}{\phi_0} \; and \; \phi_0 = \frac{R_p}{3}\sqrt{\frac{k}{D_{TA}^e}}$$

Here we are going to use everything we know about the effectiveness factor to calculate the true *k* and then calculate the effectiveness factor with this value.

$$\phi_0 = \frac{R_p}{3}\sqrt{\frac{k}{D_{TA}^e}} = \frac{0.25}{3}\sqrt{\frac{k}{1\;10^{-3}}} = 2.6\sqrt{k}$$

The reaction is pseudo-1st order, therefore:

$$\eta = \frac{observed\; rate}{rate\; in\; the\; absence\; of\; diffusion} = \frac{k_{obs}C_{AS}}{k\;C_{AS}} = \frac{k_{obs}}{k}$$

Note that the observed rate was given in $cm^3/(s\; g_{cat})$ which is different than the k_{obs} defined in η or the *k* defined in ϕ_0. These rate constants are defined on a volume basis (units: s^{-1}) and not corrected based on the amount of catalyst, therefore to calculate k_{obs}, we use:

$$\eta = \frac{k_{obs}}{k} = \frac{0.8\text{cm}^3\text{s}^{-1}g_{cat}^{-1} \times 1.2\; g_{cat}\; cm^{-3}}{k} = \frac{0.96}{k}$$

$$\eta = \frac{\tanh\left(2.635\sqrt{k}\;\right)}{2.635\sqrt{k}} = \frac{0.96}{k}$$

Solving for *k*, we get: $k = 6.4\; s^{-1}$

$$\eta = \frac{\tanh\left(2.635\sqrt{k}\;\right)}{2.635\sqrt{k}} = \frac{0.96}{k} = 0.15$$

There are significant diffusion limitations!

Just to demonstrate that we get similar answers, we can also use the other method:

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

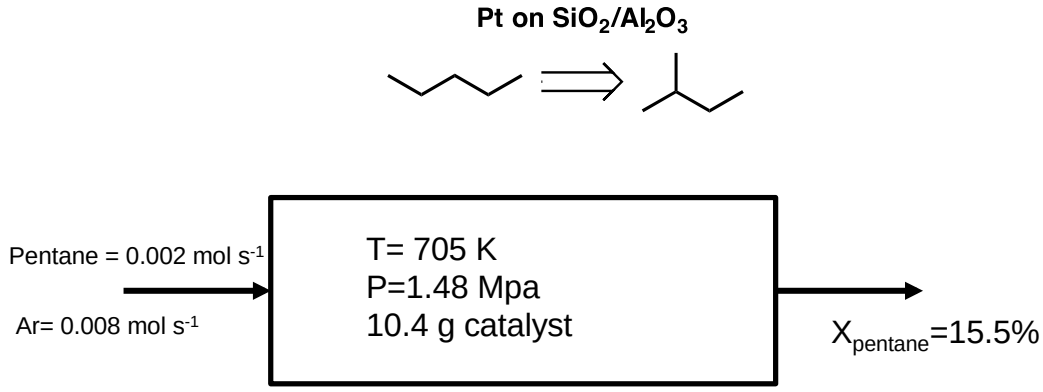
with: $\phi = R_p\sqrt{\frac{k}{D_{TA}^e}} = 0.25\sqrt{\frac{k}{1\;10^{-3}}} = 7.905\sqrt{k}$

$$\eta = \frac{3}{7.905\sqrt{k}}\left[\frac{1}{\tanh\left(7.905\sqrt{k}\right)} - \frac{1}{7.905\sqrt{k}}\right] = \frac{0.96}{k}$$

Leading to $k = 7.1\; s^{-1}$ and $\eta = 0.14$ which is a vey similar result!

Problem 3

The catalytic cracking of pentane to isopentane was accomplished in an isothermal differential continuous flow reactor (which acts like a CSTR) containing a supported platinum catalyst on SiO_2/Al_2O_3:



The reaction has an effectiveness factor of 0.42.

