DEPARTMENT OF CHEMICAL ENGINEERING

Ch E 345 - Chemical Reactor Design
Seminar #3

February 3, 2017

1. The following irreversible first-order reactions occur at constant density:

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

where $k_1 = 0.15$ min^{-1}; $k_2 = 0.05$ min^{-1}. This reaction system is to be analyzed in continuous flow reactors with a volumetric feed rate of 150 L/min and feed composition C_{A0}. Find the production rate of R (that is, C_R/C_{A0}) for each of the following reactor systems:

(a) A single CSTR with volume of 300 L

(b) Two CSTRs in series, each with volume of 150 L

(c) Two CSTRs in parallel, each with volume of 150 L and with the feed stream equally divided between them.

2. Consider the vapour-phase dehydration of ethanol over a catalyst. The rate of ethanol dehydration to diethyl ether at temperatures of 110 to 135 °C is given by the rate function:

$$(-r_A) = \frac{k_s K_A^2 \left(P_A^2 - \frac{1}{K_1} P_W P_E \right)}{\left(1 + K_A P_A + K_W P_W\right)^2} \quad \frac{\text{mol}}{\text{s} \cdot \text{g cat}}$$

where $A = C_2H_5OH$, $W = H_2O$ and $E = (C_2H_5)_2O$. The constants are:

$$k_s = 1.5 \times 10^8 \exp\left(\frac{-12424}{T}\right) \frac{\text{mol}}{\text{s} \cdot \text{gcat}}, \qquad K_A = 2.0 \times 10^{-7} \exp\left(\frac{4741}{T}\right) \text{ kPa}^{-1},$$

$$K_1 = 0.25 \exp\left(\frac{1842}{T}\right), \qquad K_W = 1.0 \times 10^{-9} \exp\left(\frac{7060}{T}\right) \text{ kPa}^{-1}$$

with T in K and P_i in kPa. The overall reaction for ethanol dehydration to diethyl ether is:

$$2A \rightleftharpoons W + E$$

(a) Convert the above rate expression to concentration units, *i.e.* replace the P_A, P_E and P_W and C_A, C_E and C_W. Use mol/m^3 for concentration units and assume ideal gas behavior.

(b) Calculate the equilibrium fractional conversion of ethanol if pure ethanol is fed to a reactor at a total pressure of 300 kPa and 130°C.

(c) The ethanol dehydration is to be carried out with a two reactor system, specifically, a PFR followed by a CSTR. Pure ethanol vapor is fed to the PFR at a rate of 0.25 mol/h. Each reactor contains 20.0 g of catalyst (ion exchange resin) and both reactors are operated at 300 kPa and 130°C. Calculate the steady-state fractional conversion of ethanol at the exit of the PFR and at the exit of the CSTR.

(d) Repeat part (c), but change the order of the two reactors.

Solution to Problem 1

The kinetics of each reaction are first order. Therefore the two rate equations are written:

$$\left(-r_{\mathrm{A}}\right) = k_1 C_{\mathrm{A}} \quad \text{and} \quad \left(r_{\mathrm{S}}\right) = k_2 C_{\mathrm{R}}$$

The system is constant density, so the volumetric flow rate is constant.

Part (a)

Perform a mole balance on species R for a single CSTR. Species R is formed by the first reaction and destroyed in the second reaction. The net rate of formation of R is therefore:

$$r_{\mathrm{R}} = k_1 C_{\mathrm{A}} - k_2 C_{\mathrm{R}}$$

The reactor mole balance is

$$-F_{\mathrm{R}E} + \left(k_1 C_{\mathrm{A}E} - k_2 C_{\mathrm{R}E}\right) V = 0$$

The mole balance for species A is

$$F_{\mathrm{A}0} - F_{\mathrm{A}E} - k_1 C_{\mathrm{A}E} V = 0$$

As the density is constant, the mole balances can be written in terms of concentration and volumetric flowrate.

$$-C_{\mathrm{R}E} + \left(k_1 C_{\mathrm{A}E} - k_2 C_{\mathrm{R}E}\right) \frac{V}{Q} = 0$$

$$C_{\mathrm{A}0} - C_{\mathrm{A}E} - k_1 C_{\mathrm{A}E} \frac{V}{Q} = 0$$

The solution is to be expressed in terms of the ratio $\frac{C_{\mathrm{R}E}}{C_{\mathrm{A}O}}$, so divide both equations

$$\frac{-C_{\mathrm{R}E}}{C_{\mathrm{A}0}} + \left(k_1 \frac{C_{\mathrm{A}E}}{C_{\mathrm{A}0}} - k_2 \frac{C_{\mathrm{R}E}}{C_{\mathrm{A}0}}\right) \frac{V}{Q} = 0 \qquad (1)$$

$$1 - \frac{C_{\mathrm{A}E}}{C_{\mathrm{A}0}} - k_1 \frac{C_{\mathrm{A}E}}{C_{\mathrm{A}0}} \frac{V}{Q} = 0 \qquad (2)$$

