ChE-403 Problem Set 3.1

Week 9

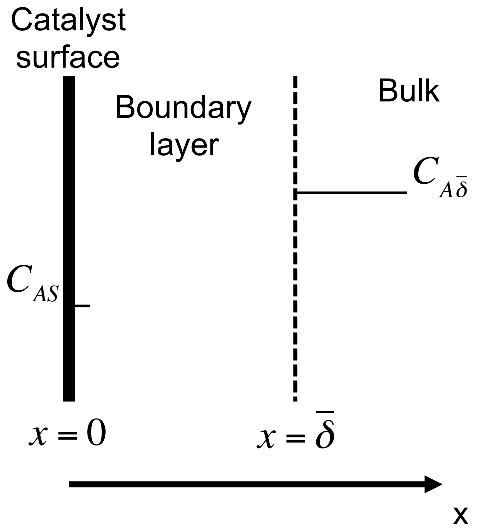
Problem 1

Consider Ficks Law in 1 dimension:

$$\dot{n}_A = -D_{A,B}\frac{d\mathrm{C_A}}{dx}$$

If this describes diffusion in a boundary layer then there is no accumulation term. There is no source term either as the reaction only occurs at the catalyst surface. Therefore, the flux must be constant ($\dot{n}_A = cst$). With that information, can you solve this equation with the following boundary conditions?

with:
$\mathrm{C_A} = C_{AS}$ @ $x = 0$
$\mathrm{C_A} = C_{A\bar{\delta}}$ @ $x = \bar{\delta}$



Calculate $\mathrm{C_A}$ and $\dot{n}_A$.

Solution:

If $\dot{n}_A = cst$. Then,

$$\frac{d\dot{n}_A}{dx} = 0 = -D_{A,B}\frac{d^2\mathrm{C_A}}{dx^2}$$

or

$$\frac{d^2\mathrm{C_A}}{dx^2} = 0$$

Let’s integrate:

$$\frac{dC_A}{dx} = cst2$$

Let’s integrate again:

$$C_A = cst1 + cst2\ x$$

with:
$C_A = C_{AS}$ @ $x = 0$

$$C_A = cst1 = C_{AS} \text{ @ } x = 0$$

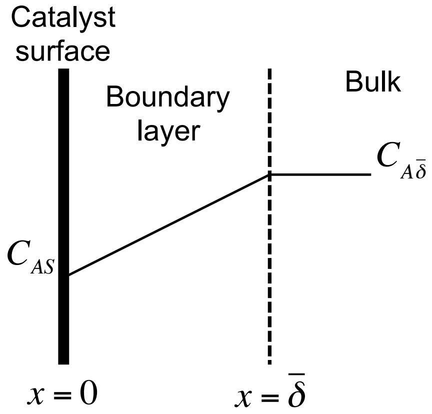
with:
$C_A = C_{A\bar{\delta}}$ @ $x = \bar{\delta}$

$$C_A = C_{AS} + cst2\ \bar{\delta}\ = C_{A\bar{\delta}}$$

$$\rightarrow cst2 = \frac{C_{A\bar{\delta}} - C_{AS}}{\bar{\delta}}$$

$$C_A = C_{AS} + \frac{C_{A\bar{\delta}} - C_{AS}}{\bar{\delta}} x$$

$\dot{n}_A = -D_{A,B}\frac{dC_A}{dx} = -\frac{D_{A,B}}{\bar{\delta}}(C_{A\bar{\delta}} - C_{AS})$ This is a linear function:



Problem 2

Let's look at the combustion of a coal particle in a controlled burner. The reaction is so fast that all the oxygen is consumed at the surface of the coal. This is an entirely external mass transfer limited process. The rate is given by:

$$r = k_s C_s = \bar{k} \exp\left(-\frac{E}{R_g T_s}\right) C_s$$

With:

$\bar{k} = 10^6\ m\ min^{-1}$

$E = 100\ kJ/mol$

T_s: Surface temperature

C_s: Surface concentration of O_2

$C_{bulk} = 2\ mol/m^3$

$T_B = 500°C$

$\Delta H_r = -150 \frac{kJ}{mol}$

$h_t = 0.5\ kJ\ min^{-1} K^{-1} m^{-2}$

$\bar{k}_c = 0.5\ m\ min^{-1}$

a) What is the maximum T° difference between the bulk gas and the particle? What is the observed reaction rate under those conditions?

b) What is the *actual* surface reaction temperature and concentration and therefore the *actual* reaction rate? (you will need a solver for this, but if you can get to the point where you need the solver, that's really the point of the problem).

