REB, The Book
Example 6.6.4 Solution

An adiabatic, steady-state CSTR with a volume of 500 cm^3 is going to be used to convert A and B into Y and Z according to reaction (1). A liquid solution flowing at 1.0 cm^3 s^{-1} and containing equal amounts of A and B (0.015 mol cm^{-3}) at 50 °C will be used. The heat capacity of the fluid is essentially equal to that of the solvent, and can be considered to be constant and equal to 0.35 cal g^{-1} K^{-1}. The density of the fluid, also constant, is 0.93 g cm^{-3}. The rate expression for reaction (1) is given in equation (2), and the heat of reaction (1) may be assumed to be constant and equal to –20 kJ mol^{-1}. The rate coefficient displays Arrhenius temperature dependence with a pre-exponential factor equal to 3.24 x 10^{12} cm^3 mol^{-1} s^{-1}, and an activation energy of 105.0 kJ mol^{-1}. How many steady states are possible at these conditions, and what are the conversion and outlet temperature for each of them?

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

$$r_1 = k_1 C_A C_B \tag{2}$$

Assignment Summary

<u>Reaction</u>

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

<u>Rate Expression</u>

$$r_1 = k_1 C_A C_B \tag{2}$$

<u>Reactor</u>: Adiabatic, steady-state CSTR

<u>Given Constants</u>: V = 500 cm^3, $\dot{V}_{in}$ = 1.0 cm^3 s^{-1}, $C_{A,in}$ = 0.015 mol cm^{-3}, $C_{B,in}$ = 0.015 mol cm^{-3}, T_{in} = (50 + 273.15) K, $\tilde{C}_p$ = 0.35 cal g^{-1} K^{-1}, ρ = 0.93 gm cm^{-3}, ΔH_1 = –20 kJ mol^{-1}, $k_{0,1}$ = 3.24 x 10^{12} cm^3 mol^{-1} s^{-1}, and E_1 = 105.0 kJ mol^{-1}.

Parameter:

T for multiplicity plot

Deliverables: f_A and T for each of 3 steady states

Formulation of the Equations

Reactor Model Equations:

$$0 = \dot{n}_{A,in} - \dot{n}_A - Vr_1 = \epsilon_1 \tag{3}$$

$$0 = \dot{n}_{B,in} - \dot{n}_B - Vr_1 = \epsilon_2 \tag{4}$$

$$0 = -\dot{n}_Y + Vr_1 = \epsilon_3 \tag{5}$$

$$0 = -\dot{n}_Z + Vr_1 = \epsilon_4 \tag{6}$$

$$0 = -\dot{V}_{in}\rho\tilde{C}_p\left(T - T_{in}\right) - Vr_1\Delta H_1 = \epsilon_5 \tag{7}$$

Reactor Model Variables:

$\dot{n}_A$, $\dot{n}_B$, $\dot{n}_Y$, $\dot{n}_Z$, and T_{in} for multiplicity plot

$\dot{n}_A$, $\dot{n}_B$, $\dot{n}_Y$, $\dot{n}_Z$, and T for calculating steady states

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

$$\dot{n}_{A,in} = \dot{V}_{in}C_{A,in} \tag{8}$$

$$r_1 = k_1C_AC_B \tag{2}$$

$$k_1 = k_{0,1}\exp\left(\frac{-E_1}{RT}\right) \tag{9}$$

$$C_A = \frac{\dot{n}_A}{\dot{V}} \tag{10}$$

$$\dot{V} = \dot{V}_{in} \tag{11}$$

$$C_B = \frac{\dot{n}_B}{\dot{V}} \tag{12}$$

$$\dot{n}_{B,in} = \dot{V}_{in} C_{B,in} \tag{13}$$

<u>Additional Uncomputable Unknowns:</u>

$$\underline{T} = \left[-25, \cdots, 350\right] + 273.15 \text{ K} \qquad \text{(for multiplicity plot)} \tag{14}$$

<u>ATE Solver Inputs</u>:

1. For multiplicity plot
   a. Initial guesses for the reactor model variables

$$\forall T_n \in \underline{T} \quad \begin{array}{ll} n = 1 & \begin{pmatrix} \dot{n}_{A,guess} = \dot{n}_{A,in} \\ \dot{n}_{B,guess} = \dot{n}_{B,in} \\ \dot{n}_{Z,guess} = 0 \\ T_{in,guess} = T_n - 1K \end{pmatrix} \\ n > 1 & \begin{pmatrix} \dot{n}_{A,guess} = \dot{n}_A \Big|_{T_{n-1}} \\ \dot{n}_{B,guess} = \dot{n}_B \Big|_{T_{n-1}} \\ \dot{n}_{Z,guess} = \dot{n}_Z \Big|_{T_{n-1}} \\ T_{in,guess} = T_{in} \Big|_{T_{n-1}} \end{pmatrix} \end{array} \tag{15}$$

   b. Residuals function that
      i. receives guesses for the reactor model variables
      ii. returns the residuals corresponding to the reactor model equations
2. For calculating steady states
   a. Initial guesses for the reactor model variables.

