

The reactor cannot be used because it will exceed the specified maximum temperature of 585°R.

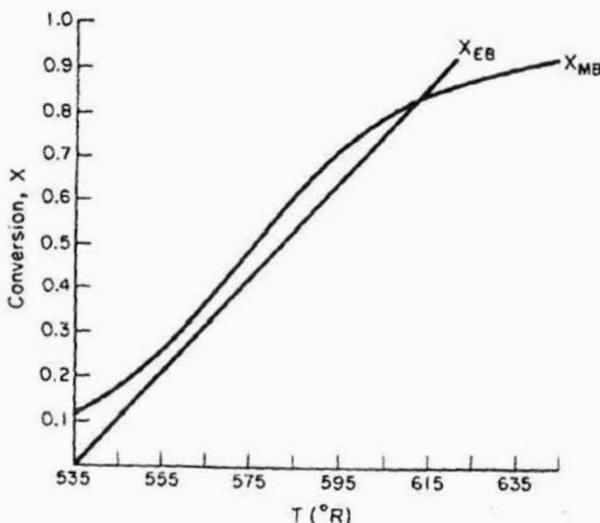


Figure E8-8.2 The conversions X_{EB} and X_{MB} as a function of temperature.

Example 8-9 CSTR with a Cooling Coil

A cooling coil has been located in equipment storage for use in the hydration of propylene oxide discussed in Example 8-8. The cooling coil has 40 ft² of cooling surface and the cooling water flow rate inside the coil is sufficiently large that a constant coolant temperature of 85°F can be maintained. A typical overall heat-transfer coefficient for such a coil is 100 Btu/h·ft²·°F. Will the reactor satisfy the previous constraint of 125°F maximum temperature if the cooling coil is used?

Solution

If we assume that the cooling coil takes up negligible reactor volume, the conversion calculated as a function of temperature from the mole balance is the same as that in Example 8-8 [Equation (E8-8.10)].

1. **Combining the mole balance, stoichiometry, and rate law**, we have, from Example 8-8,

$$X_{MB} = \frac{\tau k}{1 + \tau k} = \frac{(2.084 \times 10^{12}) \exp(-16,306/T)}{1 + (2.084 \times 10^{12}) \exp(-16,306/T)} \quad (\text{E8-8.10})$$

T is in °R.

2. **Energy balance.** Neglecting the work by the stirrer, we combine Equations (8-27) and (8-50) to write

$$\frac{UA(T_a - T)}{F_{A0}} - X[\Delta H_{Rx}^\circ(T_R) + \Delta C_p(T - T_R)] = \sum \Theta_i C_{p_i}(T - T_0) \quad (\text{E8-9.1})$$

Energy Balance

Solving the energy balance for X_{EB} yields

$$X_{EB} = \frac{\sum \Theta_i C_{p_i} (T - T_0) + [UA(T - T_a)/F_{A0}]}{-[\Delta H_{R_x}^{\circ}(T_R) + \Delta C_p(T - T_R)]} \quad (E8-9.2)$$

The cooling coil term in Equation (E8-9.2) is

$$\frac{UA}{F_{A0}} = \left(100 \frac{\text{Btu}}{\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F}} \right) \frac{(40 \text{ ft}^2)}{(43.04 \text{ lb mol/h})} = \frac{92.9 \text{ Btu}}{\text{lb mol} \cdot ^\circ\text{F}} \quad (E8-9.3)$$

Recall that the cooling temperature is

$$T_a = 85^\circ\text{F} = 545^\circ\text{R}$$

The numerical values of all other terms of Equation (E8-9.2) are identical to those given in Equation (E8-8.12) but with the addition of the heat exchange term.

$$X_{EB} = \frac{403.3(T - 535) + 92.9(T - 545)}{36,400 + 7(T - 528)} \quad (E8-9.4)$$

We now have two equations [(E8-8.10) and (E8-9.4)] and two unknowns, X and

The POLYMATH program and solution to these two Equations (E8-8.10), X and (E8-9.4), X_{EB} , are given in Tables E8-9.1 and E8-9.2. The exiting temperature and conversion are 103.7°F (563.7°R) and 36.4%, respectively, i.e.,

$$T = 564^\circ\text{R} \text{ and } X = 0.36$$

TABLE E8-9.1. POLYMATH: CSTR WITH HEAT EXCHANGE

Equations:

