REB, The Book
Example 7.4.2 Solution

A jacketed, 10 L BSTR is going to be used to process an aqueous solution of A and B. The reactor jacket is perfectly mixed with a volume of 1400 cm^3, a heat transfer coefficient of 138 cal ft^{-2} min^{-1} K^{-1} and a heat transfer area of 1200 cm^2. Cooling water at 40 °C flows into the jacket at a rate of 100 g min^{-1}. Both the reacting fluid and the cooling water may be taken to have a density of 1 g cm^{-3} and a heat capacity of 1 cal g^{-1} K^{-1}.

Solutions containing A, B, X, Y, and Z are ideal, and there is no heat of mixing. The reactor will be charged by mixing two separate solutions, one containing only reagent A and the other containing only reagent B, giving a 10 L charge with initial concentrations of 5 mol A $L^{-1}$and 7 mol B L^{-1}. At the time the reactor is charged, the cooling water temperature is 40 °C. Reactions (1) and (2) will occur in the reactor. The heat of reaction (1) is −16.7 kcal mol^{-1}, and that for reaction (2) is −14.3 kcal mol^{-1}. The rate expression for reaction (1) is given in equation (3) where the pre-exponential factor for the rate coefficient is 9.74 x 10^9 L mol^{-1} min^{-1} and the activation energy is 20.1 kcal mol^{-1}. The rate expression for reaction (2) is given in equation (4) where the pre-exponential factor for the rate coefficient is 2.38 x 10^{13} min^{-1} and the activation energy is 25.3 kcal mol^{-1}.

What initial temperature is needed in order to convert 45% of the A in 30 min, and with that initial temperature what will the final temperature, the outlet exchange fluid temperature, and the selectivity for X over Z equal? Discuss ways to increase the selectivity.

$$A + B \rightarrow X + Y \tag{1}$$

$$A \rightarrow Z \tag{2}$$

$$r_1 = k_1 C_A C_B \tag{3}$$

$$r_2 = k_2 C_A \tag{4}$$

Assignment Summary

Reactions

$$A + B \rightarrow X + Y \quad (1)$$

$$A \rightarrow Z \quad (2)$$

Rate Expressions

$$r_1 = k_1 C_A C_B \quad (3)$$

$$r_2 = k_2 C_A \quad (4)$$

Reactor: liquid-phase, non-isothermal BSTR

Given Constants: V = 10 L, V_{ex}= 1.4 L, U = 138 cal ft^{-2} min^{-1} K^{-1}, A = 1200 cm^2, $T_{ex,in}$ = 40 °C, $\dot{m}_{ex}$ = 100 g min^{-1}, ρ = 1.0 g cm^{-3}, ρ_{ex} = 1.0 g cm^{-3}, $\tilde{C}_p$ = 1.0 cal g^{-1} K^{-1}, $\tilde{C}_{p,ex}$ = 1.0 cal g^{-1} K^{-1}, $C_{A,0}$ = 5.0 M, $C_{B,0}$ = 7.0 M, $T_{ex,0}$ = 40 °C, ΔH_1 = –16.7 kcal mol^{-1}, ΔH_2 = –14.3 kcal mol^{-1}, $k_{0,1}$ = 9.74 x 10^9 L mol^{-1} min^{-1}, E_1 = 20.1 kcal mol^{-1}, $k_{0,2}$ = 2.38 x 10^{13} min^{-1}, E_2 = 25.3 kcal mol^{-1}, $f_{A,f}$ = 0.45, and t_f = 30 min.

Deliverables: T_0, T_f, $T_{ex,f}$, and $S_{X/Z,f}$

Formulation of the Equations

Reactor Model Equations:

$$\frac{dn_A}{dt} = \left(-r_1 - r_2\right) V \quad (5)$$

$$\frac{dn_B}{dt} = - r_1 V \quad (6)$$

$$\frac{dn_X}{dt} = r_1 V \quad (7)$$

$$\frac{dn_Y}{dt} = r_1 V \quad (8)$$

$$\frac{dn_Z}{dt} = r_2 V \tag{9}$$

$$\frac{dT}{dt} = \frac{\dot{Q} - V\left(r_1 \Delta H_1 + r_2 \Delta H_2\right)}{\tilde{C}_p \rho V} \tag{10}$$

$$\frac{dT_{ex}}{dt} = \frac{-\dot{Q} - \dot{m}_{ex}\tilde{C}_{p,ex}\left(T_{ex} - T_{ex,in}\right)}{\rho_{ex} V_{ex} \tilde{C}_{p,ex}} \tag{11}$$

Reactor Model Variables: t, n_A, n_B, n_X, n_Y, n_Z, T, and T_{ex}

Additional Computable Unknowns: r_1, k_1, C_A, C_B, r_2, k_2, and $\dot{Q}$

$$k_i = k_{0,i} \exp\left(\frac{-E_i}{RT}\right) \quad i = 1 \text{ and } 2 \tag{12}$$

$$C_i = \frac{n_i}{V} \quad i = A \text{ and } B \tag{13}$$

$$\dot{Q} = UA\left(T_{ex} - T\right) \tag{14}$$

Additional Coupled Unknown: T_0

$$T_0 \; : \; n_A\Big|_{t=t_f} = n_{A,f} \qquad \Rightarrow \qquad 0 = n_A\Big|_{t=t_f} - n_{A,f} = \epsilon_{T_0} \tag{15}$$

