A First Course on Kinetics and Reaction Engineering

Activity 26.1

Problem Purpose

This problem will help you determine whether you have mastered the learning objectives for this unit. It illustrates a situation where a basis of calculation can be assumed, where the reactor volume must be used as the independent variable and where the final value of a dependent variable is known.

Problem Statement

A gas mixture containing 5% of the reactant A and 20% of the reactant B (balance inert, I) at 350 °C and 2 atm needs to be processed to convert 80% of the A according to irreversible reaction (1). Reaction (1) is first order in A; the pre-exponential factor is 1.4 x 10^6 min^{-1} and the activation energy is 30 kcal mol^{-1}. The heat of reaction (1) is constant and equal to −25 kcal mol^{-1}, and the constant pressure molar heat capacity of the gas mixture is approximately equal to 4 times the ideal gas constant. If an adiabatic PFR with negligible pressure drop is used, what space time will be required and what will be the outlet temperature of the gas?

$$2\,A + B \rightarrow 2\,Y + 2\,Z \qquad (1)$$

Problem Analysis

The problem specifies the use of an adiabatic PFR. No changing settings or inputs are mentioned that would lead to transient operation, so the steady state operation of the reactor will be analyzed. The rate expression is known, and we are asked to calculate reactor operating variables. Therefore, this is a steady state PFR reaction engineering problem where it will be necessary to formulate a model for the reactor in order to answer the questions asked. None of the quantities given in the problem statement are extensive, so it is permissible to assume a basis of calculation. The problem solving strategy described in the reading will be followed, with modification to suit the present problem, if needed.

Problem Solution

The first step is to associate each quantity given in the problem statement with the correct variable symbol. Reading through the problem statement, the following assignments can be made: y_A^0 = 0.05 (5% A in the feed), y_B^0 = 0.20, y_I^0 = 0.75, T^0 = 350 ºC = 623 K, P^0 = 2 atm, f_A = 0.8 (80% conversion of A), k_0 = 1.4 x 10^9 min^{-1}, E = 30 kcal mol^{-1}, $\Delta H_1(T)$ = −25 kcal mol^{-1} and $\hat{C}_{p,gas} = R$ = 1.987 x 10^{-3} kcal mol^{-1} K^{-1}.

The inlet temperature was converted to units of K so that these quantities use consistent units of K for temperature, atm for pressure, min for time, kcal for energy and mol for moles. The full composition of the feed gas is specified and since Y and Z are not included it is clear the the inlet mole fractions of these species each equal zero: y_Y^0 = 0 and y_Z^0 = 0. In addition, the problem states that there is negligible pressure drop so $P(z) = P^0$ = 2 atm.

The second step is to determine whether it is necessary to assume a basis of calculation. If you look at each of the quantities listed above, every one is an intensive quantity. Therefore we may assume a basis for the calculations. That is, we can choose a value for any one extensive quantity such as the reactor volume, inlet volumetric flow rate, inlet molar flow rate (total or any one species), etc. Any of these quantities could be chosen, but if we choose a value for the total inlet molar flow rate, it will be trivial to calculate the inlet molar flow rates of each of the reactants and products (these will be needed as initial conditions when solving the mole balance design equations).

Therefore we will use a basis of $\dot{n}^0_{total}$ = 100 mol min^{-1}. With this choice, the inlet molar flow rate of each species and the inlet volumetric flow rates can all be computed according to equations (2) and (3). In addition, since the conversion and the inlet molar flow rate of A are now know, the outlet molar flow rate of A can be computed using equation (4). The problem solving strategy presented in the informational reading notes that some students find it helpful to make a schematic diagram of the system. Figure 1 shows such a schematic for this problem. In making the schematic, equations (2) and (4) were used to calculate the inlet and outlet molar flow rates shown.

$\dot{n}^0_i = y_Y{}^0\, \dot{n}^0_{total}$ (i = A, B, I, Y and Z) (2)

