REB, The Book
Example 6.6.3 Solution

To produce Z via reaction (1), reagent A will be fed to an adiabatic 0.5 m^3 CSTR at 70 mol min^{-1}, and B will be fed at 1500 mol min^{-1} giving a total liquid feed rate of 40 L min^{-1}. The rate expression for reaction (1) is given in equation (2), where the pre-exponential factor for the rate coefficient is 1.2 x 10^9 m^3 mol^{-1} min^{-1} and the activation energy is 25.8 kcal mol^{-1}. The equilibrium constant appearing in the rate expression can be calculated using equation (3), where the pre-exponential factor is 4.2 x 10^{-18} m^3 mol^{-1} and the heat of reaction is –22.4 kcal mol^{-1}. The heat capacities of A, B, and Z are 412, 75.5, and 512 J mol^{-1} K^{-1}, respectively, and may be taken to be independent of temperature. What feed temperature will maximize the conversion of A?

$$A + B \rightarrow Z \tag{1}$$

$$r_1 = k_1 C_A C_B \left(1 - \frac{C_Z}{K_1 C_A C_B}\right) \tag{2}$$

$$K_1 = K_{0,1} \exp\left(\frac{-\Delta H_1}{RT}\right) \tag{3}$$

Assignment Summary

Reaction

$$A + B \rightarrow Z \tag{1}$$

Rate Expression

$$r_1 = k_1 C_A C_B \left(1 - \frac{C_Z}{K_1 C_A C_B}\right) \tag{2}$$

$$K_1 = K_{0,1} \exp\left(\frac{-\Delta H_1}{RT}\right) \tag{3}$$

Reactor: Adiabatic, steady-state CSTR

Given Constants: V = 0.5 m^3, $\dot{n}_{A,in}$ = 70 mol min^{-1}, $\dot{n}_{B,in}$ 1500 mol min^{-1}, $\dot{V}_{in}$ = 40 L min^{-1} $k_{0,1}$ = 1.2 x 10^9 m^3 mol^{-1} min^{-1}, E_1 = 25.8 kcal mol^{-1}, $K_{0,1}$ = 4.2 x 10^{-18} m^3 mol^{-1}, ΔH_1 = –22.4 kcal mol^{-1} $\hat{C}_{p,A}$ = 412 J mol^{-1} K^{-1}, $\hat{C}_{p,B}$ = 75.5 J mol^{-1} K^{-1}, and $\hat{C}_{p,Z}$ = 512 J mol^{-1} K^{-1}

Parameter: T_{in}

Deliverables: $f_{A,max} = \max_{T_{in}} \left(f_A\right)$, $T_{in,opt} = \arg\max_{T_{in}} \left(f_A\right)$, $T\Big|_{T_{in}=T_{in,opt}}$

Formulation of the Equations

Reactor Model Equations:

$$0 = \dot{n}_{A,in} - \dot{n}_A - Vr_1 = \epsilon_1 \tag{4}$$

$$0 = \dot{n}_{B,in} - \dot{n}_B - Vr_1 = \epsilon_2 \tag{5}$$

$$0 = -\dot{n}_Z + Vr_1 = \epsilon_3 \tag{6}$$

$$0 = -\left(\dot{n}_{A,in}\hat{C}_{p,A} + \dot{n}_{B,in}\hat{C}_{p,B}\right)\left(T - T_{in}\right) - Vr_1\Delta H_1 = \epsilon_4 \tag{7}$$

Reactor Model Variables: $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_Z$, and T

