A First Course on Kinetics and Reaction Engineering

Example 19.2

Problem Purpose

This problem illustrates the analysis of a single step in the operational protocol for a perfectly mixed batch reactor, including the treatment of the derivative of the total pressure with respect to time when the reacting fluid is an ideal gas.

Problem Statement

The rate of gas phase reaction (1) is given by the rate expression, equation (2). The pre-exponential factor, $k_{0,1}$, is equal to 265 L mol^{-1} min^{-1}, and the activation energy, E_1, is equal to 73 kJ mol^{-1}. The standard heat of reaction (1) at 298 K is equal to -165 kJ mol^{-1}. The heat capacities of A, Y and Z are given by equations (3) through (5), where the temperature must be substituted in K, and the resulting heat capacity will have units of J mol^{-1} K^{-1}.

If the reaction takes place in a constant volume, adiabatic batch reactor that is initially charged with pure A at 1000 Torr and 1225 K, how long will it take for the temperature to increase by 10 K and at that point what percentage of the original A will have been converted? How long will it take for the temperature to increase by 100 K and at that point what percentage of the original A will have been converted?

$$2A \rightarrow 2Y + Z \tag{1}$$
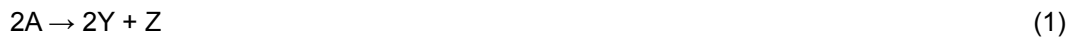
$$r_1 = k_{0,1} \exp\left\{\frac{-E_1}{RT}\right\} C_A^2 \tag{2}$$

$$\hat{C}_{p,A} = 28 + 0.05T \tag{3}$$

$$\hat{C}_{p,Y} = 26 + 0.01T \tag{4}$$

$$\hat{C}_{p,Z} = 30 + 0.005T \tag{5}$$

Problem Analysis

The reactor is a batch reactor; the reactions taking place and their corresponding rate expressions are provided, so this is a reaction engineering problem. Mole balance design equations will be written for each reactant and product, and an energy balance will be written for the reactor. Solving those equations will provide the answers to the questions posed in the problem statement.

Problem Solution

In order to model this system, a mole balance design equation for each of the three reagents (A, Y and Z) and an energy balance design equation will need to be written. The general mole balance design equation is given in equation (6) and the general energy balance design equation is given in equation (7).

$$\frac{dn_i}{dt} = V \sum_{\substack{j=all \\ reactions}} v_{i,j} r_j \tag{6}$$

$$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all \\ species}} \left(n_i \hat{C}_{p,i} \right) + V \sum_{\substack{j=all \\ reactions}} \left(r_j \Delta H_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt} \tag{7}$$

The summation in equation (6) includes only one term since there is only one reaction taking place. Noting that the stoichiometric coefficients of A, Y and Z are -2, 2 and 1, respectively, equation (6) can be written once for each species, yielding equations (8) through (10).

$$\frac{dn_A}{dt} = -2Vr_1 \tag{8}$$

$$\frac{dn_Y}{dt} = 2Vr_1 \tag{9}$$

$$\frac{dn_Z}{dt} = Vr_1 \tag{10}$$

The energy balance design equation, equation (7), can be simplified by noting that the reactor is adiabatic ($\dot{Q} = 0$), the work term is negligible, and the fluid volume is constant and equal to the total reactor volume (and hence its derivative with respect to time is equal to zero). Making these substitutions and expanding the summations leads to equation (11).

$$0 = \left(n_A \hat{C}_{p,A} + n_Y \hat{C}_{p,Y} + n_Z \hat{C}_{p,Z} \right) \frac{dT}{dt} + Vr_1 \Delta H_1 - V \frac{dP}{dt} \tag{11}$$

In order to solve a set of ordinary differential equations (ODEs), the number of dependent variables should equal the number of equations. At present we have four ODEs (equations (8) through (11)) that contain derivatives of five dependent variables (n_A, n_Y, n_Z, T and P). To address this, the derivative of the total pressure with respect to time will be re-written using the ideal gas law, equation (12). Noting that the gas constant and the reaction volume are constant, the derivative of the pressure with respect to time can be obtained by taking the derivative of equation (12), leading, as shown, to equation (13).

$$P = \frac{n_{tot} RT}{V} = \left(\sum_{\substack{k = all \\ species}} n_k \right) \frac{RT}{V} \tag{12}$$

$$\frac{dP}{dt} = \frac{R}{V} \left\{ \left(\frac{dT}{dt} \sum_{\substack{k = all \\ species}} n_k \right) + \left(T \sum_{\substack{k = all \\ species}} \frac{dn_k}{dt} \right) \right\}$$

$$\frac{dP}{dt} = \frac{R}{V}\left\{\left((n_A + n_Y + n_Z)\frac{dT}{dt}\right) + \left(T\left(\frac{dn_A}{dt} + \frac{dn_Y}{dt} + \frac{dn_Z}{dt}\right)\right)\right\} \qquad (13)$$