Solution:

a) The maximum T° difference is given by the formula for $\Delta T_{BL,MAX}$ given in class:

$$\Delta T_{BL,MAX} = \frac{\bar{k}_c C_{bulk}\ (\Delta H_r)}{h_t} = \frac{0.5\ m\ min^{-1}\ 2\ mol/m^3\ \left(-150 \frac{kJ}{mol}\right)}{0.5\ kJ\ min^{-1} K^{-1} m^{-2}} = -300K$$

$\Delta T_{BL,MAX}$ occurs when the reaction rate is so fast that C_s is effectively zero and the rate is only given by mass transfer:

$$r_{obs} = \bar{k}_c (C_{bulk} - C_S) = \bar{k}_c C_{bulk} = 0.5\ m\ min^{-1} 2 \frac{mol}{m^3} = 1 \frac{mol}{\min m^2}$$

b) Here both the reaction and mass transfer control the reaction and therefore must be equal in a continuous process. Therefore, we have:

$$r_{surface} = k_s C_S = \bar{k}_c (C_{bulk} - C_S)$$

$$C_S = \frac{\bar{k}_c C_{bulk}}{k_s + \bar{k}_c} = \frac{\bar{k}_c C_{bulk}}{\bar{k}\,\exp\left(-\frac{E}{R_g T_s}\right) + \bar{k}_c}$$

$$= \frac{0.5\, m\, min^{-1}\; 2\, mol/m^3}{100\, kJ/mol\, \exp\left(-\frac{100\, kJ/mol}{8.315\; 10^{-3}\, \frac{kJ}{mol\, K}\, T_s}\right) + 0.5\, m/min}$$

At this point there are two unknown values : C_S and T_S. We need one more equation. We can use:

$$r_{obs}\, (\Delta H_r) = \dot{q} = h_t(T_B - T_S)$$

Where $r_{obs} = \bar{k}_c(C_{bulk} - C_S)$

Therefore, we have: $\bar{k}_c(C_{bulk} - C_S)(\Delta H_r) = h_t(T_B - T_S)$

$$0.5\, m\, min^{-1}\, \left(2\frac{mol}{m^3} - C_S\right)\left(-150\frac{kJ}{mol}\right) = 0.5 kJ\, min^{-1} K^{-1} m^{-2} (773\, K - T_S)$$

$$C_S = 12.3 - 6.67\; 10^{-3} T_s$$

$$12.3 - 6.67\; 10^{-3} T_s = \frac{1}{100\, \exp\left(-\frac{1}{8.315\; 10^{-5} T_S}\right) + 0.5}$$

Solving for T_s:

$$T_s = 1061$$

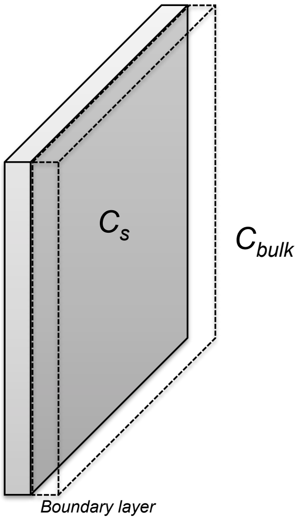
$$C_S = 0.081\, mol\, m^{-3}$$

$$r_{obs} = \bar{k}_c(C_{bulk} - C_S) = 0.96\, mol\, m^{-2} min^{-1}$$

This is quite close to what we had before. Therefore, it is mostly mass transfer that is controlling the reaction and C_s is close to zero.

