

Fall 2021 CBE 60546 Advanced Chemical Reaction Engineering
Homework 6 Solutions

Problem 8.1

F. Salvador, J. L. Gonzalez, and M. A. Herraes [Int. J. Chem. Kinet., 14, 875 (1982)] studied the kinetics of the isomerization of cholest-5-en-3-one in cyclohexane in the presence of trichloroacetic acid as a catalyst. The stoichiometry of this reaction is $A \rightarrow B$, where A refers to cholest-5-en-3-one and B to cholest-4-en-one. Species A and B both form association complexes with trichloroacetic acid. In the presence of excess acid, the kinetics of the isomerization reaction are described by a rate expression that is pseudo first-order in A:

$$r = k_{observed}(A)$$

At 25.4°C the observed rate constant is $1.087 \times 10^{-3} \text{ s}^{-1}$ for the concentration of trichloroacetic acid employed ($7.37 \times 10^{-3} \text{ M}$).

Consider this reaction as it takes place in a semibatch reactor operating at 25.4°C. Initially, this reactor contains 20 L of a cyclohexane solution that contains the desired amount of trichloroacetic acid, but no A. The reactor is fed with a cyclohexane solution containing species A ($2 \times 10^{-3} \text{ M}$) and trichloroacetic acid ($7.37 \times 10^{-3} \text{ M}$). The feed stream enters at 25.4°C. at a constant rate of 5 L/min for a total time of 30 min. Subsequently, the reactor functions as a batch reactor.

The reactor is well stirred during both phases of the reaction. Prepare plots of the concentrations of species A and B as functions of time for a total elapsed time of 100 min. At what time does the concentration of species A pass through a maximum? How much total time is necessary to convert 98% of the A fed to the reactor into B?

Solve the problem by dividing it into two sections:

Section 1: $0 \leq t \leq 30 \text{ min}$

A semibatch reactor can be seen as a batch reactor with an inlet stream. Solve in terms of number of moles since volume is changing over time.

$$\frac{dn_A}{dt} = v_{in}C_{A0} - kC_A V$$

$$\frac{dn_A}{dt} = F_{A0} - kn_A$$

Integrate from zero to solve n_A as a function of time:

$$\int_0^{n_A} \frac{dn_A}{F_{A0} - kn_A} = \int_0^t dt$$
$$\ln \left[\frac{F_{A0} - kn_A}{F_{A0}} \right] = -kt$$
$$n_A = \frac{F_{A0}}{k} (1 - e^{-kt})$$

Similar method can be employed to solve for n_B , since now we know n_A as function of time:

$$\frac{dn_B}{dt} = kn_A$$

Or recognize that the reaction $A \rightarrow B$, all A converted must become B, such that:

$$n_{A,in} - n_A = n_B$$

Divide n_A and n_B by volume to find concentration, for volume is a function of time, such:

$$V = 20 + v_{in}t$$

Section 2: $t < 30 \text{ min}$

The reactor now resembles a batch reactor, for V is not changing, the differential equation simplifies to:

$$\frac{dC_A}{dt} = -kC_A$$

The integration bound now starts with $t = 30 \text{ min}$, and we know what C_A is at $t = 30$ from solving Section 1:

$$\int_{C_{A,t=30}}^{C_A} \frac{dC_A}{-kC_A} = \int_{30}^t dt$$
$$\ln \left[\frac{C_A}{C_{A,t=30}} \right] = -k(t - 30)$$
$$C_A = C_{A,t=30} \cdot e^{-k(t-30)}$$