The mole balance design equations, equations (8) through (10), can be substituted for the derivatives of the moles of the reactants and products appearing in the final term of equation (13), leading to equation (14). Substitution of equation (14) into the energy balance, equation (11), gives equation (15), which can be rearranged to give equation (16).

$$\frac{dP}{dt} = \frac{R(n_A + n_Y + n_Z)}{V}\left(\frac{dT}{dt}\right) + \frac{RT}{V}\left(-2Vr_1 + 2Vr_1 + Vr_1\right)$$

$$\frac{dP}{dt} = \frac{R(n_A + n_Y + n_Z)}{V}\left(\frac{dT}{dt}\right) + RTr_1 \qquad (14)$$

$$0 = \left(n_A \hat{C}_{p,A} + n_Y \hat{C}_{p,Y} + n_Z \hat{C}_{p,Z}\right)\frac{dT}{dt} + Vr_1\Delta H_1 - R(n_A + n_Y + n_Z)\frac{dT}{dt} - RTVr_1 \qquad (15)$$

$$\frac{dT}{dt} = \frac{-Vr_1\left(\Delta H_1 - RT\right)}{\left(n_A\left(\hat{C}_{p,A} - R\right) + n_Y\left(\hat{C}_{p,Y} - R\right) + n_Z\left(\hat{C}_{p,Z} - R\right)\right)} \qquad (16)$$

Upon reading through the problem statement, we can see that only intensive quantities are provided. Therefore, we are free to choose a basis for the calculation. Here it will be convenient to choose the reaction volume as the basis, equation (17).

V = 1 L (assumed basis) $\qquad (17)$

At this point we have four ODEs, equations (8) through (10) and (16) that contain four dependent variables. Specifically, the independent variable is t, and the dependent variables are n_A, n_Y, n_Z and T. These design equations represent a complete model for the batch reactor as described in the problem statement. The problem specification provides enough information to calculate the initial value of the dependent variables, so the design equations can be solved numerically using software for the solution of initial-value ODEs. Supplemental Unit S5 provides a brief overview of how such software works. There are many software packages you can use in order to do this; you should pick the one you are most comfortable using. No matter what software you elect to use, you will need to provide three things as input to that software:

- the initial values of the independent and dependent variables
- the final value of either t or one of the dependent variables
- code that evaluates each of the derivatives given a value for t and values for each of the dependent variables along with the additional information provided in the problem specification or found in handbooks or other reference volumes

Let's begin by considering the initial values. At the start of the processing step described in the problem, the elapsed time for that step is zero ($t = 0$). The problem also notes that at that time, the only species present in the reactor is A. Therefore n_Y, and n_Z are each equal to zero at $t = 0$. The initial moles of A are not specified, but the pressure (P^0 = 1000 Torr) and temperature (T^0 = 1225 K) are, and that information can be used to calculate the initial moles of A using the ideal gas law, equation (18), and the reaction volume chosen as the basis for the calculations. As just noted, the initial temperature is specified to equal 1225 K in the problem statement, providing the last initial value.

$$n_A\left(t=0\right)=n_A^0=\frac{P^0V}{RT^0}\qquad(18)$$

The second thing that must be provided in order to solve the design equations is either the final value of t or the final value of one of the dependent variables. In this problem, we are asked to calculate the final time, so that clearly is not given. Instead, we are asked to calculate the time required for the temperature to increase by 10 K and by 100K. Since we know the initial temperature to be 1225 K, that means the final temperature is 1235 in the first case and 1325 K in the second case.

The final thing that must be provided in order to solve the design equations numerically is code that evaluates each of the derivatives (i. e. the right hand sides of equations (8) through (10) and (16)) given values for the independent and dependent variables and the other information provided in the problem statement. Looking at the mole balances, the only quantities that appear on the right hand sides of those equations are the reaction volume, the value of which was selected as the basis for the calculation and the rate of the reaction. The rate can be calculated using equation (2); the pre-exponential factor, activation energy and ideal gas constant are given in the problem statement or known. The temperature is one of the dependent variables, so it will be given. The only other quantity is the concentration of A, and that is trivial to calculate using equation (19) since the moles of A is a dependent variable and will be given.