Nonlinear equations

- [1] $f(X) = X - (403.3(T - 535) + 92.9(T - 545)) / (36400 + 7(T - 528)) = 0$
 [2] $f(T) = X - \tau k / (1 + \tau k) = 0$

Explicit equations

- [1] $\tau = 0.1229$
 [2] $A = 16.96 \times 10^{12}$
 [3] $E = 32400$
 [4] $R = 1.987$
 [5] $k = A \exp(-E/(R \cdot T))$

Solution output to Polymath program in Table E8-9.1 is shown in Table E8-9.2.

TABLE E8-9.2. EXAMPLE 8-8 CSTR WITH HEAT EXCHANGE

Variable	Value	f(x)	Ini Guess
X	0.3636087	2.243E-11	0.367
T	563.72893	-5.411E-10	564
tau	0.1229		
A	1.696E+13		
E	3.24E+04		
R	1.987		
k	4.6489843		

We can now use the glass lined reactor



Living Example Problem

8.7 Multiple Steady States

In this section we consider the steady-state operation of a CSTR in which a first-order reaction is taking place. We begin by recalling the hydrolysis of propylene oxide, Example 8-8.

If one were to examine Figure E8-8.2, one would observe that if a parameter were changed slightly, the X_{EB} line could move slightly to the left and there might be more than one intersection of the energy and mole balance curves. When more than one intersection occurs, there is more than one set of conditions that satisfy *both* the energy balance and mole balance; consequently, there will be multiple steady states at which the reactor may operate.

We begin by recalling Equation (8-54), which applies when one neglects shaft work and ΔC_p (i.e., $\Delta C_p = 0$ and therefore $\Delta H_{Rx} = \Delta H_{Rx}^\circ$).

$$-X\Delta H_{Rx}^\circ = C_{p0}(1 + \kappa)(T - T_c) \quad (8-54)$$

where

$$C_{p0} = \sum \Theta_i C_{p_i}$$

$$\kappa = \frac{UA}{C_{p0}F_{A0}}$$

and

$$T_c = \frac{T_0 F_{A0} C_{p0} + UA T_a}{UA + C_{p0} F_{A0}} = \frac{\kappa T_a + T_0}{1 + \kappa} \quad (8-57)$$

Using the CSTR mole balance $X = \frac{-r_A V}{F_{A0}}$, Equation (8-54) may be rewritten as

$$(-r_A V / F_{A0})(-\Delta H_{Rx}^\circ) = C_{p0}(1 + \kappa)(T - T_c) \quad (8-58)$$

The left-hand side is referred to as the *heat-generated term*:

$G(T)$ = Heat-generated term

$$G(T) = (-\Delta H_{Rx}^\circ)(-r_A V / F_{A0}) \quad (8-59)$$

The right-hand side of Equation (8-58) is referred to as the *heat-removed term* (by flow and heat exchange) $R(T)$:

$R(T)$ = Heat-removed term

$$R(T) = C_{p0}(1 + \kappa)(T - T_c) \quad (8-60)$$

To study the multiplicity of steady states, we shall plot both $R(T)$ and $G(T)$ as a function of temperature on the same graph and analyze the circumstances under which we will obtain multiple intersections of $R(T)$ and $G(T)$.

8.7.1 Heat-Removed Term, $R(T)$

Vary Entering Temperature. From Equation (8-60) we see that $R(T)$ increases linearly with temperature, with slope $C_{p0}(1 + \kappa)$. As the entering temperature T_0 is increased, the line retains the same slope but shifts to the right as shown in Figure 8-14.

