REB, The Course
Class 12 Learning Activity Solution

Examples 6.6.4 and 6.6.6 from REB, The Book analyzed an adiabatic, steady-state CSTR with a volume of 500 cm^3 that was going to be used to convert A and B into Y and Z according to reaction (1). A liquid solution flowing at 1.0 $cm^3\ s^{-1}$ and containing equal amounts of A and B (0.015 mol cm^{-3}) at 50 °C was going be used. The heat capacity of the fluid is essentially equal to that of the solvent, and can be considered to be constant and equal to 0.35 cal $g^{-1}\ K^{-1}$. The density of the fluid, also constant, is 0.93 g cm^{-3}. The rate expression for reaction (1) is given in equation (2), and the heat of reaction (1) may be assumed to be constant and equal to –20 kJ mol^{-1}. The rate coefficient displays Arrhenius temperature dependence with a pre-exponential factor equal to 3.24 x 10^{12} $cm^3\ mol^{-1}\ s^{-1}$, and an activation energy of 105.0 kJ mol^{-1}.

Example 6.6.4 showed that three steady states are possible for this reactor, and Example 6.6.6 showed that the high temperature (265 °C) and low temperature (50.1 °C) steady states are stable while the steady state at 138 °C is unstable. One possible startup procedure for this reactor is to fill it with pure solvent, heat the solvent to some initial temperature, and then initiate the feed flow. Compare the transient outlet temperature vs. time for initial temperatures of 180 °C and 190 °C.

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

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

Assignment Summary

Reaction

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

Rate Expression

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

Reactor: transient, liquid-phase, adiabatic CSTR

Given Constants: V = 500 cm^3, $\dot{V}_{in}$ = 1.0 cm^3 s^{-1}, $C_{A,in}$ = 0.015 mol cm^{-3}, $C_{B,in}$ = 0.015 mol cm^{-3}, T_{in} = (50 + 273.15) K, $\tilde{C}_p$ = 0.35 cal g^{-1} K^{-1}, ρ = 0.93 gm cm^{-3}, ΔH_1 = –20 kJ mol^{-1}, $k_{0,1}$ = 3.24 x 10^{12} cm^3 mol^{-1} s^{-1}, and E_1 = 105.0 kJ mol^{-1}, $C_{A,0} = 0$, $C_{B,0} = 0$, $C_{Y,0} = 0$, and $C_{Z,0} = 0$.

Parameter: $\underline{T}_0 = \left(\left[180, 190\right] + 273.15\right)$ K

Deliverables: $\underline{T}$ vs. $\underline{t}$ as a graph for two values of T_0.

Formulation of the Equations

Reactor Model Equations:

$$\frac{d\dot{n}_A}{dt} = \frac{\dot{V}_{in}}{V}\left(\dot{n}_{A,in} - \dot{n}_A - Vr_1\right) \tag{3}$$

$$\frac{d\dot{n}_B}{dt} = \frac{\dot{V}_{in}}{V}\left(\dot{n}_{B,in} - \dot{n}_B - Vr_1\right) \tag{4}$$

$$\frac{d\dot{n}_Y}{dt} = \frac{\dot{V}_{in}}{V}\left(-\dot{n}_Y + Vr_1\right) \tag{5}$$

$$\frac{d\dot{n}_Z}{dt} = \frac{\dot{V}_{in}}{V}\left(-\dot{n}_Z + Vr_1\right) \tag{6}$$

$$\frac{dT}{dt} = \frac{-\tilde{C}_p\rho\dot{V}_{in}\left(T - T_{in}\right) - Vr_1\Delta H_1}{V\tilde{C}_p\rho} \tag{7}$$

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

Additional Computable Unknowns: $\dot{n}_{A,in}$, r_1, k_1, C_A, $\dot{V}$, C_B, and $\dot{n}_{B,in}$

$$\dot{n}_{i,in} = \dot{V}_{in}C_{i,in} \quad i = A \text{ and } B \tag{8}$$

$$k_1 = k_{0,1}\exp\left(\frac{-E_1}{RT}\right) \tag{9}$$

$$C_i = \frac{\dot{n}_i}{\dot{V}} \quad i = A \text{ and } B \tag{10}$$

$$\dot{V} = \dot{V}_{in} \tag{11}$$

$$\dot{n}_{B,in} = \dot{V}_{in} C_{B,in} \tag{12}$$

Additional Uncomputable Unknown:

$$\underline{T}_0 \tag{13}$$

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 1 for each $T_{0,n}$ in $\underline{T}_0$.
2. Stopping criterion that t equals the final value shown in Table 1.
3. Derivatives function that
   a. receives values of the reactor model variables at the start of an integration step
   b. returns the values of the reactor model equation derivatives

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

Variable	Initial Value	Final Value
t	0	t_f = 1 h
$\dot{n}_A$	0	
$\dot{n}_B$	0	
$\dot{n}_Y$	0	
$\dot{n}_Z$	0	
T	$T_{0,n}$	

Implementation of the Calculations

The Python script, activity_12.py, that was written to perform the calculations accompanies this solution.