$$C_A=\frac{n_A}{V}\qquad(19)$$

In order to write code to evaluate the derivative of the temperature with respect to time, equation (16), we will need to first calculate the heat of reaction and the heat capacities. (The calculation of the rate was just discussed; n_A, n_Y, n_Z and T are dependent variables and therefore their values will be given; the volume was chosen as the basis for the calculations and the gas constant is known.) The heat capacities can be calculated using equations (3) through (5) since the temperature will be given. The heat of reaction depends upon the temperature. As discussed in Unit 2, the heat of reaction can be calculated from the standard heat at 298 K (given in the problem statement) and the heat capacities as shown in equation (20). Writing the heat capacities as $\hat{C}_{p,i}=a_i+b_iT$ and substituting into equation (20) along with the stoichiometric coefficients leads to equation (21)

$$\Delta H_j^0(T) = \Delta H_j^0(298 \text{ K}) + \sum_{\substack{i= \text{all} \\ \text{species}}} \left(v_{i,j} \int_{298K}^{T} \hat{C}_{p,i} \, dT \right) \tag{20}$$

$$\Delta H_1^0(T) = \Delta H_1^0(298 \text{ K}) + \int_{298K}^{T} \hat{C}_{p-Z} \, dT + 2\int_{298K}^{T} \hat{C}_{p-Y} \, dT - 2\int_{298K}^{T} \hat{C}_{p-A} \, dT$$

$$\Delta H_1^0(T) = \Delta H_1^0(298 \text{ K}) + \int_{298K}^{T} (a_Z + b_Z T) \, dT + 2\int_{298K}^{T} (a_Y + b_Y T) \, dT - 2\int_{298K}^{T} (a_A + b_A T) \, dT$$

$$\Delta H_1^0(T) = \Delta H_1^0(298 \text{ K}) + (a_Z + 2a_Y - 2a_A)(T - 298 \text{ K})$$
$$+ \frac{(b_Z + 2b_Y - 2b_A)}{2} \left(T^2 - (298 \text{ K})^2 \right) \tag{21}$$

Thus, at this point we can write code to evaluate the derivatives, so all the input that is needed to solve the design equations numerically is available. Doing so will yield the final value of the remaining independent and dependent variables, in this case t, n_A, n_Y and n_Z. The resulting values can be used to calculate the percentage of A that was converted using equation (22) (the final time is found directly and does not need to be calculated).

$$f_{A,\%} = \frac{n_A^0 - n_A}{n_A^0}(100\%) \tag{22}$$

Upon performing the calculations, one finds that it takes 1.45 min for the temperature to rise by 10 K, at which time 0.79% of the A has been converted, and it takes 12.1 min for the temperature to rise by 100 K at which time 7.88% of the A has been converted.

Calculation Details Using MATLAB

If you elect to use MATLAB to solve the design equations, Supplemental Unit S5 provides template files that can be used. In this problem, the equations are initial value ODEs and the final value of a dependent variable is provided, so the appropriate template file is SolvIVDifD.m. Before that file can be used, you must make six required modifications.

To begin, I made a copy of the template file and saved it as Example_19_2.m; a copy of that file accompanies this solution. Since the function name must match the filename, I changed the name of the function to Example_19_2. At the same time, knowing that I won't need to use the results from these calculations in subsequent calculations, I changed the function so that it does not return any values. However, I noted that I would need to perform the calculations for two different temperature rises, so I changed the function so that the temperature rise is passed in as an argument. The template file begins with a long set of comments describing what it does and how to use it; I replaced these comments with a brief comment stating the purpose of the modified version. None of these modifications were required. As a result of making them, the beginning of the file looks as shown in Listing 1.

```
% Modified version of the MATLAB template file SolvIVDifD.m used in the
% solution of Example 19.2 of "A First Course on Kinetics and Reaction
% Engineering."
%
function Example_19_2(deltaT)
```

Listing 1. Non-required modifications made at the beginning of the template file.

The first <u>*required*</u> modification involves entering all the known quantities from the problem statement along with constants that will be needed (from handbooks or other reference sources). As these are entered, they should be converted to a consistent set of units. For this problem, I decided to use units of L, mol, min, K, J and Torr. Notice that I entered the coefficients in equations (3) through (5) as constants `ai` and `bi` ($\hat{C}_{p,i} = a_i + b_i T$). After the given constants had been entered, I also calculated the initial moles of A, equation (18), and the final temperature, since these are also constant quantities. These modifications were made immediately following the code in Listing 1, and they are shown in Listing 2.

```
% Known quantities and constants (in L, mol, min, J, K, Torr)
k0 = 265;
E = 73000;
dH298 = -165000;
P0 = 1000;
T0 = 1225;
R = 8.314;
% Constants for heat capacities
aA = 28;
aY = 26;
aZ = 30;
bA = 0.05;
bY = 0.01;
bZ = 0.005;
V = 1; % basis
nA0 = P0*V/(62.36367*T0); % Ideal gas law
Tf = T0 + deltaT;
```

Listing 2. Results of the first required modification.