Same method goes for C_B ,

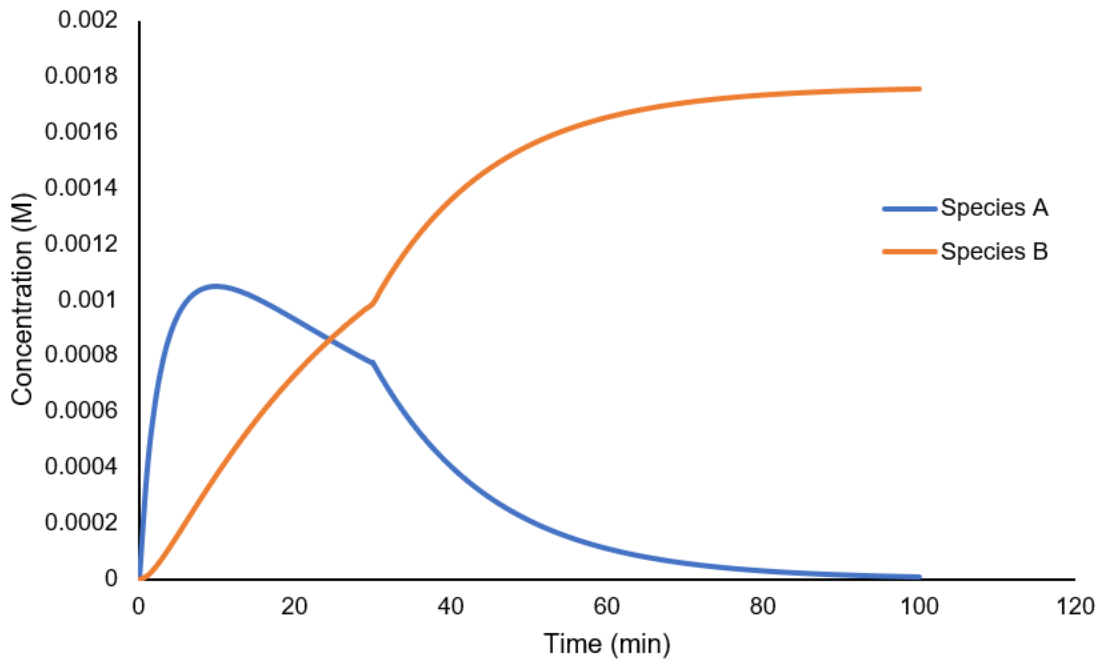
$$\frac{dC_B}{dt} = kC_A$$

Or again finding the amount of n_B by know how much n_A has been consumed, and divide by the volume at $t > 30$ min, which would be a constant value of:

$$V = 20 + (5 \text{ L/min})(30 \text{ min}) = 170 \text{ L}$$

Prepare plots of the concentrations of species A and B as functions of time for a total elapsed time of 100 min.

8.1 Part a) Concentration as function of time



To find the time at which the concentration of A is at maximum,

$$C_A = \frac{n_A}{V} = \frac{F_{A0}}{k} \frac{(1 - e^{-kt})}{20 + v_{in}t}$$

$$\frac{dC_A}{dt} = 0$$

Or use Python, Mathematica, or other computational methods to find the maximum point on the graph plotted in Part a.

At what time does the concentration of species A pass through a maximum?

$$t_{C_{A,max}} = 9.88 \text{ min}$$

To find the amount of time required to convert 98% of A to B,

$$n_A = 0.02n_{A,in}$$
$$n_{A,in} = F_{A0} \cdot t = (5 \text{ L/min})(0.002 \text{ M})(30 \text{ min}) = 0.3 \text{ mol}$$
$$n_A = 0.02(0.3 \text{ mol}) = 0.006 \text{ mol}$$

$$n_A = C_A V = C_{A,t=30} V \cdot e^{-k(t-30)} = 0.006 \text{ mol}$$

Or use Python, Mathematica, or other computational methods to find the point on the graph

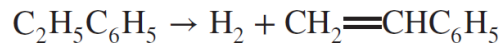
where $C_A = \frac{n_A}{V} = \frac{0.006 \text{ mol}}{170 \text{ L}} = 3.53 \times 10^{-5} \text{ M}$.