$$\dot{V}^0 = \frac{\dot{n}^0_{total} R T^0}{P^0} \quad (3)$$

$$\dot{n}^f_A = \dot{n}^0_A \left(1 - f_A\right) \quad (4)$$

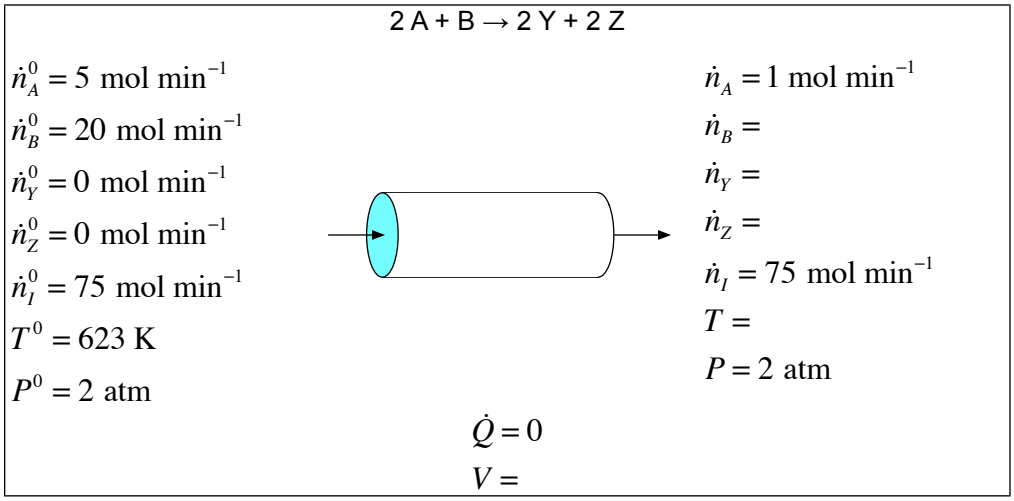


Figure 1. Schematic diagram of the steady state PFR.

The next step is to write the design equations needed to models the reactor. The general form of the mole balance for a steady state PFR is given in equation (5) and the general form of the energy balance is given in equation (6). Using equation (5), mole balances on A, B, Y and Z can be written as given in equations (7) through (10). The first term in the numerator of equation (6) is equal to zero because the reactor is adiabatic. The summation in the denominator of equation (6) can be replaced with

a single term since a heat capacity for the gas mixture is given. This leads to the energy balance in equation (11).

$$\frac{d\dot{n}_i}{dz} = \frac{\pi D^2}{4}\left(\sum_{j=1}^{N_{rxns}} \nu_{i-j} r_j\right) \tag{5}$$

$$\frac{dT}{dz} = \frac{\pi DU\left(T_e - T\right) - \frac{\pi D^2}{4}\left(\sum_{j=1}^{N_{reactions}} r_j \Delta H_j\right)}{\left(\sum_{i=1}^{N_{species}} \dot{n}_i \hat{C}_{p-i}\right)} \tag{6}$$

$$\frac{d\dot{n}_A}{dz} = -2\frac{\pi D^2}{4} r_1 = f_1\left(z, \dot{n}_A, \dot{n}_B, \dot{n}_Y, \dot{n}_Z, T\right) \tag{7}$$

$$\frac{d\dot{n}_B}{dz} = -\frac{\pi D^2}{4} r_1 = f_2\left(z, \dot{n}_A, \dot{n}_B, \dot{n}_Y, \dot{n}_Z, T\right) \tag{8}$$

$$\frac{d\dot{n}_Y}{dz} = 2\frac{\pi D^2}{4} r_1 = f_3\left(z, \dot{n}_A, \dot{n}_B, \dot{n}_Y, \dot{n}_Z, T\right) \tag{9}$$

$$\frac{d\dot{n}_Z}{dz} = 2\frac{\pi D^2}{4} r_1 = f_4\left(z, \dot{n}_A, \dot{n}_B, \dot{n}_Y, \dot{n}_Z, T\right) \tag{10}$$

$$\frac{dT}{dz} = \frac{-\frac{\pi D^2}{4} r_1 \Delta H_1\left(T\right)}{\dot{n}_{total} \hat{C}_{p,gas}} = f_5\left(z, \dot{n}_A, \dot{n}_B, \dot{n}_Y, \dot{n}_Z, T\right) \tag{11}$$

A momentum balance is not needed since the problem states that the pressure drop is negligible. Therefore the next step is to solve the design equations (7) through (11). This will be done numerically. In order to do so one must provide initial values for the independent and dependent variables, the final value of either the independent variable or one of the dependent variables and code that is given values for the independent and dependent variables and that computes the values of the functions f_1 through f_5. The schematic diagram shows that the values of all of the dependent variables are known at the inlet to the reactor, so initial conditions are that the molar flow rates of A, B, Y and Z and the temperature are equal to the values shown at the reactor inlet. The schematic also reveals that the molar flow rate of A is known at the outlet, so that can be used as the final condition.

