Ch E 345 - Chemical Reactor Design
Seminar #2

January 27, 2017

1. Consider a plug flow reactor with a reversible isothermal gas phase reaction:

$$A + B \rightleftharpoons C$$

The reactor feed consists of a mixture of 50% A and 50% B. The reaction rate is:

$$(-r_A) = k_1 C_A C_B - k_2 C_C^2$$

The inlet temperature is 500 K and the total pressure is 200 kPa. The volumetric feed flowrate is 10 m^3/s. The rate constants have values of:

$$k_1 = 0.1 \frac{m^3}{mol \cdot s} \text{ and } k_2 = 0.05 \frac{m^3}{mol \cdot s}.$$

(a) Calculate the conversion of A in a reactor of volume 10 m^3.
(b) Calculate the maximum conversion of A in an infinitely long reactor.

2. The reaction between ammonia and formaldehyde to give hexamine is:

$$4\,NH_3 + 6\,HCHO \rightarrow (CH_2)_6 N_4 + 6\,H_2O$$
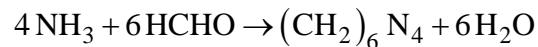
A 0.5 litre CSTR is used for the reaction. Each reactant is fed to the reactor in a separate stream, at the rate of 1.5×10^{-3} L/s each with ammonia concentration 4.0 mol/L and formaldehyde 6.4 mol/L. The reactor temperature is 36°C. Calculate the concentration of ammonia and formaldehyde in the effluent stream. The reaction rate and rate constant are:

$$(-r_A) = k\,C_A^2 C_B \quad \frac{mol\ A}{L \cdot s} \qquad k = 1.42 \times 10^3 \exp\left(\frac{-3090}{T}\right)$$

where A is ammonia and B is formaldehyde.

3.   The following reaction occurs in aqueous solution.

$$NaOH + C_2H_5(CH_3CO) \rightarrow Na(CH_3CO) + C_2H_5OH$$

$$A \quad + \quad\quad B \quad\quad\quad \rightarrow \quad\quad C \quad + \quad D$$
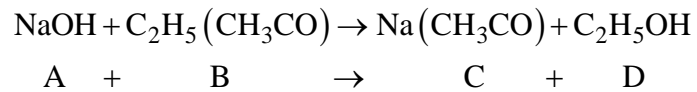
This reaction is second order and irreversible, that is: $(-r_A) = k\,C_A\,C_B$

A well mixed laboratory batch reactor is filled with a solution of 0.1 molar NaOH and ethyl acetate (component B). After 15 minutes, the conversion of NaOH is 15%.

(a) For a commercial size reactor, how much time is required to achieve 30% conversion of a solution containing 0.2 molar ethyl acetate and 0.2 molar NaOH?

(b) What reactor volume is required to produce 50 kg of sodium acetate (product C, molecular weight 66) at this 30% conversion (conditions of part (a))?

Solution to Problem 1

Part (a)

The reactor is isothermal with plug flow. It is a gas phase reaction with a change in moles on reaction. Therefore, the volumetric flowrate changes with reaction. The mole balance is:

$$-\frac{dF_A}{dV} = (-r_A) = k_1 C_A C_B - k_2 C_C^2$$

The mole balance can be written in terms of fractional conversion. Noting that

$$F_{A0} = F_{B0} \text{ and } C_A = \frac{F_A}{Q}, \quad C_B = \frac{F_B}{Q}, \quad C_C = \frac{F_C}{Q}$$

write the mole balance table:

	moles in	moles out
A	F_{A0}	$F_{A0}(1-X_A)$
B	F_{B0}	$F_{A0}(1-X_A)$
C	0	$F_{A0}X_A$
Total	$2F_{A0}$	$2F_{A0} - F_{A0}X_A$

Using the ideal gas law, we obtain a relationship between the volumetric flowrate and the molar flowrate:

$$\frac{Q}{F_t} = \frac{Q_0}{F_{t0}}$$

Therefore, by substitution:

$$Q = Q_0(1-0.5X_A)$$

Now write the mole balance in terms of conversion:

$$F_{A0}\frac{dX_A}{dV} = k_1\left(\frac{F_{A0}}{Q_0}\right)^2\left(\frac{1-X_A}{1-0.5X_A}\right)^2 - k_2\left(\frac{F_{A0}}{Q_0}\right)^2\left(\frac{X_A}{1-0.5X_A}\right)^2$$

Rearrange:

$$V = \frac{Q_0^2}{F_{A0}}\int_0^{X_A}\frac{(1-0.5X_A)^2\,dX_A}{k_1(1-X_A)^2 - k_2X_A^2}$$