How much total time is necessary to convert 98% of the A fed to the reactor into B?

$$t_{f_{A=98\%}} = 77.35 \text{ min}$$

Problem 8.6

Dehydrogenation of ethylbenzene to styrene is normally accomplished in a fixed-bed reactor. A catalyst is packed in tubes to form the fixed bed. Steam is often fed with the styrene to moderate the temperature excursions that are characteristic of adiabatic operation. The steam also serves to prolong the life of the catalyst. Consider the situation in which we model the behavior of this reactor as an isothermal plug flow reactor in which the dehydrogenation reaction occurs homogeneously across each cross section of the reactor. The stoichiometry of the primary reaction is



Consider the case for which the reaction obeys a rate law that is first-order in ethyl benzene with $k = 3.5 \times 10^{-3}\text{s}^{-1}$ at the temperature of interest (200°C), and the feed is 75% v/v H_2O , 15% $\text{C}_2\text{H}_5\text{C}_6\text{H}_5$, and 10% H_2 .

If the feed stream enters at 1 atm and behaves as an ideal gas, what space time is necessary for the laboratory-scale reactor to achieve 90% conversion? What is the mean residence time of the gas under these conditions? Which of these two times is more useful for purposes of reactor design? Why?

For the reaction of ethylbenzene dehydrogenation is a gas phase reaction, we must consider the density change in the fixed-bed reactor by using the volumetric expansion parameter, δ :

$$\delta = \frac{V(\text{at } f_a = 1) - V(\text{at } f_a = 0)}{V(\text{at } f_a = 0)}$$

Assuming ideal gas, with constant pressure and temperature, the equation can be rewritten in terms of moles:

$$\delta = \frac{n_{\text{total}}(\text{at } f_a = 1) - n_{\text{total}}(\text{at } f_a = 0)}{n_{\text{total}}(\text{at } f_a = 0)}$$

Solve for n_{total} at each conversion, either by using the ideal gas law, or consider using the volume percent:

$$n_{\text{total}}(\text{at } f_a = 0) = \text{initial number of moles} = \frac{PV}{RT}$$

$$\begin{aligned} n_{\text{total}}(\text{at } f_a = 1) &= \text{number of moles when all of the ethylbenzene has been consumed} \\ &= 1.15 \cdot n_{\text{total}}(\text{at } f_a = 0) \end{aligned}$$

$$\delta = \frac{1.15 \cdot n_{total}(at f_a = 0) - n_{total}(at f_a = 0)}{n_{total}(at f_a = 0)}$$

$$\delta = \frac{1.15 - 1}{1} = 0.15$$

The equation to find the space time of a plug flow reactor is:

$$\tau = C_{A0} \int_0^{f_A} \frac{df_A}{(-r_A)}$$

For a gas phase reaction:

$$C_A = C_{A0} \left(\frac{1 - f_A}{1 + \delta f_A} \right)$$

Simplify and solve:

$$\tau = C_{A0} \int_0^{f_A} \frac{df_A}{k C_{A0} \left(\frac{1 - f_A}{1 + \delta f_A} \right)}$$

$$\tau = \frac{1}{k} \int_0^{0.9} \frac{1 + \delta f_A}{1 - f_A} df_A$$

$$\tau = \frac{1}{k} [-0.15 f_A - 1.15 \ln(1 - f_A)] \Big|_0^{0.9}$$

$$\tau = \frac{[(-0.15 \cdot 0.9) - 1.15 \ln(1 - 0.9)] - [0 - 1.15 \ln(1)]}{3.5 \times 10^{-3} s^{-1}}$$

What space time is necessary for the laboratory-scale reactor to achieve 90% conversion?

$$\tau = 717.14 s = 11.95 min$$

The mean residence time of the plug flow reactor can be represented by the following equation:

$$\bar{t} = \int_0^{V_R} \frac{dV}{v}$$

For a gas phase reaction:

$$v = v_0(1 + \delta f_A)$$

$$dV = \frac{F_{A0} df_A}{(-r_A)}$$

Rewriting the differential equation in terms of f_A :

$$\bar{t} = \int_{f_{A,initial}}^{f_{A,final}} \frac{F_{A0} df_A}{(-r_A)v_0(1 + \delta f_A)}$$

