REB, The Book
Example 7.4.1 Solution

The liquid-phase reaction between A and B, equation (1), is irreversible. At the conditions of interest, the heat of reaction is constant and equal to –101.2 kJ mol^{-1}. The rate expression is given in equation (2), where the rate coefficient exhibits Arrhenius temperature dependence with a pre-exponential factor of 5.11 x 10^4 L mol^{-1} s^{-1} and an activation energy of 74.8 kJ mol^{-1}.

Two solutions, one containing only reagent A at 180 °C and one containing only reagent B at 180 °C, are charged to an adiabatic BSTR producing 1900 L of solution initially containing 2.9 mol A L^{-1} and 3.2 mol B L^{-1} at 180 °C. The solution is ideal and has a constant heat capacity of 1.23 cal g^{-1} K^{-1} and a constant density of 1.02 g cm^{-3}. Plot the concentrations of A, B, Y, and Z, the reacting fluid temperature, and the instantaneous reaction rate for the first 2 h of reaction, and comment upon the shapes of the graphs.

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

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

Assignment Summary

Reaction

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

Rate Expression

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

Reactor: liquid-phase, adiabatic BSTR

Given Constants: ΔH_1 = –101.2 kJ mol^{-1}, $k_{0,1}$ = 5.11 x 10^4 L mol^{-1} s^{-1}, E_1 = 74.8 kJ mol^{-1}, T_0 = 180 °C, V = 1900 L, $C_{A,0}$ = 2.9 mol A L^{-1}, $C_{B,0}$ = 3.2 mol B L^{-1}, $\tilde{C}_p$ = 1.23 cal g^{-1} K^{-1}, ρ = 1.02 g cm^{-3}, and t_f = 2 h.

Deliverables: C_A, C_B, C_Y, C_Z, T, and r_1 vs. t as graphs

Formulation of the Equations

Reactor Model Equations:

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

$$\frac{dn_B}{dt} = -r_1 V \tag{4}$$

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

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

$$\frac{dT}{dt} = -\frac{r_1 \Delta H_1}{\rho \tilde{C}_p} \tag{7}$$

Reactor Model Variables: t, n_A, n_B, n_Y, n_Z, and T

Additional Computable Unknowns: r_1, k_1, C_A, C_B

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

$$C_i = \frac{n_i}{V} \quad i = A \text{ and } B \tag{9}$$

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 1
2. Stopping criterion that t equals the final value shown in Table 1
3. Derivatives function that
    a. receives the BSTR model variables (t, n_A, n_B, n_Y, n_Z, and T) at the start of an integration step

b. returns the corresponding values of the CSTR model derivatives

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

Variable	Initial Value	Final Value
t	0	t_f
n_A	$n_{A,0} = C_{A,0}V$	
n_B	$n_{B,0} = C_{B,0}V$	
n_Y	0	
n_Z	0	
T	T_0	

Deliverables Equations:

$$\underline{C}_i = \frac{\underline{n}_i}{V} \quad i = A, B, Y, \text{ and } Z \tag{10}$$

$$\underline{r}_1 = k_{0,1} \exp\left(\frac{-E_1}{R\underline{T}}\right)\underline{C}_A\underline{C}_B \tag{11}$$

Implementation of the Calculations

The Python script, example_7_4_1.py, that was written to perform the calculations accompanies this solution.

Results and Discussion

The calculations were performed as described above, and the results are shown in Figures 1 through 3.

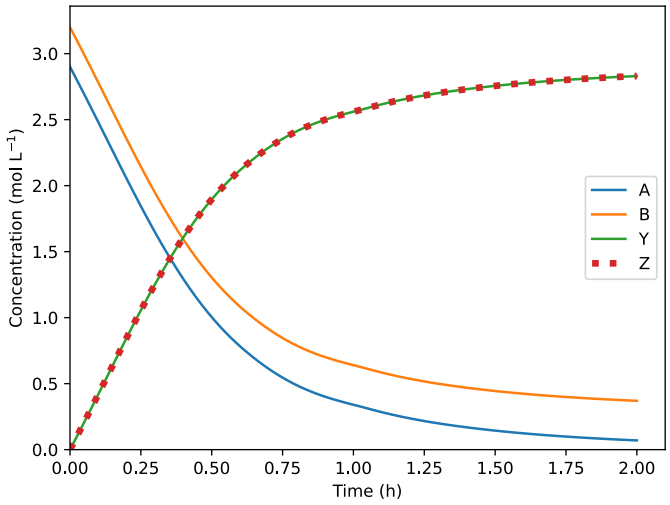

Figure 1. Concentration profiles during the first 2 h of reaction.

