A First Course on Kinetics and Reaction Engineering

Example 27.1

Problem Purpose

This problem will help you determine whether you have mastered the learning objectives for this unit. It illustrates a situation where a PFR transient can be analyzed using only the steady state PFR design equations.

Problem Statement

This example examines the start up of the PFR from Example 3 of Unit 26. A perfectly insulated tubular reactor with a diameter of 10 cm and a length of 5 m is initially being flushed with pure water at a temperature of 25 °C, flowing at a rate of 75 L min^{-1}. To start up the reactor, a valve is used to switch from pure water at the inlet to an aqueous solution containing A and B at concentrations of 1.0 and 1.2 M, respectively. This feed stream is at a constant temperature of 30 °C and flows at the same rate as the water it replaces, 75 L min^{-1}. Reagents A and B react according to reaction (1) with a rate of reaction that is accurately described by equation (2). The heat of reaction (1) is -10,700 cal mol^{-1} and may be assumed to be constant. The heat capacity of the solution and the density of the solution may be taken to be constant and equal to those of water (1.0 cal g^{-1} K^{-1} and 1.0 g cm^{-3}). The pressure drop in the reactor is negligible. Plot the molar flow rate of A and the temperature as a function of distance into the reactor 0.131 minutes after the feed was started. Plot the same variables three more times as a function of distance into the reactor 0.262 min, 0.393 min and 0.524 min after the feed was started. (Note: the four times specified correspond to one-fourth of the space time, one-half of the space time, three fourths of the space time and the space time.)

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

$$r_1 = \left(8.72\times10^5 \text{ L mol}^{-1} \text{ min}^{-1}\right)\exp\left\{\frac{-7200 \text{ cal mol}^{-1}}{RT}\right\}C_AC_B \tag{2}$$

Problem Analysis

This problem describes the start-up of a PFR, and reactor start-up is inherently a transient process. This is not a kinetics problem because the rate expression is known. Thus, it is a reaction engineering problem, more specifically a transient PFR reaction engineering problem. To solve the problem it will be necessary to construct an accurate mathematical model for the reactor. Normally one would start with transient mole balances on every reactant and product, a transient energy balance and a transient mechanical energy balance. Here, the latter is not needed because the problem states that the pressure drop is negligible.

The informational reading pointed out that some transient PFR problems can be solved using only the steady-state forms of the design equations. For this to be true, the change that initiates the transient must only affect fluid that enters the reactor after the change is made; it cannot affect fluid that is already within the reactor at the time the change is made. That condition is satisfied in the present problem. The inlet concentrations and temperature are changed, but the flow rate remains the same. A fluid element somewhere within the reactor will be unaffected by such a change. In particular, the flow rate of that element, its temperature and the temperature of the wall it touches will remain the same. The axial variation of the composition and temperature along the length of a reactor can be referred to as the temperature-composition profile. When a change of the kind under consideration here occurs, the transient consists of a front that propagates from the inlet of the reactor to its outlet over the course of one space time. The temperature-composition profile between the inlet and the front will be equal to the final steady state temperature-composition profile while the temperature-composition profile between the front and the reactor outlet will be equal to the steady state temperature-composition profile prior to the change. Thus, to answer the question, all that is needed is to compute the steady state temperature-composition profile before the change and the steady state temperature-composition profile after the change.

Problem Solution

As just noted, to answer the question, all we need are the steady state temperature-composition profiles before and after the change. Before the change, the molar flow rate of A was zero everywhere within the reactor (because the reactor contained pure water) and the temperature was equal to 25 °C (298.15 K) everywhere within the reactor. We calculated the molar flow rate of A and the temperature along the reactor for the new steady state (after the change) in Example 3 of Unit 26. You should review that example if you don't recall how to calculate the molar flow rate and temperature profiles for the conditions that apply after the change.