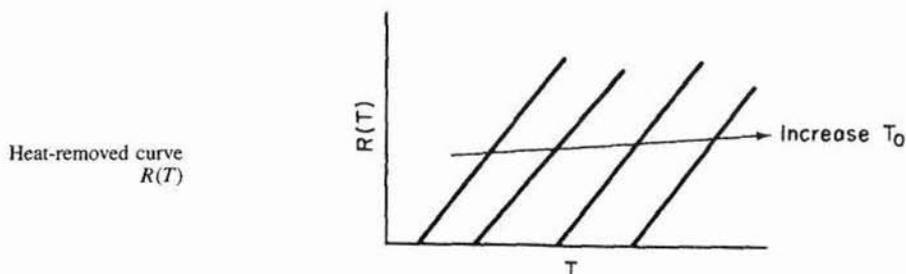


Figure 8-14 Variation of heat removal line with inlet temperature.

Vary Non-adiabatic Parameter κ . If one increases κ by either decreasing the molar flow rate F_{A0} or increasing the heat-exchange area, the slope increases and the ordinate intercept moves to the left as shown in Figure 8-15, for conditions of $T_a < T_0$:

$$\kappa = 0 \quad T_c = T_0$$

$$\kappa = \infty \quad T_c = T_a$$

If $T_a > T_0$, the intercept will move to the right as κ increases.

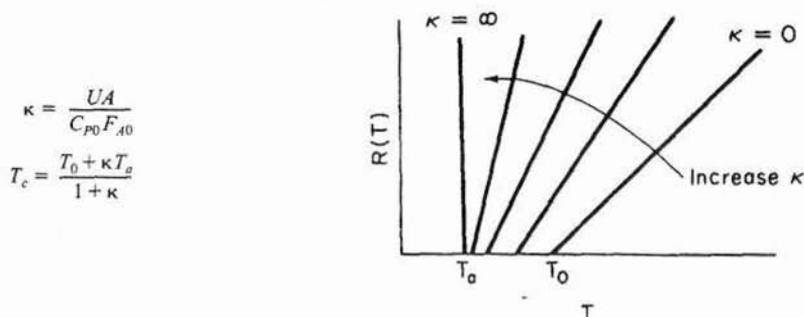


Figure 8-15 Variation of heat removal line with κ ($\kappa = UA/C_{p0}F_{A0}$).

8.7.2 Heat of Generation, $G(T)$

The heat-generated term, Equation (8-59), can be written in terms of conversion. (Recall: $X = -r_A V / F_{A0}$)

$$G(T) = (-\Delta H_{R_x}^0)X \quad (8-61)$$

To obtain a plot of heat generated, $G(T)$, as a function of temperature, we must solve for X as a function of T using the CSTR mole balance, the rate law, and stoichiometry. For example, for a first-order liquid-phase reaction, the CSTR mole balance becomes

$$V = \frac{F_{A0}X}{kC_A} = \frac{v_0 C_{A0}X}{kC_{A0}(1-X)}$$

Solving for X yields

$$X = \frac{\tau k}{1 + \tau k}$$

1st-order reaction

Substituting for X in Equation (8-61), we obtain

$$G(T) = \frac{-\Delta H_{Rx}^{\circ} \tau k}{1 + \tau k} \quad (8-62)$$

Finally, substituting for k in terms of the Arrhenius equation, we obtain

$$G(T) = \frac{-\Delta H_{Rx}^{\circ} \tau A e^{-E/RT}}{1 + \tau A e^{-E/RT}} \quad (8-63)$$

Note that equations analogous to Equation (8-63) for $G(T)$ can be derived for other reaction orders and for reversible reactions simply by solving the CSTR mole balance for X . For example, for the second-order liquid-phase reaction

2nd-order reaction

$$X = \frac{(2\tau k C_{A0} + 1) - \sqrt{4\tau k C_{A0} + 1}}{2\tau k C_{A0}}$$

the corresponding heat generated is

$$G(T) = \frac{-\Delta H_{Rx}^{\circ} [(2\tau C_{A0} A e^{-E/RT} + 1) - \sqrt{4\tau C_{A0} A e^{-E/RT} + 1}]}{2\tau C_{A0} A e^{-E/RT}} \quad (8-64)$$

At very low temperatures, the second term in the denominator of Equation (8-63) for the first-order reaction can be neglected so that $G(T)$ varies as

Low T

$$G(T) = -\Delta H_{Rx}^{\circ} \tau A e^{-E/RT}$$

(Recall that ΔH_{Rx}° means the heat of reaction is evaluated at T_R .)