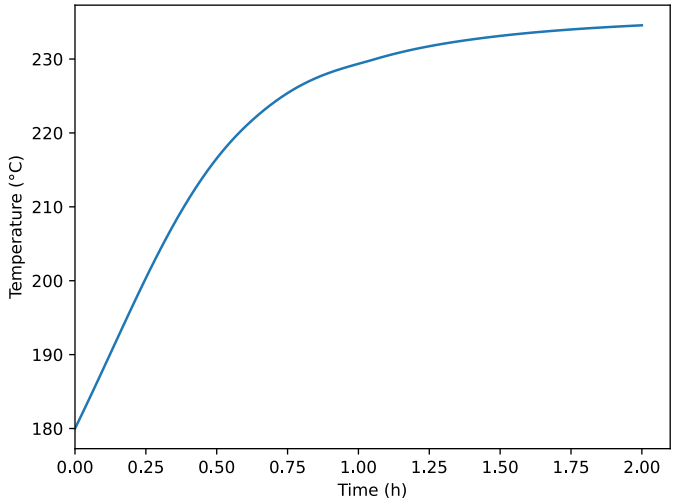

Figure 2. Temperature profile during the first 2 h of reaction.

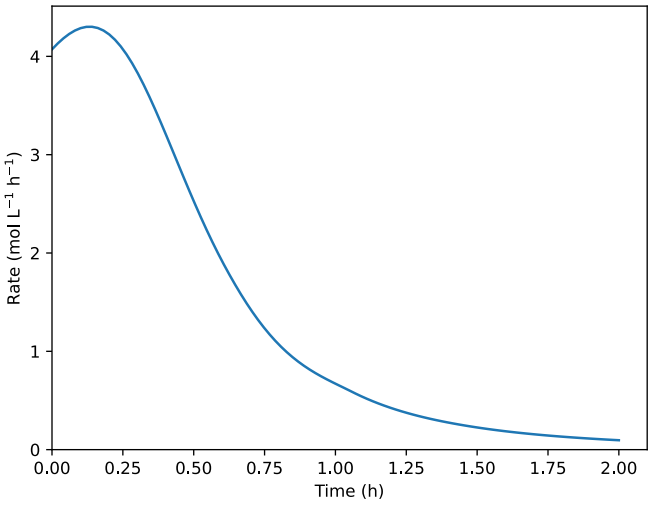

Figure 3. Instantaneous rate profile during the first 2 h of reaction.

Figure 1 shows that the concentrations of the reactants, A and B, decrease monotonically during the first two hours of operation while the concentrations of the products, Y and Z, increase. Figure 2 shows that the temperature increases steadily, too. The variation of the instantaneous reaction rate shown in Figure 3 is different. Initially it increases, but then it passes through a maximum after which it steadily decreases. A qualitative analysis shows that the variations in the concentrations, temperature and rate are expected.

At t = 0, the concentrations of the reagents and the temperature are all at their initial values. At that point the rate is positive, so after a short interval of time the concentrations of A and B will have decreased slightly and the concentrations of Y and Z will have increased slightly due to the occurrence of the reaction. Because the reaction is exothermic and the reactor operates adiabatically, the temperature will have increased due to the heat released by the reaction.

The rate could either increase or decrease during this short interval. The concentrations of the reactants, A and B, are decreasing, and this alone would cause the rate to decrease. However, at the same time the temperature is increasing, and that alone would cause the rate to increase. Generally, at the start of the reaction the exponential dependence of the rate upon the temperature will be stronger than its

dependence upon the reactant concentrations, and the rate will increase. This is seen to be the case in Figure 3. (Had the heat of reaction been very small, leading to a small increase in the temperature, it is possible that the rate would have decreased, especially if the activation was also small).

To summarize, during that initial short interval of time, plots of the concentrations of Y and Z, the temperature, and the rate vs. time all have positive slopes while the concentrations of A and B have negative slopes. During the next short interval of time, the rate is larger than during the first interval of time. As a consequence, the concentrations and temperature will change more during the second interval. That means that the curvature of the temperature, Y concentration, and Z concentration profiles is initially concave upward and the curvature of the A and B concentration profiles is initially concave downward. Again during this second short interval, opposing effects on the rate are associated with the decreasing reactant concentrations and the increasing temperature.

It is hard to see in Figures 1 and 2, but because initially the rate is increasing, the concentrations of A and B are decreasing faster and faster and the concentrations of Y and Z and the temperature are increasing faster and faster. These trends cannot continue indefinitely, if they did, C_Y, C_Z, and T would approach positive infinity and C_A and C_B would approach negative infinity.

In fact, the curvature does change because at some point the effect of decreasing reactant concentrations upon the rate becomes stronger than the effect of increasing temperature. At the point where the two effects become equal, the rate reaches a maximum. Beyond the maximum, the effect of decreasing reactant concentration dominates and the rate decreases. This is seen in Figure 3 where the instantaneous rate passes through a maximum.

At the point where the rate reaches its maximum value, the concentration and temperature profiles exhibit an inflection point. (Again, in this example this is very, very subtle and cannot be discerned in the figures.) Beyond that point, the C_Y, C_Z, and T profiles are concave downward and the C_A and C_B profiles are concave upward. That is, the changes over time become smaller and smaller. This behavior can continue indefinitely. Eventually the concentrations and temperature will stop changing and

become constant. In this example, A is the limiting reactant, and the reaction is irreversible, so the concentrations and temperature will become constant when C_A becomes equal to zero.

Deliverables

The concentration, temperature and instantaneous rate profiles during the first 2 h of reaction are shown in Figures 1, 2, and 3.