Assuming the reaction is first-order in pentane and the diffusivity is primarily of the Knudsen type, estimate the tortuosity $\bar{\tau}$ of the perfectly spherical catalyst pellets that have a diameter of 3.2 mm. You can assume that the gases act ideally and that the catalyst has uniform cylindrical pores. You can also assume that the pentane concentration in the reactor is an average of the incoming and outgoing concentration and that external mass transfer can be neglected.

Additional data:

Pore volume of the catalyst: 0.48 $cm^3\ g^{-1}$
Surface area of the catalyst: 240 $m^2\ g^{-1}$
Pellet density: 1.332 $g\ cm^{-3}$
Pellet porosity: 0.59

Solution:

Let's first find the average mole fraction of A (pentane) in the reactor:

$$x_A = \frac{0.2\left(1+(1-0.155)\right)}{2} = 0.1845$$

In an ideal gas, the concentration is simply:

$$C_A = \frac{P_A}{RT} = \frac{x_A P}{RT} = \frac{0.1845\ 1.48\ 10^6 Pa}{8.314\ kg\ m^2\ mol^{-1}\ K^{-1} s^{-2}\ 705K} = 46.6 \frac{mol}{m^3} = 4.66\ 10^{-5} \frac{mol}{cm^3}$$

We can calculate the observed rate based on the conversion (and normalize it based on the catalyst quantity):

$$r_{obs} = \frac{0.002\ mol\ s^{-1} * 0.155}{10.4\ g_{cat}} = 2.98\ 10^{-5}\ mol\ s^{-1} g_{cat}^{-1}$$

We can use this to calculate a *k*:

$$\eta = \frac{\text{Apparent rate}}{Rate\ without\ diffusion} = \frac{k_{obs} C_A}{k C_A} = \frac{2.98\ 10^{-5}\ mol\ s^{-1} g_{cat}^{-1}}{k\ 4.66\ 10^{-5} \frac{mol}{cm^3}} = 0.42$$

$$\rightarrow k = 1.52\ cm^3\ g_{cat}^{-1}\ s^{-1}$$

We can also use η to calculate the thiele modulus:

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

Using a solver, we get that $\phi = 5.94$

We can use ϕ and *k* to calculate D_{TA}^e. However, *k* is per gram of catalyst, but in the Thiele Modulus, the rate is defined as per pellet volume. Therefore, we have to multiply by the density of the pellet to get *k* in units per volume of pellet:

$$k = 1.52\ cm^3\ g_{cat}^{-1}\ s^{-1}\ \ 1.332 g_{cat}\ cm^{-3} = 2.02\ s^{-1}$$

$$\phi^2 = \frac{R_p^2 k}{D_{TA}^e} \rightarrow D_{TA}^e = \frac{R_p^2 k}{\phi^2} = \frac{(0.32/2)^2 cm^2\ 2.02\ s^{-1}}{5.94^2} = 1.47\ 10^{-3}\ cm^2 s^{-1}$$

Here, diffusion is mostly due to Knudsen diffusion, therefore: $D_{TA}^e \approx D_{KA}^e$

If we have uniform cylindrical pores, it's as if we had 1 long pore of volume $\pi R_{pore}^2 h$ and of surface $2\pi R_{pore} h$. Since we know the surface and the volume, we can calculate R_{pore}:

$$\frac{Volume}{Surface} = \frac{0.48\ \text{cm}^3\ \text{g}_{\text{cat}}^{-1}}{240\ 10^4\ cm^2\ \text{g}_{\text{cat}}^{-1}} = \frac{R_{pore}}{2} \rightarrow R_{pore} = 4\ 10^{-7}\ cm = 4\ nm$$

$$D_{KA} = 9.7\ 10^3\ R_{pore}\left(\frac{T}{M_A}\right)^{1/2} = 9.7\ 10^3\ 4\ 10^{-7}\ cm\left(\frac{705}{72.15}\right)^{1/2} = 0.0121\ cm^2 s^{-1}$$

$$D_{KA}^e = \frac{\bar{\varepsilon}_p}{\bar{\tau}} D_{KA} \rightarrow \bar{\tau} = \frac{\bar{\varepsilon}_p}{D_{KA}^e} D_{KA} = 4.86$$