Simplify and solve:

$$\bar{t} = \int_{f_{A,initial}}^{f_{A,final}} \frac{v_0 C_{A0} df_A}{(-r_A)v_0(1 + \delta f_A)}$$

$$\bar{t} = \int_{f_{A,initial}}^{f_{A,final}} \frac{v_0 C_{A0} df_A}{(-k C_A)v_0(1 + \delta f_A)}$$

$$\bar{t} = \int_{f_{A,initial}}^{f_{A,final}} \frac{v_0 C_{A0} df_A}{\left(-k C_{A0} \left(\frac{1 - f_A}{1 + \delta f_A}\right)\right) v_0(1 + \delta f_A)}$$

$$\bar{t} = \frac{-1}{k} \int_{f_{A,initial}}^{f_{A,final}} \frac{df_A}{\left(\frac{1 - f_A}{1 + \delta f_A}\right) (1 + \delta f_A)} = \frac{-1}{k} \int_0^{0.9} \frac{df_A}{1 - f_A}$$

$$\bar{t} = \frac{-1}{k} [\ln(1 - f_A)] \Big|_0^{0.9}$$

$$\bar{t} = \frac{-(\ln(1 - 0.9) - \ln(1))}{3.5 \times 10^{-3} \text{ s}^{-1}}$$

What is the mean residence time of the gas under these conditions?

$$\bar{t} = 657.14 \text{ sec} = 10.95 \text{ min}$$

Which of these two times is more useful for purposes of reactor design? Why?

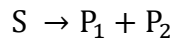
The space time is more useful for the purpose of reactor design, for you can find information regarding the volume of the reactor with space time. Mean residence time does not necessarily provide insight regarding reactor design, since it only describes how long a particle stays inside a reactor on average.

Problem 8.12

Researchers in both industry and academia have employed immobilized enzymes as biocatalysts. Immobilization usually involves attaching enzymes to solid supports and packing the supports in a tube through which liquid flows. One application has involved conversion of the lactose in dairy fluids to glucose and galactose, which would permit conversion of the whey produced in cheese manufacture to useful by-products. By averaging over the void spaces between solid particles and the particles themselves, one can obtain an effective rate expression per unit volume of the bed of biocatalyst. The rate expression is

$$r = \frac{kS}{S + K_M[1 + (P_1/K_I)]}$$

for a reaction of the type



At a given temperature the parameters k , K_M , and K_I are constants. K_M is known as a Michaelis constant and K_I as an inhibition constant. S and P_1 are the concentrations of reactant S and product P_1 , respectively. What effective space time for a tubular reactor will be required to obtain 80% conversion of the lactose at 40°C, where $K_M = 0.0528$ M, $K_I = 0.0054$ M, and $k = 5.53$ mol/(L · min). The initial lactose concentration is 0.149 M.

The space time of a tubular reactor can be described by the following equation:

$$\tau = S_0 \int_0^{f_S} \frac{df_S}{(-r_S)}$$

Since the catalytic conversion of lactose happens in the aqueous phase, we do not need to consider the volumetric expansion. The equation will simply be:

$$\tau = S_0 \int_0^{f_S} \frac{df_S}{\left(\frac{kS}{S + K_M[1 + (P_1/K_I)]} \right)}$$

Rewriting concentration of S in terms of conversion:

$$S = S_0(1 - f_S)$$

Since we know the reaction is: $S \rightarrow P_1 + P_2$

For every mole of S consumed, one mole of P_1 and one mole P_2 will be generated. Thus:

$$P_1 = f_S S_0$$

Plug in, simplify and solve:

$$\tau = S_0 \int_0^{f_S} \frac{(S + K_M[1 + (P_1/K_I)])}{kS} df_S$$

$$\tau = S_0 \int_0^{f_S} \frac{S_0(1 - f_S) + K_M \left[1 + \frac{f_S S_0}{K_I}\right]}{kS_0(1 - f_S)} df_S$$

$$\tau = \frac{1}{k} \int_0^{f_S} \frac{S_0(1 - f_S) + K_M + \frac{K_M f_S S_0}{K_I}}{(1 - f_S)} df_S$$

$$\tau = \frac{1}{k} \int_0^{f_S} \left[S_0 + \frac{K_M}{(1 - f_S)} + \frac{K_M f_S S_0}{K_I(1 - f_S)} \right] df_S$$