Having just specified the initial and final conditions, the only other thing needed is computer code that is given the values of the independent and dependent variables and uses those value to evaluate the functions f_1 through f_5. Therefore, we need to go through equations (7) through (11) and show how to calculate every quantity that appears. As we begin to do so, the first quantity we encounter is the tube diameter, D. The tube diameter is not specified in the problem statement, and we cannot calculate its

value. We could try using a different basis for our calculations, but no matter what extensive quantity we selected, other than D itself, we still would not be able to calculate the value of D. If we chose to specify D as the basis for our calculations, we would not be able to calculate the initial values (inlet molar flow rates). The key to resolving this dilemma was discussed in the informational reading. When a steady state PFR operates adiabatically with a negligible pressure drop, the reactor diameter only appears in the design equations within the term $\pi D^2/4$. As described in the informational reading, this term can be combined with dz, leading to a change in the independent variable from z to the cumulative reactor volume, V. That is to say, equation (12) can be substituted into the design equations (7) through (11), leading to the equivalent design equations given in equations (13) through (17).

$$\frac{\pi D^2}{4} dz = dV \tag{12}$$

$$\frac{d\dot{n}_A}{dV} = -2r_1 = f_1'\left(V, \dot{n}_A, \dot{n}_B, \dot{n}_Y, \dot{n}_Z, T\right) \tag{13}$$

$$\frac{d\dot{n}_B}{dV} = -r_1 = f_2'\left(V, \dot{n}_A, \dot{n}_B, \dot{n}_Y, \dot{n}_Z, T\right) \tag{14}$$

$$\frac{d\dot{n}_Y}{dV} = 2r_1 = f_3'\left(V, \dot{n}_A, \dot{n}_B, \dot{n}_Y, \dot{n}_Z, T\right) \tag{15}$$

$$\frac{d\dot{n}_Z}{dV} = 2r_1 = f_4'\left(V, \dot{n}_A, \dot{n}_B, \dot{n}_Y, \dot{n}_Z, T\right) \tag{16}$$

$$\frac{dT}{dV} = \frac{-r_1 \Delta H_1\left(T\right)}{\dot{n}_{total} \hat{C}_{p,gas}} = f_5'\left(V, \dot{n}_A, \dot{n}_B, \dot{n}_Y, \dot{n}_Z, T\right) \tag{17}$$

The initial and final conditions needed to solve equations (13) through (17) remain the same except the initial condition for the independent variable is that V = 0 instead of z = 0. Thus, to solve equations (13) through (17), the only other thing we need is code that is given values for the independent and dependent variables (V, $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_Y$, $\dot{n}_Z$ and T) and uses those values to evaluate the functions f_1' through f_5'. Going through those functions variable by variable, we find that $\hat{C}_{p,gas}$ and $\Delta H_1^0(T)$ have already been specified, so the code only needs to compute r_1 and $\dot{n}_{total}$ in order to evaluate the functions.

The problem states that the reaction is first order in A, and the units on the pre-exponential factor indicate that the concentration of A should be used (not the partial pressure). Hence, the rate can be calculated using equation (18), where the values of the pre-exponential factor and the activation energy have already been specified. The concentration that appears in equation (18) can be evaluated using the ideal gas law, equation (19). In that equation, the value of the pressure has already been specified and the values of the molar flow rate of A and the temperature will be given. The total molar flow rate is simply

the sum of the species molar flow rates, equation (20), where the molar flow rate of I is a known constant, and the other molar flow rates will be given to the code as input.

$$r_1 = k_0 \exp\left(\frac{-E}{RT}\right) C_A \tag{18}$$

$$C_A = \frac{\dot{n}_A}{\dot{V}} = \frac{\dot{n}_A}{\left(\frac{\dot{n}_{total} RT}{P}\right)} = \frac{\dot{n}_A P}{\dot{n}_{total} RT} \tag{19}$$

$$\dot{n}_{total} = \dot{n}_A + \dot{n}_B + \dot{n}_Y + \dot{n}_Z + \dot{n}_I \tag{20}$$

At this point, the design equations (13) through (17) can be solved numerically. Doing so will yield the values of the unknown independent and dependent variables at the final condition, that is, at the reactor outlet. Thus, solving the equations will yield the volume of the PFR, V, and the outlet temperature, T. The problem asks for the outlet temperature and the space time. The latter is found, by definition, using equation (21), the PFR volume found by solving the design equations and the inlet volumetric flow rate found using equation (3).

$$\tau = \frac{V}{\dot{V}^0} \tag{21}$$

When the equations are solved as just described, one finds that the outlet temperature is 872.3 K and the space time is equal to 0.44 min. It is important to realize that the value of V found by solving the design equations only applies for the chosen basis because it is an extensive quantity. In contrast, the outlet temperature and the space time are intensive quantities, so those values will be the same no matter what basis is chosen.