REB, The Book
Example 6.6.2 Solution

Reactants A and B can react irreversibly to produce either a desired product, D, or an undesired product, U, as shown in equations (1) and (2). The rate expressions for reactions (1) and (2) are given in equations (3) and (4), respectively. In those rate expressions, the pre-exponential factors for k_1 and k_2 are 10.2 gal mol^{-1} min^{-1} and 17.0 gal mol^{-1} min^{-1}, respectively, and the activation energies are 15.3 kJ mol^{-1} and 23.7 kJ mol^{-1}, respectively. A liquid mixture containing 10 mol A gal^{-1} and 12 mol B gal^{-1} at 350 K is fed to an adiabatic 25 gal CSTR at a rate of 12.5 gal min^{-1}. If the standard heats of reactions (1) and (2) at 298 K are -12.0 and -21.3 kJ mol^{-1}, respectively, and if the reagents form an ideal liquid mixture with the temperature-independent heat capacities of A, B, D and U equal to 85, 125, 200 and 170 J mol^{-1} K^{-1}, what are the conversion of the limiting reagent, the outlet selectivity (in mol D per mol U) and the outlet temperature?

$$A + B \rightarrow D \qquad (1)$$

$$A + B \rightarrow U \qquad (2)$$

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

$$r_2 = k_2 C_A C_B \qquad (4)$$

Assignment Summary

Reactions

$$A + B \rightarrow D \qquad (1)$$

$$A + B \rightarrow U \qquad (2)$$

Rate Expressions

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

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

Reactor: Adiabatic, liquid-phase, steady-state CSTR

Given Constants: $k_{0,1}$ = 10.2 gal mol^{-1} min^{-1}, $k_{0,2}$ = 17.0 gal mol^{-1} min^{-1}, E_1 = 15.3 kJ mol^{-1}, E_2 = 23.7 kJ mol^{-1}, $C_{A,in}$ = 10 mol gal^{-1}, $C_{B,in}$ = 12 mol gal^{-1}, T_{in} = 350 K, V = 25 gal, $\dot{V}_{in}$ = 12.5 gal min^{-1}, $\Delta H_1\Big|_{298K}$ = –12.0 kJ mol^{-1}, $\Delta H_2\Big|_{298K}$ = –21.3 kJ mol^{-1}, $\hat{C}_{p,A}$ = 85 J mol^{-1} K^{-1}, $\hat{C}_{p,B}$ = 125 J mol^{-1} K^{-1}, $\hat{C}_{p,D}$ = 200 J mol^{-1} K^{-1}, and $\hat{C}_{p,U}$ = 170 J mol^{-1} K^{-1}.

Deliverables: f_A, $S_{D/U}$, and T

Formulation of the Equations

Reactor Model Equations:

$$0 = \dot{n}_{A,in} - \dot{n}_A + V\left(-r_1 - r_2\right) = \epsilon_1 \tag{5}$$

$$0 = \dot{n}_{B,in} - \dot{n}_B + V\left(-r_1 - r_2\right) = \epsilon_2 \tag{6}$$

$$0 = -\dot{n}_D + V r_1 = \epsilon_3 \tag{7}$$

$$0 = -\dot{n}_U + V r_2 = \epsilon_4 \tag{8}$$

$$\begin{aligned} 0 = &-\left(\dot{n}_{A,in}\hat{C}_{p,A} + \dot{n}_{B,in}\hat{C}_{p,B}\right)\left(T - T_{in}\right) \\ &-V\left(r_1 \Delta H_1 + r_2 \Delta H_2\right) = \epsilon_5 \end{aligned} \tag{9}$$

Reactor Model Variables: $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_D$, $\dot{n}_U$, and T.

Additional Computable Unknowns: $\dot{n}_{A,in}$, r_1, k_1, C_A, C_B, $\dot{V}$, r_2, k_2, $\dot{n}_{B,in}$, ΔH_1, and ΔH_2.

$$\dot{n}_{A,in} = \dot{C}_{A,in}\dot{V}_{in} \tag{10}$$

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

$$k_1 = k_{0,1}\exp\left(\frac{-E_1}{RT}\right) \tag{11}$$

$$C_A = \frac{\dot{n}_A}{\dot{V}_{in}} \tag{12}$$

$$C_B = \frac{\dot{n}_B}{\dot{V}_{in}} \tag{13}$$

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

$$k_2 = k_{0,2} \exp\left(\frac{-E_2}{RT}\right) \tag{14}$$

$$\dot{n}_{B,in} = \dot{C}_{B,in}\dot{V}_{in} \tag{15}$$

$$\Delta H_1 = \Delta H_1\Big|_{298K} + \left(\hat{C}_{p,D} - \hat{C}_{p,A} - \hat{C}_{p,B}\right)(T - 298) \tag{16}$$

$$\Delta H_2 = \Delta H_2\Big|_{298K} + \left(\hat{C}_{p,U} - \hat{C}_{p,A} - \hat{C}_{p,B}\right)(T - 298) \tag{17}$$

<u>ATE Solver Inputs</u>:

1. Initial guesses for the reactor model variables.

$$\dot{n}_{i,guess} = \dot{n}_{i,in} \qquad i = A, B, D, \text{ and } U \tag{18}$$

$$T_{guess} = T_{in} + 5K \tag{19}$$

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

<u>Deliverables Equations</u>:

$$f_A = \frac{\dot{n}_{A,in} - \dot{n}_A}{\dot{n}_{A,in}} \tag{20}$$

$$S_{D/U} = \frac{\dot{n}_D}{\dot{n}_U} \tag{21}$$

Implementation of the Calculations

The Python script, example_6_6_2.py, that was written to perform the calculations accompanies this solution.

Results and Discussion

The ATE solver did converge using the initial guess shown in equations (18) and (19). The conversion of A in the reactor is 54.9%, the selectivity is 8.39 mol D per mol U, and the outlet temperature is 383 K. There could be other steady-states, so the calculations were repeated using a wide range of guesses for the temperature. The solver converged to the same solution in each case, suggesting there are no other steady states. If a more definitive determination, a plot of the outlet temperature as a function of the inlet temperature should be generated and examined to see whether more than one outlet temperatures are possible at the present inlet temperature of 350 K.

The products, D and U, are produced in two parallel reactions. Reactions of this type were analyzed qualitatively in the REB Class 8 Learning Activity. The analysis showed that unlike series reactions (see REB, The Book Example 5.5.2) the reaction time does not strongly affect the selectivity. It suggested that if the activation energies for the two parallel reactions were sufficiently different, the initial temperature might affect the selectivity.

Here the activation energy for reaction (2) is larger than that for reaction (1), so increasing the temperature will increase k_2 more thank_1, resulting in a lower selectivity for D over U. Thus, the selectivity for D over U can be increased by decreasing the temperature. However, if everything else remains fixed, decreasing the temperature will decrease the conversion. That is, decreasing the temperature will increase the selectivity but decrease the conversion while increasing the temperature will decrease the selectivity but increase the conversion.

To verify this prediction, the feed temperature was decreased to 325 K and the calculations were repeated. The selectivity did indeed increase to 10.6 mol D per mol U, and the conversion decreased to 46.7%. Increasing the temperature to 375 K gives a selectivity of6.9 mol D per mol U and a conversion of 61.5%.

Deliverables

Operation of the adiabatic CSTR as described in this assignment results in 54.9% conversion of A with a selectivity of 8.39 mol D per mol U, and an outlet temperature of 383 K.