Using the ideal gas law:

$$PQ_0 = 2F_{A0}R_g T \implies F_{A0} = \frac{PQ_0}{2R_g T}$$

Therefore:

$$V = \frac{2Q_0 R_g T}{P} \int_0^{X_A} \frac{1 - X_A + 0.25X_A^2}{0.1 - 0.2X_A + 0.1X_A^2 - 0.05X_A^2} dX_A$$

Substitute the numbers:

$$10 = \frac{(2)(10)(8.314)(500)}{(200,000)(0.1)} \int_0^{X_A} \left(\frac{1 - X_A + 0.25X_A^2}{1 - 2X_A + 0.5X_A^2} \right) dX_A$$

The integral can be evaluated analytically.

$$2.406 = 0.25 \left[2X_A + 4\ln\left(1 - 2X_A + 0.5X_A^2\right) + 6 \int_0^{X_A} \frac{dX}{1 - 2X_A + 0.5X_A^2} \right]$$

$$\left[-\ln\left(1 - 2X_A + 0.5X_A^2\right) - 2 \int_0^{X_A} \frac{dX}{1 - 2X_A + 0.5X_A^2} \right]\left[+ \int_0^{X_A} \frac{dX}{1 - 2X_A + 0.5X_A^2} \right]$$

The remaining integral is also evaluated analytically. After simplification, we obtain:

$$2.406 = \left[\frac{0.5}{\sqrt{2}} \ln\left[\frac{X_A - 2 - \sqrt{2}}{X_A - 2 + \sqrt{2}} \right] + 0.5X_A \right]_0^{X_A}$$

Introduce the integration limits:

$$6.804 = 0.5X_A + \ln\left[\frac{X_A - 3.414}{X_A - 0.5858} \right] - \ln(5.828)$$

Attempts to solve the preceding equations prove difficult. Therefore we adopt a different strategy. Write the mole balance in terms of the differential equation:

$$\frac{dX_A}{dV} = k_1 \left(\frac{P}{2R_g TQ_0} \right)\left(\frac{1 - X_A}{1 - 0.5X_A} \right)^2 - k_2 \left(\frac{P}{2R_g TQ_0} \right)\left(\frac{X_A}{1 - 0.5X_A} \right)^2$$

$$\frac{dX_A}{dV} = \frac{(0.1)(200,000)}{(2)(8.314)(500)(10)} \left[\left(\frac{1 - X_A}{1 - 0.5X_A} \right)^2 - \frac{1}{2}\left(\frac{X_A}{1 - 0.5X_A} \right)^2 \right]$$

$$\frac{dX_A}{dV} = 0.241 \left[\frac{1 - 2X_A + X_A^2 - 0.5X_A^2}{1 - X_A + 0.25X_A^2} \right]$$

When this equation is integrated numerically, it is seen that the differential equation essentially becomes equal to zero when $V = 1.424$. At this point, the conversion is $X_A = 0.586$, and corresponds to an equilibrium. The remaining reactor volume is wasted because no further reaction occurs.

Part (b)

For an infinitely long reactor, the reaction will achieve equilibrium. At equilibrium the net rate of reaction is zero:

$$\left(-r_A \right) = k_1 C_A C_B - k_2 C_C^2 = 0$$

At the reactor exit, the equation can be written:

$$k_1 \frac{F_A F_B}{Q_2} - k_2 \frac{F_C^2}{Q_2} = 0$$

Each molar flowrate can be written in terms of the inlet molar flowrate of A . Noting that $F_{A0} = F_{B0}$ gives:

$$F_A = F_{A0}\left(1 - X_A\right) \qquad F_B = F_{A0}\left(1 - X_A\right) \qquad F_C = F_{A0}X_A$$

Substitute:

$$k_1 \frac{F_{A0}^2}{Q^2}\left(1 - X_A\right)^2 - k_2 \frac{F_{A0}^2 X_A^2}{Q^2} = 0$$
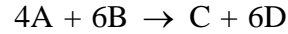
Rearrange:

$$0.1\left(1 - X_A\right)^2 - 0.05X_A^2 = 0$$

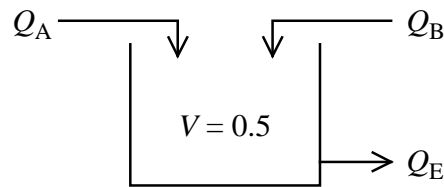or:

$$\sqrt{2}\left(1 - X_A\right) = X_A$$
$$1.414 = 2.414\,X_A$$

Finally, solve for the fractional conversion of $X_A = 0.586$.

Solution to problem 2

The reaction is written in terms of A, B, C, D :

$$4A + 6B \rightarrow C + 6D$$

The reaction takes place in liquid solution and so the density is assumed to be constant. Note that each reactant is fed to the reactor in a separate stream.