Problem 3

A second order irreversible reaction has a surface rate constant of $1.8\ 10^{-4} m^4\, mol^{-1} s^{-1}$ and takes place on the surface of a catalyst that can be considered to be a 1 dimensional non-porous slab:



We assume the reaction takes place at steady state and we have the following parameters:

$k = 1.8\ 10^{-4} m^4\, mol^{-1} s^{-1}$
$\bar{k}_c = 0.2\ cm\, s^{-1}$
$C_{bulk} = 0.1\ mol/L$

What is the observed rate at these conditions?
How does it compare to the maximum observed rate?

A $C_{bulk} = 0.1\ mol/L$ is actually the saturation concentration. Imagine you were to prepare a series of dilutions up to a C_{bulk} of 0.05 mol/L and measure the observed rate. What would a plot of this look like? What is the danger for such an experiment if you did not know anything about the reaction you were studying?

Solution:

$$r_{obs} = kC_S^2 = \bar{k}_c(C_{bulk} - C_S)$$

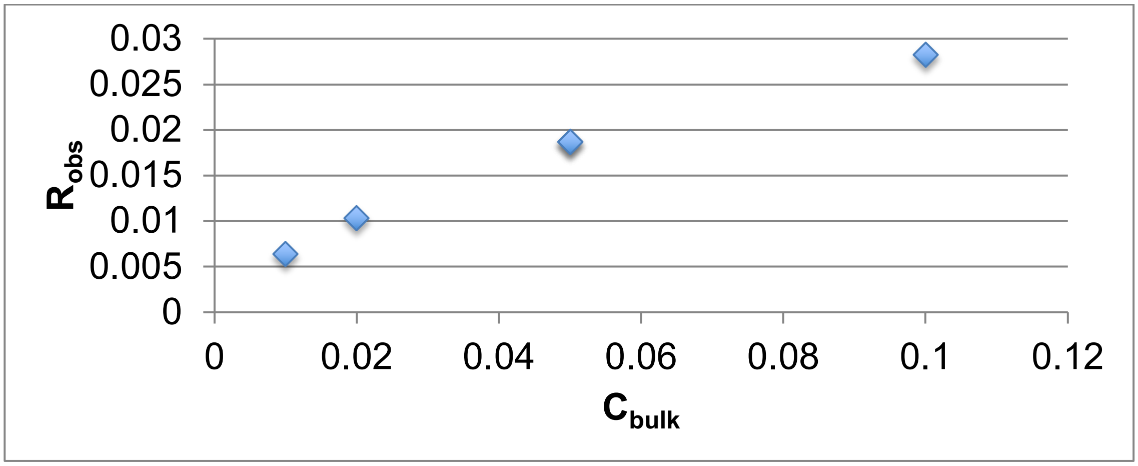
$$kC_S^2 + \bar{k}_c C_S - \bar{k}_c C_{bulk} = 0$$

$$C_S = \frac{-\bar{k}_c + \sqrt{\bar{k}_c^2 + 4k\bar{k}_c C_{bulk}}}{2k}$$
$$= \frac{-0.2cm\, s^{-1} + \sqrt{0.04cm^2 s^{-2} + 4\ \ 1.8\ 10^4\ cm^4\, mol^{-1} s^{-1}\ 0.2cm\, s^{-1}\ 0.1\ 10^{-3}\ mol\ cm^{-3}}}{2\ (1.8\ 10^{-4} m^4\ mol^{-1} s^{-1} = 1.8\ 10^4\ cm^4\ mol^{-1} s^{-1})}$$
$$= 0.028\ 10^{-3}\ mol\ cm^{-3} = 0.028\ mol\ L^{-1}$$

The observed rate is:
$r_{obs} = kC_s^2 = 1.8\ 10^4\ \ (0.028\ 10^{-3})^2 = 1.4\ 10^{-5}\ mol\ cm^{-2} s^{-1}$

$r_{max} = kC_{bulk}^2 = 1.8\ 10^4 (0.1\ 10^{-3})^2 = 1.8\ 10^{-4}\ mol\ cm^{-2} s^{-1}$ which is roughly 10x faster.

The observed rate plotted for concentrations between 0.1 and 0.05 mol/L is:



This pattern could easily be confused with a first order reaction if one is not careful!