The second <u>*required*</u> modification involves entering the code to evaluate the right hand side of the ODEs when they are written in the form shown in equation (23). The equations were written in that form in the problem solution above, but here the equations are provided as a vector quantity. Thus, it is necessary to map the dependent variables used in the problem statement (n_A, n_Y, n_Z and T) to a vector `z`, and the corresponding derivatives are mapped to a vector `dzdt`. I find it useful at the start of the internal function that will evaluate the derivatives, to define local variables with the names used in the problem statement. This modification is not required, but in my opinion, it makes the code more readable and easier to debug. In addition, the list of variables here serves as a reminder of the mapping of the problem statement variables to the vector `z`. Here the heat capacities, heat of reaction and rate are first calculated

as described previously in this solution. The derivatives are then evaluated using equations (8) through (10) and (16), saving the results in the vector dzdt. The resulting code is shown in Listing 3.

$$\frac{d\underline{z}}{dt} = \underline{f}(\underline{z}, t) \tag{23}$$

```
      % Function that evaluates the ODEs
   function dzdt = odeqns(t,z)
      nA = z(1);
      nY = z(2);
      nZ = z(3);
      T = z(4);
      cpA = aA + bA*T;
      cpY = aY + bY*T;
      cpZ = aZ + bZ*T;
      dH = dH298 + (aZ + 2*aY - 2*aA)*(T-298) + 0.5*(bZ + 2*bY -
   2*bA)*(T^2-298^2));
      r = k0*exp(-E/R/T)*(nA/V)^2;
      dzdt = [
         -2*V*r
         2*V*r
         V*r
         -V*r*(dH - R*T)/(nA*(cpA-R) + nY*(cpY-R) + nZ*(cpZ-R));
      ];
   end % of internal function odeqns
```

Listing 3. Results of the second required modification.

The third _required_ modification involves providing the initial values of the independent and dependent variables. The only variable requiring calculation is the initial moles of A which is calculated using equation (17). The initial values of the dependent variables are entered as a vector named z0, and they must use the same mapping of the problem variables to the vector z0 as was used previously for z. The results of performing this modification are shown in Listing 4.

```
   % Initial values
   t0 = 0.0;
   z0 = [
      nA0
      0
      0
      T0
   ];
```

Listing 4. Results of the third required modification.

The fourth and fifth _required_ modifications involve providing the final value of one dependent variable, in this problem T. The first step (fourth modification) is to select a value for t_f that is much greater than the actual final time. Of course, you don't know what the final time is at this point, so all you can do is set t_f to a large number. It is important to check the answer to make sure that the final time that is reported is smaller than this value; otherwise, you need to make this value larger and repeat the

execution of the function, Example_19_2. For this problem, I arbitrarily set t_f to 100,000 min, so I'll need to check the final time that is calculated and make sure it is less than 100,000 min.

The second step (fifth modification) is to provide the final condition. Basically, this involves adding the code to calculate the value of a variable named stop_when. The variable, stop_when, should equal zero when the final condition is reached. Here the final condition we want to reach is that the temperature should equal 1325 K. When I entered the data from the problem statement, I used Tf to represent this final temperature. Hence, noting that z(4) represents the temperature, the final condition is given by equation (24). I can rearrange that equation so that there is a zero on the left-hand side as shown in equation (25). Clearly, the final condition will be reached when the right hand side of equation (25) equals zero. Therefore, for the fifth required modification, I set the variable stop_when equal to the right hand side of equation (25). The results of these two modifications are shown in Listing 5.

$$z(4) = T_f \tag{24}$$

$$0 = T_f - z(4) \tag{25}$$

```
tf = 100000;
options = odeset('Events',@stop);
    [t, zz, te, ze, ie] = ode45(@odeqns,[t0, tf],z0,options);
% NOTE: For stiff equations replace ode45 with ode15s

% Function that provides the integration stopping criterion
function [stop_when, isterminal, direction] = stop(t,z)
    isterminal = 1;
    direction = 0;

    stop_when = Tf - z(4);
end % of internal function stop
```

Listing 5. Results of the fourth and fifth required modifications.

The sixth and final _required_ modification is to use the results from solving the ODEs to calculate whatever the problem requested. Here all that is required is the calculation of the conversion according to equation (22). The results of these modifications are shown in Listing 6.

```
t_f_min = t_f
T_f = z(4)
pct_converted = 100*(nA0 - z(1))/(nA0)
```

Listing 6. Results of the sixth required modification.

Once the file containing all the modifications had been saved, it was executed by typing Example_19_2(10) at the MATLAB command prompt. This caused the calculations for the first part to be carried out. The function was then executed a second time with an argument of 100 to perform the calculations for the second part of the question. The resulting output is shown in Listing 7.

```
>> Example_19_2(10)

t_f_min =

    1.4513

T_f =

       1235

pct_converted =

    0.7929

>> Example_19_2(100)

t_f_min =

   12.1776

T_f =

       1325

pct_converted =

    7.8781
```

Listing 7. Results of executing the modified template file.