Additional Computable Unknowns: r_1, k_1, C_A, $\dot{V}$, C_B, C_Z, and K_1

$$r_1 = k_1 C_A C_B \left(1 - \frac{C_Z}{K_1 C_A C_B}\right) \tag{2}$$

$$k_1 = k_{0,1}\exp\left(\frac{-E_1}{RT}\right) \tag{8}$$

$$C_A = \frac{n_A}{\dot{V}} \tag{9}$$

$$\dot{V} = \dot{V}_{in}$$

$$C_B = \frac{n_B}{\dot{V}} \tag{11}$$

$$C_Z = \frac{n_Z}{\dot{V}} \tag{12}$$

$$K_1 = K_{0,1} \exp\left(\frac{-\Delta H_1}{RT}\right) \tag{3}$$

Additional Uncomputable Unknown: T_{in}

$$\underline{T}_{in} = \left(\left[75,\cdots,125\right] + 273.15\right) \text{ K} \tag{13}$$

ATE Solver Inputs:

1. Initial guesses for the reactor model variables.

$$\forall T_{in,n} \in \underline{T}_{in} \qquad \begin{matrix} n = 1 \\ \\ \\ n > 1 \end{matrix} \qquad \begin{pmatrix} \dot{n}_{A,guess} = \dot{n}_{A,in} \\ \dot{n}_{B,guess} = \dot{n}_{B,in} \\ \dot{n}_{Z,guess} = \dot{n}_{Z,in} \\ T_{guess} = T_{in,n} + 5K \end{pmatrix} \\ \begin{pmatrix} \dot{n}_{A,guess} = \dot{n}_A\big|_{T_{in,n-1}} \\ \dot{n}_{B,guess} = \dot{n}_B\big|_{T_{in,n-1}} \\ \dot{n}_{Z,guess} = \dot{n}_Z\big|_{T_{in,n-1}} \\ T_{guess} = T\big|_{T_{in,n-1}} \end{pmatrix} \tag{14}$$

2. Residuals function that
    a. receives guesses for the reactor model variables
    b. returns the residuals corresponding to the reactor model equations

Deliverables Equations:

$$\forall T_{in,n} \in \underline{T}_{in} \qquad f_{A,n} = \frac{\dot{n}_{A,in} - \dot{n}_A\Big|_{T_{in,n}}}{\dot{n}_{A,in}} \tag{15}$$

$$f_{A,max} = \max_{T_{in}} \left(\underline{f}_A \right) \tag{16}$$

$$T_{in,opt} = \arg\max_{T_{in}} \left(\underline{f}_A \right) \tag{17}$$

$$T\Big|_{T_{in}=T_{in,opt}} \tag{18}$$

Implementation of the Calculations

The Python script, example_6_6_3.py, that was written to perform the calculations accompanies this solution.

Results and Discussion

A range of inlet temperatures between 75 and 125 °C was chosen for analysis, equation (13). The ATE solver converged for the initial guess shown in equation (14). Figure 1 shows the conversion for each inlet temperature in the range. The conversion does pass through a maximum, indicating that the chosen range of inlet temperatures did not need to be adjusted.