ATE Solver Inputs:

1. Initial guesses for the coupled unknown, T_0

$$T_{0,guess} = T_{ex,in} + 5\,K \tag{16}$$

2. Residuals function that
    a. receives a guess for T_0
    b. uses it to solve the BSTR design equations
    c. returns the residual ϵ_{T_0}

IVODE Solver Inputs:

1. Initial values of the reactor model variables given in Table 1
2. Stopping criterion that t equals the final value shown in Table 1.
3. Derivatives function that
   a. receives the reactor model variables (t, n_A, n_B, n_X, n_Y, n_Z, T, and T_{ex}) at the start of an integration step
   b. returns the corresponding values of the reactor model derivatives

Table 1. Initial and final values of the design equation variables.-1

Variable	Initial Value	Final Value
t	0	t_f
n_A	$n_{A,0} = C_{A,0}V$	$n_{A,f} = n_{A,0}\left(1 - f_{A,f}\right)$
n_B	$n_{B,0} = C_{B,0}V$	
n_X	0	
n_Y	0	
n_Z	0	
T	T_0	
T_{ex}	$T_{ex,0}$	

Deliverables Equations:

$$T_f = \underline{T}\Big|_{t_f} \tag{17}$$

$$T_{ex,f} = \underline{T}_{ex}\Big|_{t_f} \tag{18}$$

$$S_{X/Z,f} = \left.\left(\frac{n_X}{n_Z}\right)\right|_{t_f} \tag{19}$$

Implementation of the Calculations

The Python script, example_7_4_2.py, that was written to perform the calculations accompanies this solution. It defines a BSTR model function and a BSTR derivatives function that solve the BSTR design equations, (5) through (11), given an initial temperature. T_0. It also defines a coupled unknown residual function that uses a guess for T_0 to solve the design equations and calculate the residual, ϵ_{T_0}, corresponding to the implicit equation for T_0, equation (15). The calculations start by solving equation (15) for T_0 using an ATE solver. That result is then used to solve the BSTR design equations, after which the deliverables are calculated.

Results and Discussion

The initial temperature must be 65 °C for the conversion to equal 45% after 30 min of reaction. At that time, the temperature of the reacting fluid will be 92.5 °C, the exit temperature of the exchange fluid will be 68.2 °C, and the selectivity will equal 4.2 mol X per mol Z.

When two reactions are taking place, it is quite common for the product of one reaction to be desired and the product of the other reaction to be undesired. That raises the question, "what can a reaction engineer do to change the selectivity?" There isn't a single, universal answer to that question. However, for parallel reactions it is often useful to write an expression for the instantaneous selectivity. In this system, the instantaneous selectivity for X over Z is given by the net rate of generation of X divided by the net rate of generation of Z as shown in equation (20).

$$S_{X/Z,inst} = \frac{\sum_j r_{X,j}}{\sum_j r_{Z,j}} = \frac{r_1}{r_2} = \frac{k_1 C_A C_B}{k_2 C_A} = \frac{k_{0,1}\exp\left(\frac{-E_1}{RT}\right)}{k_{0,2}\exp\left(\frac{-E_2}{RT}\right)} C_B$$

$$S_{X/Z,inst} = \frac{k_{0,1}}{k_{0,2}} \exp\left(\frac{E_2 - E_1}{RT}\right) C_B \qquad (20)$$

The final selectivity will equal the integral of the instantaneous selectivity from t_0 to t_f. Noting that E_2 is greater than E_1, equation (20) suggests two ways to increase the instantaneous selectivity for X over Z. The first is to maintain a high concentration of B. The second is to decrease the mean temperature during the reaction. In a batch reactor, the only way to increase the average concentration of B is to increase the initial amount. The average temperature could be decreased by using a lower initial temperature or by changing the exchange fluid flow rate or inlet temperature. One point to bear in mind is that decreasing the mean temperature will decrease both reaction rates, not just the undesired rate. As a consequence, to keep the conversion the same, a longer reaction time would be necessary.

To test these predictions, a simulation was performed where the initial temperature was reduced to 55 °C, keeping the conversion the same at 45%. The results showed that the selectivity will increase to 5.5 mol X per mol Z, but the reaction time will increase to 87 min. Given economic data and other operating constraints, an engineer could optimize the performance of this reactor through simulation of this kind.

Deliverables

In order to convert 45% of the A in 30 min, an initial temperature of 65 °C is required. With that initial temperature, the temperature of the reacting fluid will be 92.5 °C, the exit temperature of the exchange fluid will be 68.2 °C, and the selectivity will equal 4.2 mol X per mol Z.