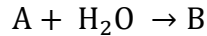
$$\tau = \frac{1}{k} \left[S_0 f_S - K_M \ln(1 - f_S) - \frac{K_M S_0 (f_S + \ln(1 - f_S))}{K_I} \right] \Bigg|_0^{0.8}$$

What effective space time for a tubular reactor will be required to obtain 80% conversion?

$$\tau = 15.01 \text{ sec} = 0.25 \text{ min}$$

Problem 8.36

A single CSTR is to be employed to effect a hydration reaction in perchloric acid solution:



Under appropriate conditions the reaction is pseudo first-order in reactant A. For these conditions the rate constant is equal to $2.7 \times 10^{-2} \text{ min}^{-1}$. Consider operation of a reactor with a volume of 9.0 m^3 to which an aqueous solution of the reactant is being fed at a rate of 100 L/min . The feed concentration of reactant A is equal to 0.5 M .

- (a) Determine the effluent concentration of species A for the indicated operating conditions if steady state conditions prevail in the reactor.
- (b) If the volumetric flow rate is increased to 150 L/min , prepare a plot of the effluent concentration of species A as a function of time from the time at which the increase is made until 100 min later. How long does it take the effluent concentration of species A to equal 0.175 M ? The reactor continues to operate at the same temperature and with the same concentration of reactant in the feed stream. Note that there is no accumulation of the liquid phase in the CSTR.

The concentration of species in a CSTR can be described by the following equation:

$$\text{Accumulation} = \text{In} - \text{Out} + \text{Reaction}$$

$$\frac{dC_A}{dt} = \frac{C_{A,in}}{\tau} - \frac{C_{A,out}}{\tau} + r_A$$

Assuming a pseudo first-order reaction, the rate law can be written as:

$$r_A = -kC_A$$

Plug into differential equation:

$$\frac{dC_A}{dt} = \frac{C_{A,in}}{\tau} - \frac{C_{A,out}}{\tau} - kC_A$$

At steady state, the concentration of A inside the CSTR is no longer changing, therefore:

$$0 = \frac{C_{A,in}}{\tau} - \frac{C_{A,out}}{\tau} - kC_A$$

Plug in and solve:

$$0 = \frac{C_{A0}}{\tau} - \frac{C_A}{\tau} - kC_A$$

$$C_A = \frac{C_{A0}}{(1 + \tau k)}$$

$$\tau = \frac{V}{v_0} = \frac{9000 \text{ L}}{100 \text{ L/min}} = 90 \text{ min}$$

$$C_A = \frac{0.5 \text{ M}}{(1 + [90 \cdot 2.7 \times 10^{-2}])} = 0.145 \text{ M}$$

Determine the effluent concentration of species A for the indicated operating conditions if steady state conditions prevail in the reactor.

$$C_A = 0.145 \text{ M}$$

Once the reactor is operating at steady state, the flow rate has been changed from 100 L/min to 150 L/min. With everything else remain the same, to find when C_A reaches 0.175 M:

$$\frac{dC_A}{dt} = \frac{C_{A0}}{\tau} - \frac{C_A}{\tau} - kC_A$$

For residence time now equals:

$$\tau = \frac{V}{v_0} = \frac{9000 \text{ L}}{150 \text{ L/min}} = 60 \text{ min}$$

