REB, The Book
Example 8.4.1 Solution

A strong acid, A (15 M), at 20 °C is going to be neutralized using a strong base, B (15 M NaOH), also at 20 °C, equation (1). If the acid and the base were simply mixed together, they would react violently, releasing enough energy to raise their temperature to over 225 °C. Instead, a 10 L SBSTR will be used to neutralize 5.0 L of the acid. The acid will initially be present in the reactor, and the base will be added a rate of 0.25 L min^{-1} until 5 L of the base have been added. The reacting fluid will exchange heat with 2.5 L cooling water in a perfectly mixed shell. Chilled water at 20 °C will enter the shell at a rate of 2.5 L min^{-1}. The heat transfer area is 2150 cm^2 and the heat transfer coefficient is 73 cal cm^{-2} h^{-1} K^{-1}. At the time the acid is charged to the reactor, the cooling water temperature within the heat exchanger is 20 °C. The density and heat capacity of the acid solution, base solution, and cooling water can all be taken to be those of water, 1 g cm^{-3} and 1 cal g^{-1} K^{-1}. The neutralization reaction, equation (1), is irreversible with a heat of reaction equal to –13.7 kcal mol^{-1}. The reaction is first order in both acid and base with a pre-exponential factor of 8.11 x 10^{12} L mol^{-1} s^{-1} and an activation energy of 17.7 kcal mol^{-1}, equation (2). The pressure in the reactor will be constant and equal to 1 atm. Plot the acid concentration and the reactor temperature as functions of time while the base is being added.

$$A + B \rightarrow S + W \tag{1}$$

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

Assignment Summary

<u>Reaction</u>

$$A + B \rightarrow S + W \tag{1}$$

<u>Rate Expressions</u>

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

Reactor: Non-isothermal SBSTR

Given Constants: $C_{A,0}$ = 15 M, T_0 = 20 °C, $C_{B,in}$ = 15 M, T_{in} = 20 °C, V = 10 L, V_A = 5.0 L, $\dot{V}_{in}$ = 0.25 L min^{-1}, V_B = 5 L, V_{ex} = 2.5 L, $T_{ex,in}$ = 20 °C, $\dot{V}_{ex,in}$ = 2.5 L min^{-1}, A_{ex} = 2150 cm^2 , U = 73 cal cm^2 h^{-1} K^{-1}, $T_{ex,0}$ = 20 °C, ρ = ρ_{ex} = 1 g cm^{-3}, $\tilde{C}_p$ = $\tilde{C}_{p,ex}$ = 1 cal g^{-1} K^{-1}, ΔH_1 = –13.7 kcal mol^{-1}, $k_{0,1}$ = 8.11 x 10^{12} L mol^{-1} s^{-1}, E_1 = 17.7 kcal mol^{-1}, and P = 1 atm.

Deliverables: $\underline{C_A}$ and $\underline{T}$ vs. $\underline{t}$ as graphs

Formulation of the Equations

Reactor Model Equations:

$$\frac{dn_A}{dt} = -\, r_1 V \tag{3}$$

$$\frac{dn_B}{dt} = \dot{n}_{B,in} - r_1 V \tag{4}$$

$$\frac{dn_S}{dt} = r_1 V \tag{5}$$

$$\frac{dn_W}{dt} = r_1 V \tag{6}$$

$$\rho V \tilde{C}_p \frac{dT}{dt} - P\frac{dV}{dt} = \dot{Q} - \rho \dot{V}_{in} \tilde{C}_p \left(T - T_{in}\right) - V r_1 \Delta H_1 \tag{7}$$

$$\rho V_{ex} \tilde{C}_p \frac{dT_{ex}}{dt} = -\, \dot{Q} - \dot{m}_{ex} \tilde{C}_p \left(T_{ex} - T_{ex,in}\right) \tag{8}$$

$$\frac{dV}{dt} = \dot{V}_{in} \tag{9}$$

Reactor Model Variables: $\underline{t}$, $\underline{n}_A$, $\underline{n}_B$, $\underline{n}_S$, $\underline{n}_W$, $\underline{T}$, $\underline{T}_{ex}$, and $\underline{V}$

Additional Computable Unknowns: k_1, C_A, C_B, $\dot{n}_{B,in}$, $\dot{Q}$, and $\dot{m}_{ex}$

$$k_1 = k_{0,1} \exp\left(\frac{-E_1}{RT}\right) \tag{10}$$

$$C_i = \frac{n_i}{V} \qquad i = A \text{ and } B \tag{11}$$

$$\dot{n}_{B,in} = \dot{V}_{in} C_{B,in} \tag{12}$$

$$\dot{Q} = UA_{ex}\left(T_{ex} - T\right) \tag{13}$$

$$\dot{m}_{ex} = \rho \dot{V}_{ex} \tag{14}$$

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 1.
2. Stopping criterion that V equals the final value shown in Table 1.
3. Residuals/Derivatives function that
    a. receives the reactor model variables at the start of an integration step
    b. calculates the additional unknowns
    c. evaluates and returns the reactor design equation derivatives

$$\frac{dT}{dt} = \frac{\dot{Q} - \rho \dot{V}_{in} \tilde{C}_p \left(T - T_{in}\right) - V r_1 \Delta H_1 + P \dot{V}_{in}}{\rho V \tilde{C}_p} \tag{15}$$

$$\frac{dT_{ex}}{dt} = \frac{-\dot{Q} - \dot{m}_{ex} \tilde{C}_p \left(T_{ex} - T_{ex,in}\right)}{\rho V_{ex} \tilde{C}_p} \tag{16}$$

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

Variable	Initial Value	Final Value
t	0	
n_A	$n_{A,0} = C_{A,0}V_A$	
n_B	0	
n_S	0	
n_W	0	
T	T_0	
T_{ex}	$T_{ex,0}$	
V	$V_0 = V_A$	$V_f = V_A + V_B$

Deliverables Equation:

$$\underline{C}_A = \frac{\underline{n}_A}{\underline{V}} \tag{17}$$

Implementation of the Calculations

The Python script, example_8_4_1.py, that was written to perform the calculations accompanies this solution. It defines an SBSTR model function and and SBSTR derivatives function that solve the design equations using an IVODE solver. Those functions are used to calculate the reactor model variables and generate the requested graphs.