We are first asked to plot the molar flow rate of A and the temperature as a function of distance into the reactor 0.131 minutes after the feed was started. To do this, we simply calculate how far into the reactor the front will have moved. Since we have plug flow, this is just equal to the linear velocity of the fluid multiplied by the elapsed time. The linear velocity is just the volumetric flow rate divided by the cross sectional area of the reactor. Therefore equation (3) is use to calculate l, the instantaneous axial position of the front.

$$l = \frac{\dot{V}}{\left(\frac{\pi D^2}{4}\right)} t \tag{3}$$

Substituting the volumetric flow rate and tube diameter given in the problem statement into equation (3) shows that the front will be located 1.25 m into the reactor after 0.131 min. This is consistent with the information given in the problem statement which indicates that this time is one-fourth of the reactor space time, because 1.25 m is one-fourth of the total reactor length, 5m. With this knowledge, the requested profiles can be plotted using the steady state solutions. Any fluid element at an axial position farther into the reactor than 1.25 m will have a molar flow rate of A and a temperature representative of the steady state prior to the change; that is, the molar flow rate of A will equal zero and the temperature will equal 298.15 K. Any fluid element at an axial position less than 1.25 m will have a flow rate and temperature representative of the steady state that will eventually be reached at the new feed conditions (this was calculated in Example 3 of Unit 26). Hence, the profiles will look as shown in Figure 1.

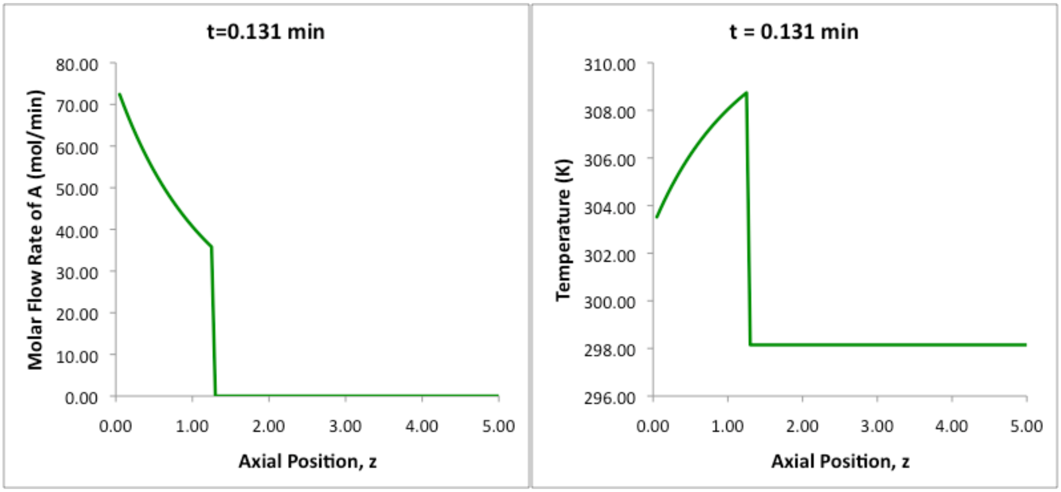

Figure 1. Molar flow rate of A and temperature profiles in the reactor 0.131 min after the feed composition and temperature were changed.

The plots for the other three times are prepared in a similar manner, leading to Figures 2 through 4. Notice that the jump from properties characteristic of the new inlet conditions to properties characteristic of the old inlet conditions, that is, the front, propagates from the inlet of the reactor (at time equal to zero) to the outlet of the reactor (at a time equal to the space time of the reactor, 0.524 min in this case). In any real reactor, there is likely to be some small amount of mixing and thermal conductivity in the axial direction so that the front would not be quite as sharp and the ideal PFR model suggests. If the four molar flow rate profiles were all plotted on the same graph, a figure identical to Figure 27.1 in the information reading results.