The two feed streams have equal flowrates. Thus

$$Q_A = Q_B \quad \text{and} \quad Q_E = Q_A + Q_B$$

The mole balance on A is:

$$Q_A C_{A0} - Q_E C_{AE} - k_1 C_{AE}^2 C_{BE} V = 0$$

The mole balance for B is:

$$Q_B C_{B0} - Q_E C_{BE} - \left(\frac{6}{4}\right) k C_{AE}^2 C_{BE} V = 0$$

Note the factor $\dfrac{6}{4}$ accounts for the stoichiometry. Six moles of B are consumed for each 4 moles of A that react. From the two mole balances:

$$C_{BE} = \frac{1}{Q_E}\left[Q_B C_{B0} - \frac{6}{4} Q_A C_{A0} + \frac{6}{4} Q_E C_{AE} \right]$$

$$C_{BE} = \frac{C_{B0}}{2} - 0.75 C_{A0} + 1.5 C_{AE}$$

Substitute the inlet concentrations:

$$C_{BE} = 3.2 - 3 + 1.5C_{AE} = 0.2 + 1.5C_{AE}$$

The reaction rate constant at $36°C \equiv 309 \text{ K}$ is

$$k = 1.43 \times 10^3 \exp\left(-\frac{3090}{309}\right) = 6.49 \times 10^{-2}$$

The mole balance for A is:

$$2.0 - C_{AE} - \frac{6.49 \times 10^{-2}}{3 \times 10^{-3}} 0.5C_{AE}^2 \left(0.2 + 1.5C_{AE}\right) = 0$$

or:

$$2.0 - C_{AE} - 10.82 C_{AE}^2 \left(0.2 + 1.5C_{AE}\right) = 0$$

simplify:
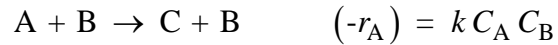
$$2.0 - C_{AE} - 2.164 C_{AE}^2 - 16.23 C_{AE}^3 = 0$$

Solve iteratively for $C_{AE} = 0.42 \dfrac{\text{mol}}{\text{L}}$.

Then by back substitution $C_{BE} = 0.83 \dfrac{\text{mol}}{\text{L}}$.

Solution to Problem 3

The reaction occurs in the liquid phase so constant density is assumed. The reaction stoichiometry and rate expression are:

$$A + B \rightarrow C + B \qquad (-r_A) = k\, C_A\, C_B$$

Because the reaction is second order, the conversion depends on the initial concentration. The rate constant is unknown and must be determined from the information provided. We consider the experimental batch reactor. The mole balance is:

$$-\frac{1}{V}\frac{d N_A}{dt} = (-r_A) = k\, C_A\, C_B$$

At time $t = 0$, we have $C_{A0} = C_{B0} = 0.1\ \dfrac{\text{mol}}{\text{L}}$. In terms of fractional conversion, we can write:

$$C_{A0}\frac{d X_A}{dt} = k\, C_{A0}^2\left(1 - X_A\right)^2$$

Rearrange and integrate:

$$\frac{d X_A}{\left(1 - X_A\right)^2} = k\, C_{A0}\, dt \qquad \left.\frac{1}{1 - X_A}\right|_0^{X_A} = k\, C_{A0}\, t\big|_0^t$$

or, rearranging:

$$k\, C_{A0}\, t = \left(\frac{X_A}{1 - X_A}\right)$$

Substitute the values of $t = 15\ \text{min}$ and $X_A = 0.15$.

$$k\,(0.1)(15) = \left(\frac{0.15}{1 - 0.15}\right)$$

Solve for $k = 0.1176\ \dfrac{\text{L}\cdot\text{min}}{\text{mol}}$.

Part (a)

To determine the time required to achieve 30% conversion starting from $C_{A0} = C_{B0} = 0.2 \dfrac{mol}{L}$,

we can simply substitute into the mole balance:

$$kC_{A0}t = \frac{X_A}{1 - X_A}$$

Substitute:

$$(0.1176)(0.2)(t) = \frac{0.3}{1 - 0.3}$$

Solve for $t = 18.21$ min.

Part (b)

We want to produce 50 kg of C. This mass corresponds to:

$$\frac{50 \text{ kg}}{66 \ \dfrac{\text{kg}}{\text{mol}}} = 0.7576 \text{ kmol} \equiv 757.58 \text{ mol}$$

for a conversion of 30% with $C_{A0} = 0.2 \dfrac{mol}{L}$, the final concentration of C is:

$$0.2 \ \frac{mol}{L} \times 0.3 = 0.06 \ \frac{mol}{L}$$

If the reactor is to contain 757.58 mol, the volume must be:

$$\frac{757.58 \text{ mol}}{0.06 \ \dfrac{mol}{L}} = 12,626 \text{ L}$$