Results and Discussion

The design equations were solved as described above. The concentration of acid during the time when base is being added to the reactor is shown in Figure 1, and the temperature during that time is shown in Figure 2. The concentration decreases steadily for two reasons. First, it is being diluted by the added base and second it is reacting with the base. The final concentration of acid is less than 0.02 M.

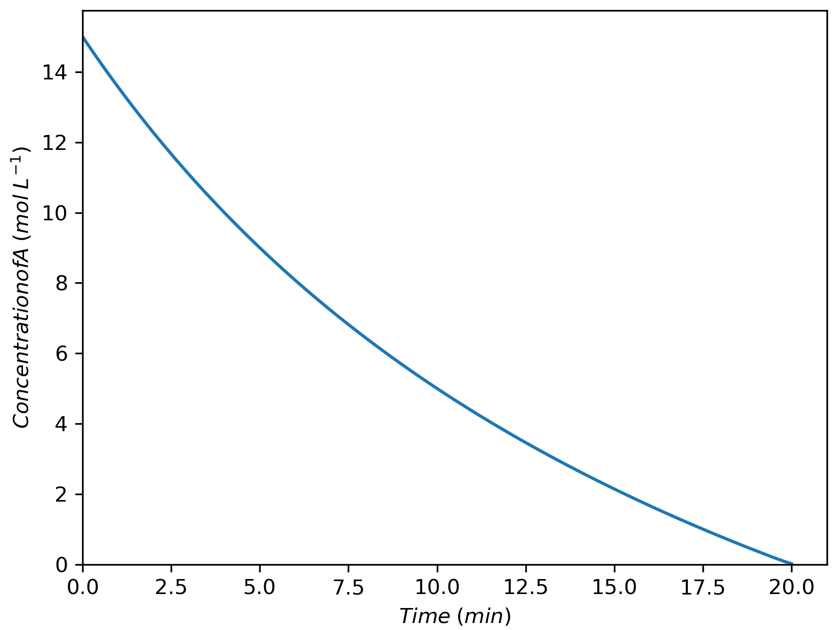

Figure 1. Concentration of acid while base is being added to the SBSTR.

The temperature increases steadily during processing. This indicates that heat is being released by the reaction faster than it is being removed by the external cooling fluid. The assignment narrative noted that if the concentrated acid and base were mixed instantaneously, they would react violently and release sufficient heat to raise the temperature to 225 °C. The heat exchanger would not be able to remove heat that rapidly enough to keep the temperature under control. Figure 2 shows that by operating as an SBSTR and adding the base slowly over time, the temperature can be safely controlled. The final temperature is 52.7 °C.

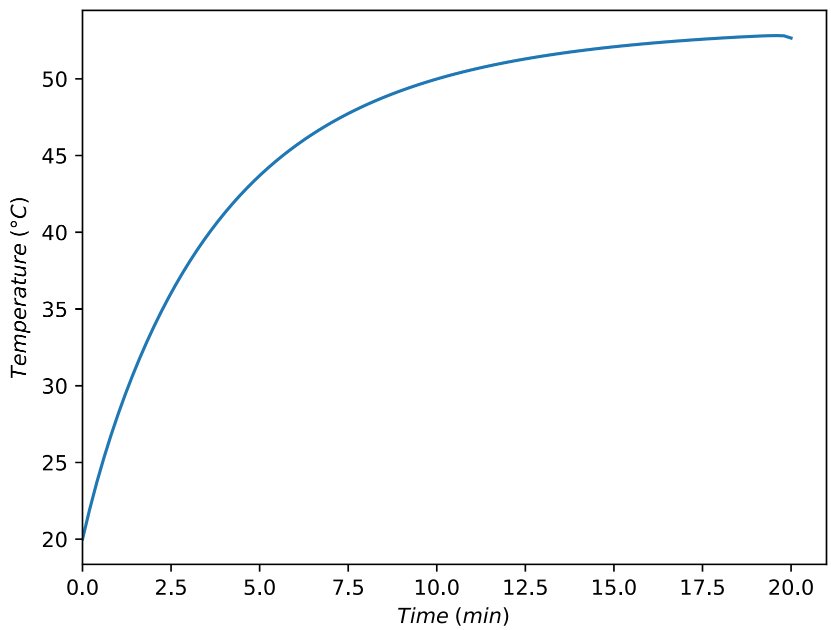

Figure 2. Reacting fluid temperature while base is being added to the SBSTR.

Deliverables

The concentration and temperature profiles during the addition of the base to the SBSTR are shown in Figures 1 and 2, respectively. At the instant the addition of the base to the reactor is completed, the concentration of acid is less than 0.02 M and the temperature of the reacting fluid is 52.7 °C