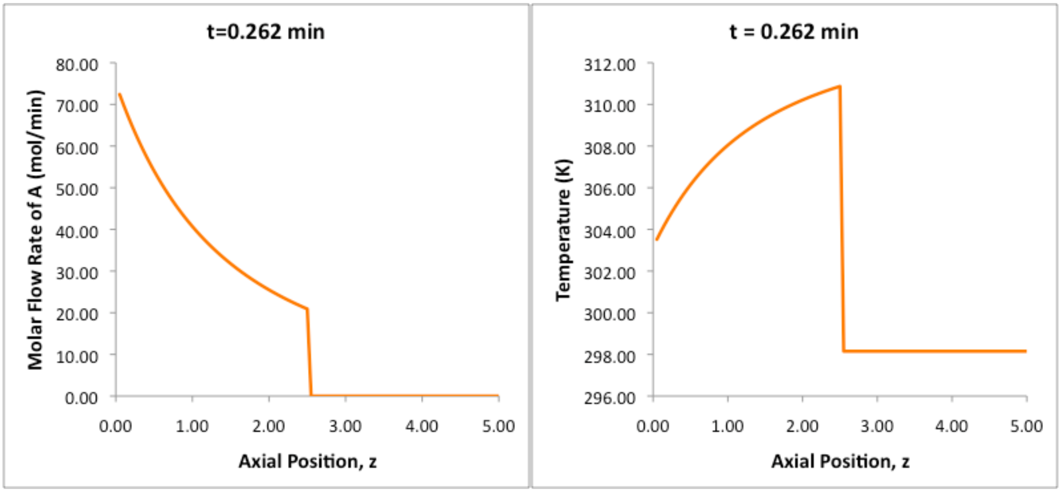

Figure 2. Molar flow rate of A and temperature profiles in the reactor 0.262 min after the feed composition and temperature were changed.

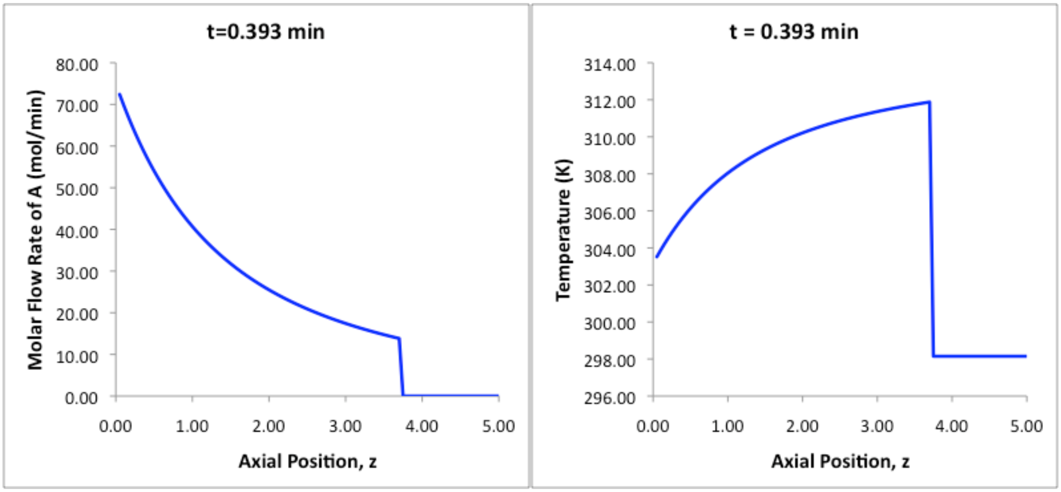

Figure 3. Molar flow rate of A and temperature profiles in the reactor 0.393 min after the feed composition and temperature were changed.