Solve the differential from steady-state C_A to $C_A=0.175\text{M}$

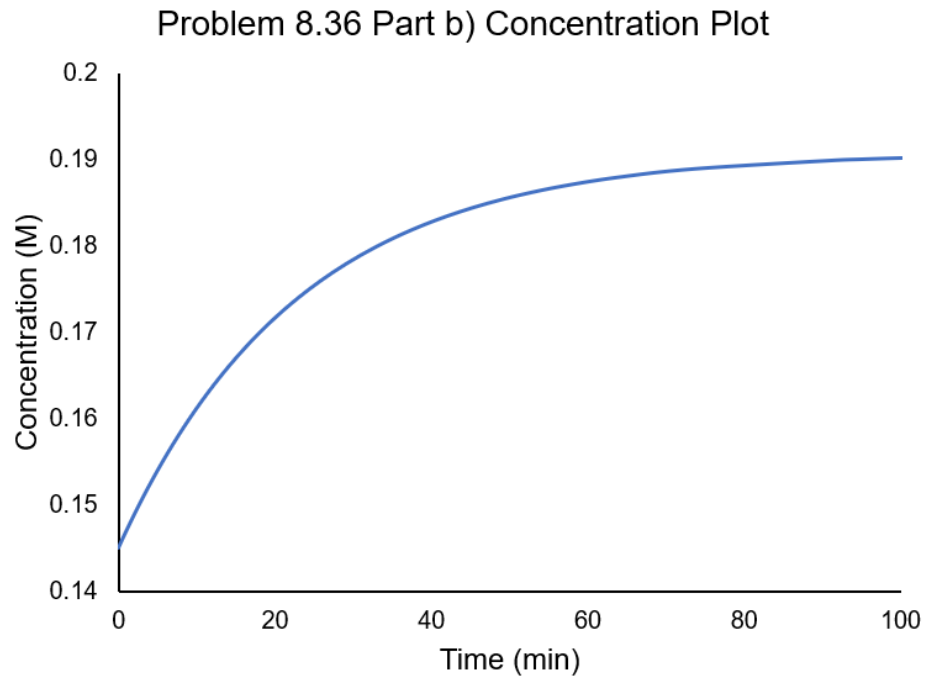
$$\int_{0.145}^{0.175} \frac{dC_A}{\frac{C_{A0}}{\tau} - \frac{C_A}{\tau} - kC_A} = \int_0^t dt$$

$$t = \left[\frac{-\tau \ln(C_{A0} - C_A(1 + \tau k))}{(1 + \tau k)} \right] \Bigg|_{0.145}^{0.175}$$

How long does it take the effluent concentration of species A to equal 0.175 M?

$$t = 24 \text{ min}$$

Prepare a plot of the effluent concentration of species A as a function of time from the time at which the increase is made until 100 min later.



Problem 8.40

A cascade of three identical CSTRs is currently employed to carry out an irreversible pseudo first-order reaction with water (W). The stoichiometry is



Each reactor has a volume of 500 gallons. In the presence of the acid form of an ion-exchange resin currently employed as a catalyst, the reaction is known to be first-order in species P, but the effective rate constant currently associated with this catalyst is uncertain because of losses of the solid maintained in suspension to attrition. If the cascade is operated such that the temperature of the contents of each reactor is 50°C, a flow rate of 25 gal/min leads to an overall conversion of species P of 93.6% (for the cascade). The concentration of species P in the feed stream is 2.2 M.

- (a) What is the value of the pseudo first-order rate constant for these operating conditions? What are the concentrations of species P and R leaving each reactor?
- (b) Consider the possibility of increasing by 40% the production capacity of the reactor network described above by employing different temperatures in the reactors in the cascade subject to the following constraints:
1. The overall conversion is to be held constant at 93.6%. The new feed rate is to be 35 gal/min.
 2. The first reactor in the cascade is to continue to operate at 50°C. The second and third reactors are both to operate at the same temperature, but this temperature remains to be determined.

Address the following questions: At what temperature should the second and third reactors be operated if the activation energy for the reaction is 18 kcal/mol? What are the concentrations of species P and R leaving each reactor?

A cascade of CSTR can be generally described using the following equation:

$$\tau = \frac{V_{Ri}}{v_0} = \frac{C_{A,(i-1)} - C_{A,i}}{-r_{Ai}}$$

Since the reaction is first-order in species P, the rate law can be written as:

$$r_p = -kC_P$$

Plug and solve for C_p :

$$\tau = \frac{V_{Ri}}{v_0} = \frac{C_{P,(i-1)} - C_{P,i}}{kC_{P,i}}$$
$$\tau k C_{P,i} + C_{P,i} = C_{P,(i-1)}$$
$$C_{P,i} = \frac{C_{P,(i-1)}}{(1 + \tau k)}$$