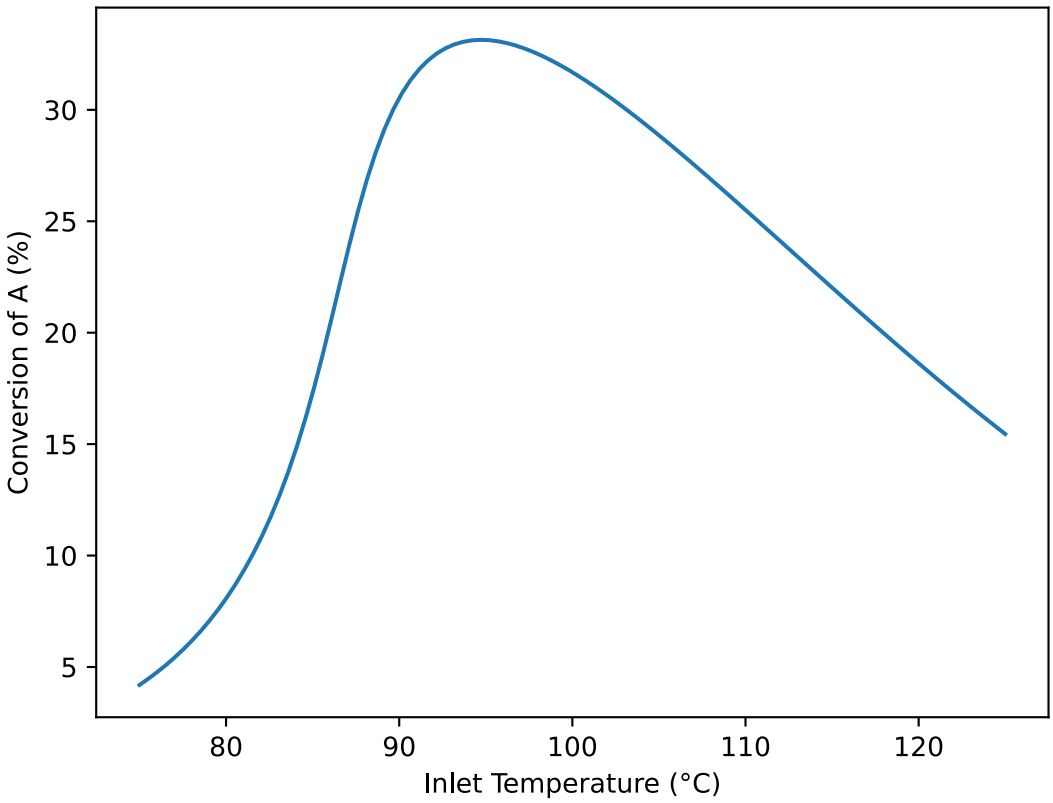

Figure 1. Conversion as a function of inlet temperature.

The calculations began at the lowest inlet temperature and then proceeded successively through the rest of the inlet temperatures. The curve does not show any discontinuities, which might occur if the solution jumped between different steady states. It is more likely, however, that the solutions are all for the same steady state, because the results from one inlet temperature were used as the guess for the next. The design equations for the first inlet temperature in the range were solved a second time using a very large guess for the temperature, and the same steady state was found. These results suggest that multiple steady states did not exist.

The results shown in Figure 1 agree with qualitative expectations. For any feed temperature heat will be released by reaction leading to an outlet temperature that is greater than the inlet temperature. The rate expression, equation (2), contains two temperature dependent terms, namely the rate coefficient, k_1, and the equilibrium

constant, K_1. The rate coefficient increases as the temperature increases, but the equilibrium constant decreases. Looking at the rate expression, the rate will increase as k_1 increases. As K_1 decreases with increasing temperature, the second term in parentheses increases. Because the second term is being subtracted from 1, the term in parentheses decreases. To summarize, as the temperature increases, k_1 increases and this alone would cause the rate to increase. As the temperature increases K_1 decreases, and this alone would cause the rate to decrease.

At lower feed temperatures, the reaction has not come close to equilibrium. As the temperature increases, the effect upon k_1 predominates and the rate increases. Consequently, the conversion increases. At intermediate feed temperatures, the reaction begins to approach thermodynamic equilibrium. As the temperature increases both k_1 and K_1 affect the rate, and consequently the rate, and by extension, the conversion, rises less steeply. At some temperature, the effects of k_1 and K_1 on the rate become equal and the rate (and conversion) reaches a maximum. At still higher temperatures, the reaction becomes close to thermodynamic equilibrium. At this point, as the temperature increases, the effect of K_1 predominates and the rate, while still positive, decreases with increasing temperature. Consequently, as the rate decreases, the conversion decreases.

Deliverables

The maximum conversion, 33%, occurs at an inlet temperature of 95 °C, and the corresponding outlet temperature is 110 °C. Lower inlet temperatures result in a lower rate that yields lower conversions. At higher temperatures, thermodynamic equilibrium limits the conversion. Because the reaction is exothermic, the equilibrium conversion decreases as the temperature increases. Thus the maximum in the conversion is due to the opposing effects of temperature on the rate coefficient and the equilibrium constant.