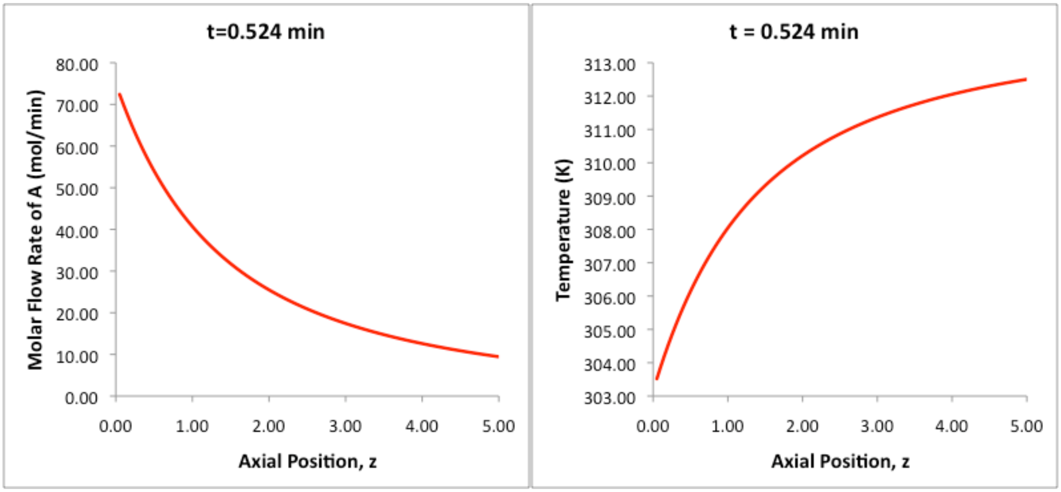

Figure 4. Molar flow rate of A and temperature profiles in the reactor 0.524 min after the feed composition and temperature were changed.

In this case, it was possible to generate the transient response of the PFR without solving the transient form of the mole and energy balance equations. Of course, if one does solve them, one expects to obtain the same result. We will now do so, first, to illustrate the formulation of the transient design equations and to see whether we do, in fact, get the same result. The general transient mole balance design equation for a PFR is given in equation (4). The fluid in this problem is a liquid and the reactor is initially filled with a fluid of the same density. Therefore, the volumetric flow rate will not change over time and so its derivative with respect to time (the last term in the design equation) can be set equal to zero. There is only one reaction taking place, so the summation reduces to a single term. After making these simplifications, the design equation can be written for each of the four species, leading to equations (5) through (8).

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \sum_{\substack{j=all\\ reactions}} \nu_{i,j} r_j - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_i}{\partial t} + \frac{\pi D^2 \dot{n}_i}{4\dot{V}^2} \frac{\partial \dot{V}}{\partial t} \tag{4}$$

$$\frac{\partial \dot{n}_A}{\partial z} = -\frac{\pi D^2}{4} r_1 - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_A}{\partial t} \tag{5}$$

$$\frac{\partial \dot{n}_B}{\partial z} = -\frac{\pi D^2}{4} r_1 - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_B}{\partial t} \tag{6}$$

$$\frac{\partial \dot{n}_Y}{\partial z} = \frac{\pi D^2}{4} r_1 - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_Y}{\partial t} \tag{7}$$

$$\frac{\partial \dot{n}_Z}{\partial z} = \frac{\pi D^2}{4} r_1 - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_Z}{\partial t} \tag{8}$$

The general transient energy balance design equation for a PFR is given in equation (9). For this problem, the pressure will not vary, either with time or position, so its derivative with respect to time can be set equal to zero. Again, there is only one reaction taking place, so the summation over the reactions will reduce to a single term. The reactor is perfectly insulated, so the heat transfer coefficient is equal to zero. Finally, the thermal properties of the fluid can be taken to equal those of water, so the summations involving the heat capacities also reduce to a single term. After making these simplifications, the energy balance given in equation (10) results.

$$\begin{aligned}\pi D U\left(T_e - T\right) = {} & \left(\sum_{\substack{i=all\\ species}} \dot{n}_i \hat{C}_{p,i} \right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \left(\sum_{\substack{j=all\\ reactions}} r_j \Delta H_j \right) \\ & + \frac{\pi D^2}{4\dot{V}} \sum_{\substack{i=all\\ species}} \left(\dot{n}_i \hat{C}_{p,i} \right) \frac{\partial T}{\partial t} - \frac{\pi D^2}{4} \frac{\partial P}{\partial t}\end{aligned} \tag{9}$$

$$\frac{\partial T}{\partial z} = -\frac{\pi D^2 \Delta H_1}{4 \rho_{fluid} \tilde{C}_{p,fluid} \dot{V}} r_1 - \frac{\pi D^2}{4\dot{V}} \frac{\partial T}{\partial t} \tag{10}$$

In order to solve the design equations, equations (5) through (8) and (10), it is necessary to specify the initial and boundary conditions. In this problem, pure water is initially flowing in the reactor. That means that initially the molar flow rate of each of the four species is equal to zero at all points within the reactor. This leads to the initial condition given in equations (11) through (14). Similarly, the water initially present in the reactor is at a temperature of 25 °C (298 K) throughout the reactor, giving initial condition (15). Once the valve is opened, the molar flow rates of each species at the inlet to the reactor and the temperature (30 °C = 303.15 K) at the inlet to the reactor are all fixed. This gives the boundary conditions presented in equations (16) through (20).

