REB, The Book
Example 6.6.6 Solution

Example 6.6.4 shows conditions where three steady states are possible when reaction (1) takes place in an adiabatic CSTR. Specifically, the reactor volume is 500 cm^3 and the feed is 1.0 cm^{-3} s^{-1} of a solution containing 0.015 mol cm^{-3} each of A and B at 50 °C. The heat capacity is 0.35 cal g^{-1} K^{-1}, and the density is 0.93 gm cm^{-3}. The heat of reaction is –20 kJ mol^{-1}, and the rate is given by equation (2) with the pre-exponential factor equal to 3.24 x 10^{12} cm^3 mol^{-1} s^{-1} and the activation energy equal to 105 kJ mol^{-1}. The steady-state conversions were 0.03, 39.9, and 97.5%, and the corresponding outlet temperatures were 50, 183, and 265 °C.

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

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

The outlet temperature for this reactor was plotted as a function of the feed temperature, and that graph is reproduced here as Figure 1, with three steady states labeled "S_{high}," "U_{mid}," and "S_{low}" Steady states S_{high} (97.5% conversion) and S_{low} (0.03% conversion) are stable while steady state U_{mid} (39.3% conversion) is unstable.

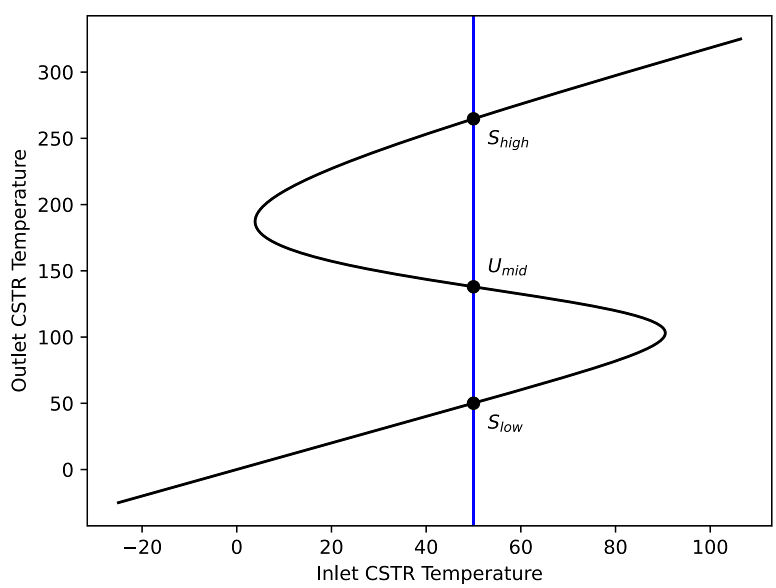

Figure 1. Steady-state temperatures prior to perturbation.

To show that steady state U_{mid} is unstable, plot the outlet temperature *vs*. time if the temperature of a CSTR at steady state U_{mid} is perturbed +1 °C, and by -1 °C holding all of the inputs constant. To show the two other steady states are stable, plot the outlet temperature *vs*. time if the temperature of a CSTR at each of those steady states is perturbed +20 °C, and by -20 °C holding all of the inputs constant.

Assignment Summary

Reaction

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

Rate Expression

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

Reactor: Transient, adiabatic CSTR

Given Constants: V = 500 cm³, $\dot{V}_{in}$ = 1.0 cm³ 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 10¹² cm³ mol⁻¹ s⁻¹, and E_1 = 105.0 kJ mol⁻¹

Parameters: $\underline{f}_{A,0} = \left[0.03, 39.9, 97.5\right]$%, $\underline{T} = \left(\left[50, 183, 265\right] + 273.15\right)$ K, and $\underline{\Delta T} = \left[20, 1, 20\right]$ K

Deliverables: Plots of $\underline{T}$ vs. $\underline{t}$ following ± 1 °C perturbations from the U_{mid} steady state and ± 20 °C perturbations form the S_{high} and S_{low} steady states.

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 $\dot{n}_{B,in}$

$$\dot{n}_{A,in} = \dot{V}_{in}C_{A,in} \tag{8}$$

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

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

$$C_A = \frac{\dot{n}_A}{\dot{V}} \tag{10}$$

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

$$C_B = \frac{\dot{n}_B}{\dot{V}} \tag{12}$$

$$\dot{n}_{B,in} = \dot{V}_{in}C_{B,in} \tag{13}$$

Additional Uncomputable Unknowns: $\underline{f}_{A,0}$, $\underline{T}_0$, and $\underline{\Delta T}$

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 1 for each $f_{A,0,n}$, $T_{0,n}$, and ΔT_n in $\underline{f}_{A,0}$, $\underline{T}_0$, and $\underline{\Delta T}$.
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 for positive and negative perturbations of the reacting fluid temperature.

Variable	Initial Value	Final Value
t	0	t_f = 1 h
$\dot{n}_A$	$\dot{n}_{A,in}\left(1-f_{A,0,n}\right)$	
$\dot{n}_B$	$\dot{n}_{B,in}-f_{A,0,n}\dot{n}_{A,in}$	
$\dot{n}_Y$	$f_{A,0,n}\dot{n}_{A,in}$	
$\dot{n}_Z$	$f_{A,0,n}\dot{n}_{A,in}$	
T	$T_{0,n}\pm\Delta T_n$	

Implementation of the Calculations

The Python script, example_6_6_6.py, that was written to perform the calculations accompanies this solution.