Substitute the known values for volume, volumetric flowrate and rate constants to get the following solution:

$$\frac{C_{AE}}{C_{A0}} = 0.7692 \qquad \frac{C_{RE}}{C_{A0}} = 0.2098$$

Part (b)

For two CSTR in series, the mole balances for A and R must be written for the two reactors.

For the first reactor, the equations are the same as in part a), albeit with a different volume.

$$-\frac{C_{RE1}}{C_{A0}} + \left(k_1 \frac{C_{AE1}}{C_{A0}} - k_2 \frac{C_{RE1}}{C_{A0}} \right) \frac{V_1}{Q} = 0 \qquad (3)$$

$$1 - \frac{C_{AE1}}{C_{A0}} - k_1 \frac{C_{AE1}}{C_{A0}} \frac{V_1}{Q} = 0 \quad (4)$$

For reactor 2, the mole balances are

$$\frac{C_{RE1}}{C_{A0}} - \frac{C_{RE2}}{C_{A0}} + \left(k_1 \frac{C_{AE2}}{C_{A0}} - k_2 \frac{C_{RE2}}{C_{A0}} \right) \frac{V_2}{Q} = 0 \qquad (5)$$

$$\frac{C_{AE1}}{C_{A0}} - \frac{C_{AE2}}{C_{A0}} - k_1 \frac{C_{AE2}}{C_{A0}} \frac{V_2}{Q} = 0 \quad (6)$$

Substitute the values ($V_1 = V_2 = 150$ L) and solve equations (3) to (6) to give values of

$$\frac{C_{AE1}}{C_{A0}} = 0.8696 \qquad \frac{C_{RE1}}{C_{A0}} = 0.1242 \qquad \frac{C_{AE2}}{C_{A0}} = 0.7562 \qquad \frac{C_{RE2}}{C_{A0}} = 0.2263$$

Part (c)

For two reactors in parallel of equal volume and flowrate, it is necessary to write the mole balance for 1 reactor only. The equations are the same as equations (1) and (2). The space time is the same as in part (a) so the solution to the problem is the same as part (a).

Solution to problem 2

Part (a):

To convert the equation to concentration use the ideal gas law:

$$C_{\mathrm{A}} = \frac{P_{\mathrm{A}}}{R_g T} \qquad C_{\mathrm{W}} = \frac{P_{\mathrm{W}}}{R_g T} \qquad C_{\mathrm{E}} = \frac{P_{\mathrm{E}}}{R_g T}$$

with $R_g = 8.314 \times 10^{-3} \dfrac{\mathrm{kJ}}{\mathrm{mol} \cdot \mathrm{K}}$ the pressure is expressed in kPa. The rate expression may therefore be written as:

$$\left(-r_{\mathrm{A}}\right) = \frac{k_s K_{\mathrm{A}}^2 R_g^2 T^2 \left(C_{\mathrm{A}}^2 - \dfrac{1}{K_1} C_{\mathrm{W}} C_{\mathrm{E}} \right)}{\left(1 + R_g T K_{\mathrm{A}} C_{\mathrm{A}} + R_g T K_{\mathrm{W}} C_{\mathrm{W}}\right)^2}$$

Part (b):

At equilibrium the net rate of reaction is zero and therefore:

$$C_{\mathrm{A}}^2 - \frac{1}{K_1} C_{\mathrm{W}} C_{\mathrm{E}} = 0$$

At 130°C, K_1 has a value of:

$$K_1 = 0.25 \exp\left(\frac{1842}{T}\right) = 0.25 \exp\left(\frac{1842}{130 + 273.15}\right) = 24.11$$

As the feed is pure ethanol, it follows that $C_{\mathrm{W}} = C_{\mathrm{E}}$. Moles are conserved on reaction so the total pressure has no effect on the equilibrium conversion. Furthermore, as moles are conserved and the pressure and temperature are constant, we can write:

$$C_{\mathrm{A}} = C_{\mathrm{A0}}(1 - X) \qquad C_{\mathrm{W}} = \frac{1}{2} C_{\mathrm{A0}} X \qquad C_{\mathrm{E}} = \frac{1}{2} C_{\mathrm{A0}} X$$

The equilibrium condition is therefore:

$$\frac{\dfrac{1}{2} C_{\mathrm{A0}} X \dfrac{1}{2} C_{\mathrm{A0}} X}{C_{\mathrm{A0}}^2 \left(1 - X\right)^2} = 24.11$$

Solving gives a value of $X = 0.905$.