at t = 0, $\dot{n}_A$ = 0 for all z (11)

at t = 0, $\dot{n}_B$ = 0 for all z (12)

at t = 0, $\dot{n}_Y$ = 0 for all z (13)

at t = 0, $\dot{n}_Z$ = 0 for all z (14)

at t = 0, T = 298.15 K for all z (15)

at z = 0, $\dot{n}_A = C_A^0\dot{V}$ (16)

at z = 0, $\dot{n}_B = C_B^0\dot{V}$ (17)

at z = 0, $\dot{n}_Y$ = 0 (18)

at z = 0, $\dot{n}_Z$ = 0 (19)

at z = 0, T = 303.15 K (20)

That completes the formulation of the design equation for the transient PFR. That is, equations (4) through (8) and (10 through (20), are in a form that is amenable to numeric solution. In this course we will not ask students to solve equations of this type and we will not go into the details of solving them. Doing so would require discretization and application of finite differences or some equivalent approach.

However, for illustrative purposes, the equations were solved numerically, and reactor profiles shown in Figure 5 were computed 0.131 minutes after the change in the feed composition and temperature.

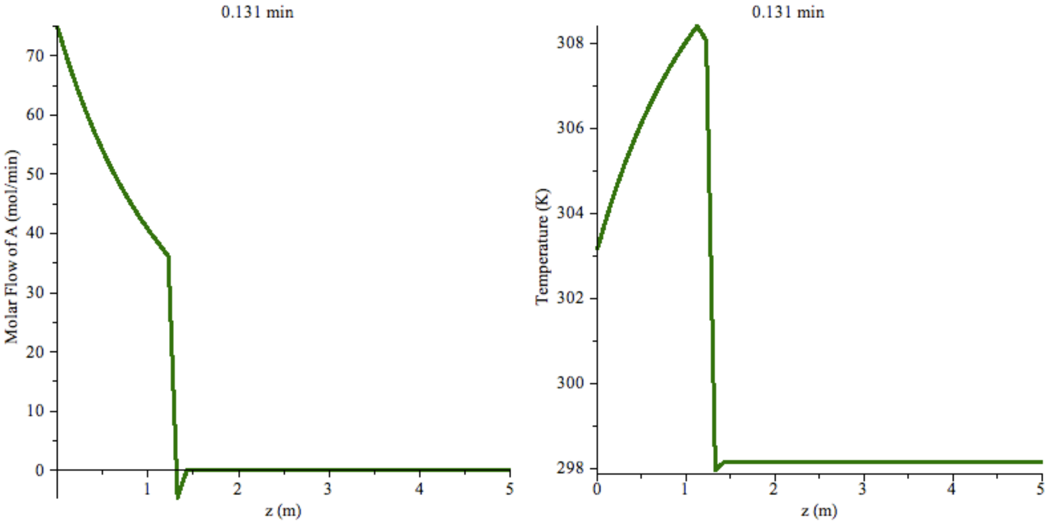

Figure 5. Molar flow rate of A and temperature profiles in the reactor 0.131 min after the feed composition and temperature were changed as calculated by numerically solving the transient design equations.

You may notice that the edge of the front is not as sharp in the plots resulting from solving the transient design equations. The top of the temperature plot is a little rounded, and both curves drop too far and then rise back to the expected value for axial positions greater than 1.25 m. This is a result of the numerical procedures (discretization and approximation of derivatives using finite differences) used to solve the equations. In fact, if the number of discretization points and the size of the time steps used in the numerical solution are not chosen properly, one might obtain results that display oscillations, etc. that are artifacts of the numerical method and have nothing to do with the solution. If you plan to solve these kinds of problem, it is strongly recommended that you take a course on numerical methods. Nonetheless, it is evident from a comparison of Figures 1 and 5 that the results are the same whether the steady state approach is used or if the transient equations are solved.

Calculation Details Using MATLAB

The numerical solution of the steady state design equations was presented in Example 26.3 and will not be duplicated here. The numerical solution of the transient design equations goes beyond the scope of this course and will not be described here.