Assuming the consumption of water in the reaction is negligible to the change in reaction volume. Then, reactors that all have the same temperature and volume, the equation can be further generalized to:

$$C_{P,i} = \frac{C_{P0}}{(1 + \tau k)^i}$$

Solve for k when $C_{P,i} = C_{P0}(1 - f) = 0.064 C_{P0}$

$$\tau = \frac{V_{Ri}}{v_0} = \frac{500 \text{ gal}}{25 \text{ gal/min}} = 20 \text{ min}$$

$$C_{P,i} = \frac{C_{P0}}{(1 + \tau k)^i}$$
$$(1 + 20k)^3 = \frac{C_{P0}}{0.064 C_{P0}}$$

What is the value of the pseudo first-order rate constant for these operating conditions?

$$k = 0.075 \text{ min}^{-1}$$

To find the concentration of both P and R in each reactor's effluent stream:

$$C_{P,i} = \frac{C_{P0}}{(1 + \tau k)^i}$$

And that

$$C_{R,i} = C_{P0} - C_{P,i}$$

What are the concentrations of species P and R leaving each reactor?

| Reactor | C _p (M) | C _R (M) |
|---------|--------------------|--------------------|
| 1 | 0.88 | 1.32 |
| 2 | 0.35 | 1.85 |
| 3 | 0.14 | 2.06 |

Given that the activation energy of the reaction is 18 kcal/mol, we can relate the reaction constant to the temperature of the reactor with the Arrhenius equation

$$k = Ae^{\frac{-E_a}{RT}}$$

For R is the ideal gas constant, 0.001987 kcal/(mol K).

Solve for the first reactor individually:

$$\tau = \frac{V_{Ri}}{v_0} = \frac{500 \text{ gal}}{35 \text{ gal/min}} = 14.3 \text{ min}$$

$$k_{\text{Reactor 1}} = 0.075 \text{ min}^{-1}$$

$$C_{P,1} = \frac{C_{P0}}{(1 + \tau k)} = \frac{2.2 \text{ M}}{(1 + 1.07)} = 1.06 \text{ M}$$

$$C_{R,1} = C_{P0} - C_{P,1} = 1.14 \text{ M}$$

Use C_{p,1} as the feed to solve for reaction condition in reactor 2 and 3:

$$C_{P,3} = \frac{C_{P0}}{(1 + \tau k)^{(3-1)}}$$

$$0.064C_{P0} = \frac{C_{P,i}}{(1 + \tau k)^2}$$

$$0.1408 \text{ M} = \frac{1.06 \text{ M}}{(1 + 14.3k)^2}$$

$$k = 0.122 \text{ min}^{-1}$$

Find the corresponding temperature:

$$k = Ae^{\frac{-E_a}{RT}}$$

$$\frac{k_1}{k_2} = e^{\frac{-E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$\ln \frac{k_1}{k_2} = \frac{-E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{0.075 \text{ min}^{-1}}{0.122 \text{ min}^{-1}} = \frac{-18 \text{ kcal/mol}}{0.001987 \text{ kcal}/(\text{mol K})} \left(\frac{1}{323 \text{ K}} - \frac{1}{T_2} \right)$$

At what temperature should the second and third reactors be operated if the activation energy for the reaction is 18 kcal/mol?

$$T_2 = 328.7 \text{ K} = 55.7 \text{ }^\circ\text{C}$$

Plug in new k value to solve for the concentration in reactor 2:

$$C_{P,2} = \frac{C_{P,1}}{(1 + \tau k)} = \frac{1.06 \text{ M}}{(1 + 1.74)} = 0.39 \text{ M}$$

$$C_{R,2} = C_{P0} - C_{P,2} = 1.81 \text{ M}$$

What are the concentrations of species P and R leaving each reactor?

| Reactor | C _p (M) | C _R (M) |
|---------|--------------------|--------------------|
| 1 | 1.06 | 1.14 |
| 2 | 0.39 | 1.81 |
| 3 | 0.14 | 2.06 |