REB, The Course
Class 17 Learning Activity Solution

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?

$$2A \rightarrow 2Y + Z \tag{1}$$

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

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

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

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

Assignment Summary

Reaction

$$2A \rightarrow 2Y + Z \tag{1}$$

Rate Expression

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

Reactor: adiabatic, gas-phase BSTR

Given Constants: $k_{0,1}$ = 265 L mol^{-1} min^{-1}, E_1 = 73 kJ mol^{-1}, $\Delta H_1^0\Big|_{289\,K}$ = –165 kJ mol^{-1}, $P_{A,0}$ = 1000 Torr, and T_0 = 1225 K

Basis: V = 1 L

Parameter: $\underline{T}_f = [1235, 1325]$ K

Deliverables: $t_{f,n}$ and $f_{A,n}$ $\forall T_{f,n} \in \underline{T}_f$

Formulation of the Equations

Reactor Model Equations:

$$\frac{dn_A}{dt} = -\,2Vr_1 \tag{6}$$

$$\frac{dn_Y}{dt} = 2Vr_1 \tag{7}$$

$$\frac{dn_Z}{dt} = Vr_1 \tag{8}$$

$$\left(n_A\hat{C}_{p,A} + n_Y\hat{C}_{p,Y} + n_Z\hat{C}_{p,Z}\right)\frac{dT}{dt} - V\frac{dP}{dt} = -\,Vr_1\Delta H_1 \tag{9}$$

$$RT\left(\frac{dn_A}{dt} + \frac{dn_Y}{dt} + \frac{dn_Z}{dt}\right) + \left(n_A + n_Y + n_Z\right)R\frac{dT}{dt} - V\frac{dP}{dt} = 0 \tag{10}$$

Reactor Model Variables: $\underline{t}$, $\underline{n}_A$, $\underline{n}_Y$, $\underline{n}_Z$, $\underline{T}$, and $\underline{P}$

Additional Computable Unknowns: r_1, k_1, C_A, $\hat{C}_{p,A}$, $\hat{C}_{p,Y}$, $\hat{C}_{p,Z}$, and ΔH_1

$$k_1 = k_{0,1}\exp\left(\frac{-E_1}{RT}\right) \tag{11}$$

$$C_A = \frac{n_A}{V} \tag{12}$$

$$\Delta H_1 = \Delta H_1^0\Big|_{298\,K} + \left(30 + 2\left(26\right) - 2\left(28\right)\right)\left(T - 298\,K\right) + \frac{0.005 + 2\left(0.01\right) - 2\left(0.05\right)}{2}\left(T^2 - \left(298\,K\right)^2\right) \tag{13}$$

<u>IVODE Solver Inputs</u> $\forall T_{f,n} \in \underline{T}_f$

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 at the start of an integration step
   b. returns the corresponding BSTR derivatives

$$\boldsymbol{M} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & \sum_i \left(n_i \hat{C}_{p,i}\right) & -V \\ RT & RT & RT & R\sum_i n_i & -V \end{bmatrix} \tag{16}$$

$$\underline{g} = \begin{bmatrix} -2Vr_1 \\ 2Vr_1 \\ Vr_1 \\ -Vr_1\Delta H_1 \\ 0 \end{bmatrix} \tag{17}$$

$$\begin{bmatrix} \frac{dn_A}{dt} \\ \frac{n_Y}{dt} \\ \frac{n_Z}{dt} \\ \frac{dT}{dt} \\ \frac{dP}{dt} \end{bmatrix} = \boldsymbol{M}^{-1}\underline{g} \tag{18}$$

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

Variable	Initial Value	Final Value
t	0	
n_A	$n_{A,0} = \frac{P_0 V}{R T_0}$	
n_Y	0	
n_Z	0	
T	T_0	$T_{f,n}$
P	P_0	

Deliverables Equations:

$$f_{A,n} = \frac{n_{A,0} - n_A\big|_{T_f,n}}{n_{A,0}} \tag{19}$$

Implementation of the Calculations

The Python script, activity_17.py, that was written to perform the calculations accompanies this solution. It defines a BSTR model function and a BSTR derivatives function that solve the BSTR design equations given a final temperature. The calculations begin by allocating storage for the final time and conversion corresponding to each final temperature. The design equations are then solved and the conversion calculated for each final temperature.

Results and Discussion

The calculations were performed as described above. The temperature increases by 10 K during the first 1.5 min, resulting in a conversion of 0.8%. After a total of 12.2 min, the temperature has increased by 100 K and the conversion is 7.9%. Apparently this reaction is quite slow, given the very high temperatures involved.

Deliverables

The reaction time and conversion for temperature increases of 10 and 100K are shown in Table 2.

Table 2. Reaction time, temperature increase, and conversion.

Reaction Time (min)	Temperature Rise (K)	Conversion (%)
1.5	10	0.8
12.2	100	7.9