$$\dot{n}_{i,guess} = \dot{n}_{i,in} \qquad i = A, B, \text{ and } Z \tag{16}$$

$$T_{guess,low} \text{ read from multiplicity plot} \tag{17}$$

$T_{guess,mid}$ read from multiplicity plot (18)

$T_{guess,high}$ read from multiplicity plot (19)

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

Deliverables Equations:

$$f_{A,low} = \frac{\dot{n}_{A,in} - \dot{n}_{A,low}}{\dot{n}_{A,in}} \tag{20}$$

$$f_{A,mid} = \frac{\dot{n}_{A,in} - \dot{n}_{A,mid}}{\dot{n}_{A,in}} \tag{21}$$

$$f_{A,high} = \frac{\dot{n}_{A,in} - \dot{n}_{A,high}}{\dot{n}_{A,in}} \tag{22}$$

Implementation of the Calculations

The Python scripts, example_6_6_4_part_A.py and example_6_6_4_part_B.py, that were written to perform the calculations for the multiplicity and steady states, respectively, accompany this solution.

Results and Discussion

When generating the multiplicity plot, the ATE solver converged with the initial guess in equation (15), and the range of values chosen in equation (14) spanned an appropriate range for the multiplicity plot, which is shown in Figure 1where it can be seen that there indeed are three steady states for inlet temperatures between ca. 4 and 90 °C. The solid red line represents an ignition point and the dashed red line, an extinction point. It is expected that the middle steady states, shown as a dashed black line, will be unstable. Guesses for the steady-state outlet temperatures at an inlet temperature of 50 °C (50, 140, and 270 °C) were read from the multiplicity plot as indicated in equations (17) through (19).

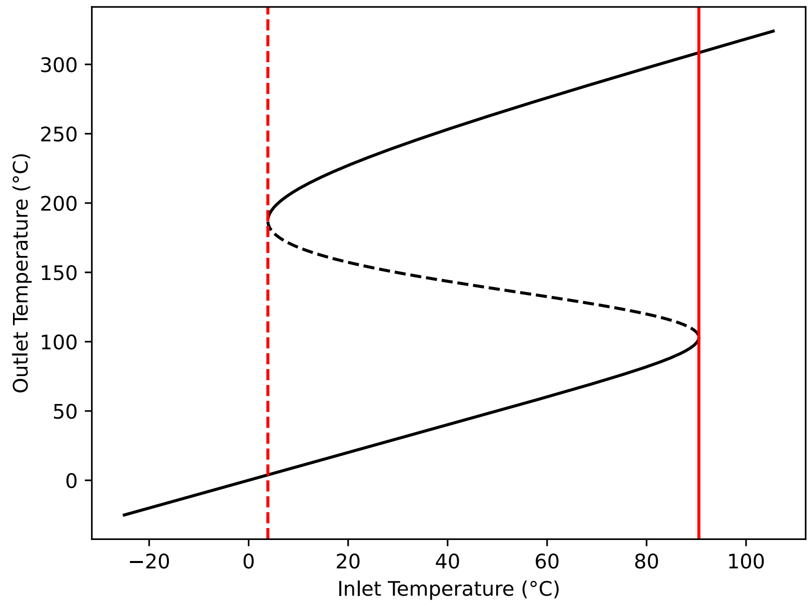

Figure 1. Outlet temperature as a function of inlet temperature.

When calculating the steady states, the ATE solver converged using the low temperature and middle temperature guesses (50 and 140 °C) read from the multiplicity plot. When the high temperature guess read from the multiplicity plot (270 °C) was used, the solver yielded a converged solution, but the conversion was over 100%. Reducing the guess to 240 °C yielded a conversion less than 100%. The results are shown in Table 1.

Table 1. Steady-state conversions and outlet temperatures

Conversion (%)	Outlet Temperature (°C)
0.03	50.1
39.9	138
97.5	265

Deliverables

There is a stable steady state with an outlet temperature of 50.1 °C where the conversion is 0.03%, and one at 265 °C with a conversion of 97.5%. A third, unstable steady state has an outlet temperature of 138 °C and a conversion of 39.9%.