Results and Discussion

The calculations were performed as described above. The value of t_f was adjusted so that the transients filled the graphs. Figure 1 shows the temperature as a function of time following perturbation from the unstable steady state by plus and minus 1 °C holding all of the inputs constant. Since none of the reactor inputs changed, the temperature would have returned to 138 °C had that been a stable steady state.

Instead, the figure shows that following a 1 °C increase in the reacting fluid temperature, it continues to increase and stabilizes at the high temperature steady state. Following a 1°C decrease in the reacting fluid temperature, it continues to decrease and stabilizes at the low temperature steady state.

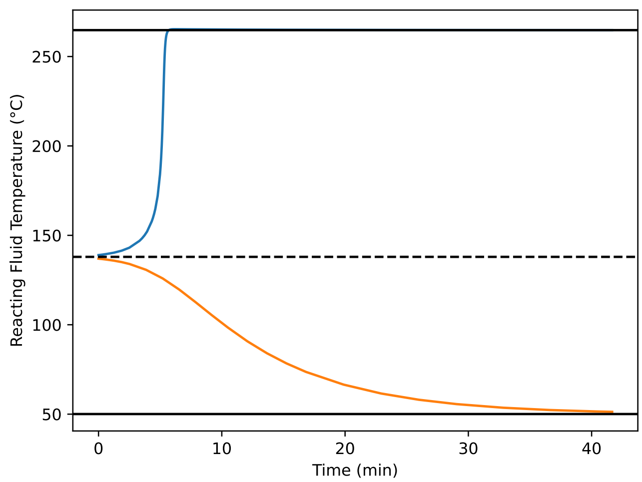

Figure 1. Reacting fluid temperature following a +1 °C (blue) and a -1 °C (orange) perturbation from the unsteady state. The dashed black line represents the unstable steady state, and the solid black lines represent the stable steady states.

For both the high temperature, Figure 2, and low temperature, Figure 3, steady states, following much larger perturbations of ± 20 °C the system returns to its original steady state. At the high temperature, the response briefly moves farther from the steady-state before reaching a maximum deviation and then returning to the steady state.

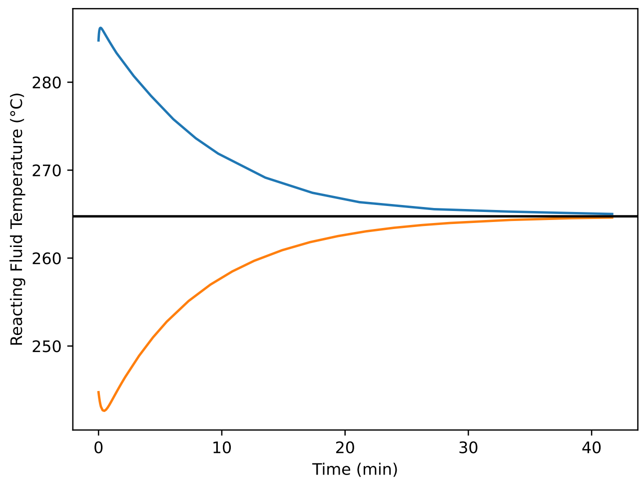

Figure 2. Reacting fluid temperature following a +1 °C (blue) and a -1 °C (orange) perturbation from the high temperature (black) steady state.

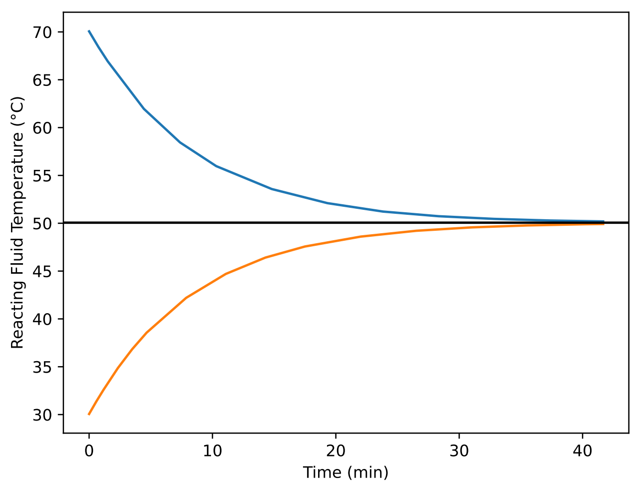

Figure 3. Reacting fluid temperature following a +1 °C (blue) and a -1 °C (orange) perturbation from the low temperature (black) steady state.

Deliverables

A 1°C change of the reacting fluid temperature from the unstable steady state initiates transient operation leading to one of the stable steady states. This shows confirms that the initial steady state is, indeed, unstable. In contrast, a 20 °C change of the reacting fluid temperature from either of the stable steady states initiates transient operation leading back to the original steady state, confirming that these initial steady states are stable.