Results and Discussion

The calculations were performed as described above. The final time was adjusted so that the transients filled graph, and the results are shown in Figure 1. When the reacting fluid is heated to 180 °C prior to starting flow of the reactants, the temperature drops and eventually becomes steady at the low temperature steady state. This is not the desired behavior because at this steady state, the conversion is only 0.03%. However, if the initial reacting fluid temperature is 190 °C the temperature initially decreases, but then passes through a minimum and eventually stabilizes at the desired high temperature steady state.

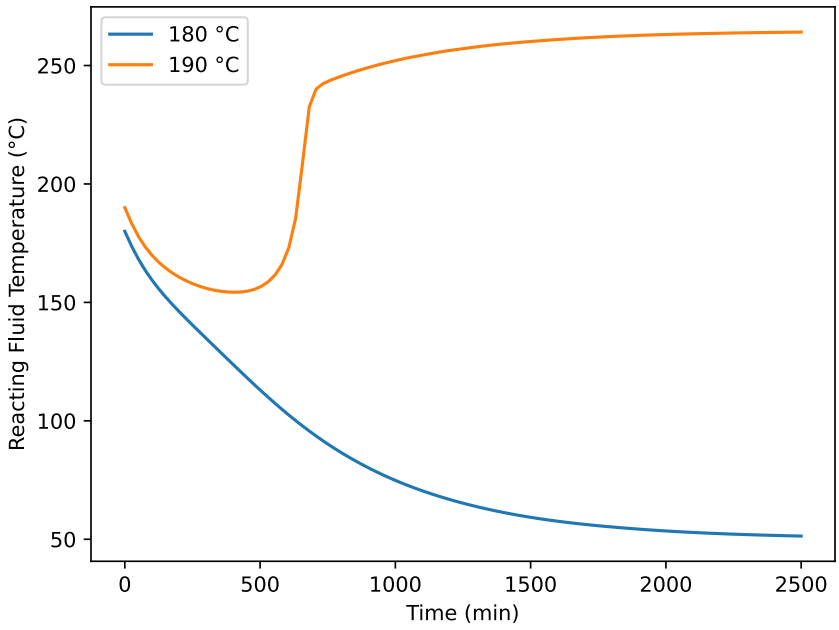

Figure 1. Effect of initial temperature on the steady-state attained during startup.

Assuming typical kinetics behavior, the reaction rate will increase with increasing reactant concentration and with increasing temperature. The feed is colder and has a higher concentration of reactant than the fluid within the reactor, so feed flowing into the reactor tends to increase the reactant concentration and decrease the temperature. The reactor is adiabatic and the reaction is exothermic, so the reaction has the opposite effect tending to increase the reactant concentration and increase the temperature.

During a very short interval of time after the feed flow starts, the temperature initially decreases in both cases, indicating that the cooling effect of the feed predominates over the heating effect of the reaction. During the next brief interval the temperature again decreases, but by less than during the first interval. Thus both profiles are decreasing with a concave upward curvature. This indicates that the effect of feed cooling again predominated over the effect of reaction during the second brief interval.

When the initial temperature is 180 °C, the cooling effect of the feed continues to predominate over the heating effect of the reaction. As a consequence the temperature profile continues to decrease with a concave upward curvature for as long as necessary until the temperature becomes constant at the low temperature steady state.

When the initial temperature is 190 °C, the temperature does not continue to decrease indefinitely, but instead reaches a minimum value. That can only occur if the heating effect of the reaction increases to the point of becoming equal to the cooling effect of the feed. Beyond that point, the heating effect of the reaction predominates and the temperature increases, maintaining a concave upward shape.

That trend cannot continue indefinitely. It would lead to an infinite temperature. Instead, the temperature profile must pass through an inflection point and become concave downward. This occurs when the effect of decreasing reactant concentration and increasing reaction temperature become equal. Beyond that point, the decreasing concentration becomes predominant, the rate decreases more and more as the reaction progresses, and the temperature profile becomes concave downward. That trend continues for a long as necessary until the temperature becomes constant at the high temperature steady state.

So to summarize, the cooling effect of the feed predominates initially. When the initial temperature is 180 °C, that never changes. However, when the initial temperature is 190 °C, the heating effect of the reaction eventually predominates over the cooling effect of the feed until ultimately, the decreasing reactant concentration becomes predominant.

Deliverables

If the CSTR filled with solvent that is preheated to 180 °C prior to starting the feed, the startup will end at the low temperature steady state, but if the solvent is preheated to 190 °C, the startup will end at the high temperature steady state.