Part (c):

At 130°C the rate constants have values of:

$$k_s = 1.5\times10^{8}\exp\left(\frac{-12424}{130+273.15}\right) = 6.2\times10^{-6}\,\frac{\text{mol}}{\text{s}\cdot\text{gcat}}$$

$$K_\text{A} = 2.0\times10^{-7}\exp\left(\frac{4741}{130+273.15}\right) = 2.56\times10^{-2}\ \text{kPa}^{-1}$$

$$K_1 = 0.25\exp\left(\frac{1842}{130+273.15}\right) = 24.11$$

$$K_\text{W} = 1.0\times10^{-9}\exp\left(\frac{7060}{130+273.15}\right) = 4.031\times10^{-2}\ \text{kPa}^{-1}$$

The feed to the reactors consists of pure ethanol at 130°C and 300 kPa. As moles are conserved on reaction and the pressure and temperature are constant, we can write:

$$P_\text{A} = P_{\text{A}0}(1-X) \qquad P_\text{W} = \frac{1}{2}P_{\text{A}0}X \qquad P_\text{E}\,\frac{1}{2}P_{\text{A}0}X$$

Substituting the values of $P_{\text{A}0}$ and the rate parameters into the rate equation gives:

$$\left(-r_\text{A}\right) = \frac{k_s\,K_\text{A}^2\,P_{\text{A}0}^2\left[\left(1-X\right)^2 - \frac{1}{4K_1}X^2\right]}{\left(1 + K_\text{A}\,P_{\text{A}0}\left(1-X\right) + \frac{K_\text{W}}{2}P_{\text{A}0}\,X\right)^2}$$

Therefore:

$$\left(-r_\text{A}\right) = \frac{3.657\times10^{-4}\left[\left(1-X\right)^2 - 1.037\times10^{-2}X^2\right]}{\left(1 + 7.68\left(1-X\right) + 6.047X\right)^2}$$

Simplify:

$$\left(-r_\text{A}\right) = \frac{3.657\times10^{-4}\left[0.99X^2 - 2X + 1\right]}{\left(8.68 - 1.634X\right)^2}\,\frac{\text{mol}}{\text{s}\cdot\text{gcat}}$$

The reactor system is a PFR followed by a CSTR. The feed flowrate is $F_{\text{A}0} = 0.25\ \text{mol/h}$ or $6.944\times10^{-5}\,\frac{\text{mol}}{\text{s}}$. The mole balance equation for the PFR in terms of catalyst mass and fractional conversion is:

$$F_{A0}\frac{dX}{dW} = (-r_A) = \frac{3.657\times10^{-4}\left[0.99X^2 - 2X + 1\right]}{(8.68 - 1.634X)^2}$$

Substituting for F_{A0} gives:

$$\frac{dX}{dW} = \frac{5.266\left[0.99X^2 - 2X + 1\right]}{(8.68 - 1.634X)^2}$$

This equation is integrated numerically for $W = 20\ g$ of catalyst. The result is:

$$X_1 = 0.619$$

The output from the PFR is fed to a CSTR. The mole balance for the CSTR is:

$$W = \frac{F_{A0}(X_2 - X_1)}{(-r_A)}$$

Therefore, with $W = 20$ g, the equation is:

$$X_1 - X_2 + \frac{105.3\left[0.99X_2^2 - 2X_2 + 1\right]}{(8.68 - 1.634X)^2} = 0$$

Solving this equation numerically gives

$$X_2 = 0.738$$

Part (d)

With the CSTR as the first reactor, the mole balance equation is:

$$W = \frac{F_{A0}X_1}{(-r_A)} \quad \text{or} \quad X_1 - \frac{105.3\left[0.99X_1^2 - 2X_1 + 1\right]}{(8.68 - 1.634X_1)^2} = 0$$

Solving this equation numerically gives $X_1 = 0.470$

The effluent from the CSTR is fed to the PFR. The mole balance equation for the PFR is the same as in part (c), except that the limits on the integral change. Solving for $W = 20$ g and $X_1 = 0.470$ gives a value of $X_2 = 0.724$.

Comment: It is seen that having the PFR before the CSTR gives a slightly higher overall conversion.