At very high temperatures, the second term in the denominator dominates, and $G(T)$ is reduced to

High T

$$G(T) = -\Delta H_{Rx}^{\circ}$$

$G(T)$ is shown as a function of T for two different activation energies, E , in Figure 8-16. If the flow rate is decreased or the reactor volume increased so as to increase τ , the heat of generation term, $G(T)$, changes as shown in Figure 8-17.

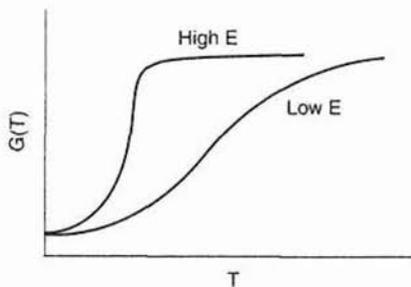


Figure 8-16 Heat generation curve.

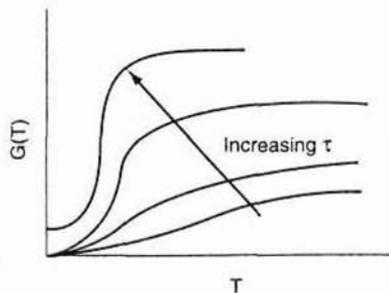


Figure 8-17 Variation of heat generation curve with space-time.

Heat-generated
curves, $G(T)$

8.7.3 Ignition-Extinction Curve

The points of intersection of $R(T)$ and $G(T)$ give us the temperature which the reactor can operate at steady state. Suppose that we begin to feed a reactor at some relatively low temperature, T_{01} . If we construct our $G(T)$ and $R(T)$ curves, illustrated by curves y and a , respectively, in Figure 8-18, we see that there will be only one point of intersection, point 1. From this point of intersection, one can find the steady-state temperature in the reactor, T_{s1} , by following a vertical line down to the T -axis and reading off the temperature as shown in Figure 8-18.

If one were now to increase the entering temperature to T_{02} , the G curve, y , would remain unchanged, but the $R(T)$ curve would move to the right as shown by line b in Figure 8-18, and will now intersect the $G(T)$ at point 2; it will be tangent at point 3. Consequently, we see from Figure 8-18 that there are two steady-state temperatures, T_{s2} and T_{s3} , that can be realized in the CSTR for the entering temperature T_{02} . If the entering temperature is increased to T_{03} , the $R(T)$ curve, line c (Figure 8-19), intersects the $G(T)$ three times and there are three steady-state temperatures. As we continue to increase T_0 , we finally reach line e , in which there are only two steady-state temperatures. By further increasing T_0 we reach line f , corresponding to T_{06} , in which we have only one temperature that will satisfy both the mole and energy balances. For the six entering temperatures, we can form Table 8-5, relating the entering temperature to the possible reactor operating temperatures. By plotting T_s as a function of T_0 , we obtain the well-known *ignition-extinction curve* shown in Figure 8-20. From this figure we see that as the entering temperature is increased, the steady-state temperature increases along the bottom line until T_{05} is reached. Any further increase in temperature beyond T_{05} and the steady-state reactor temperature will jump up to T_{s11} , as shown in Figure 8-20. The temperature at which

Both the mole and energy balances are satisfied at the points of intersection or tangency.

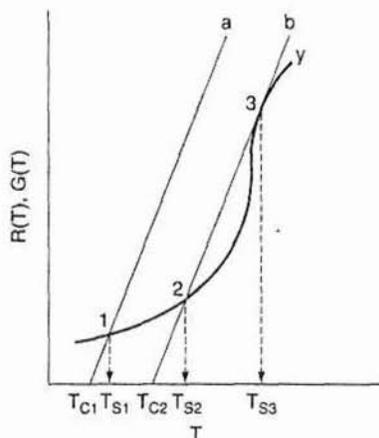


Figure 8-18 Finding multiple steady states with T_0 varied.

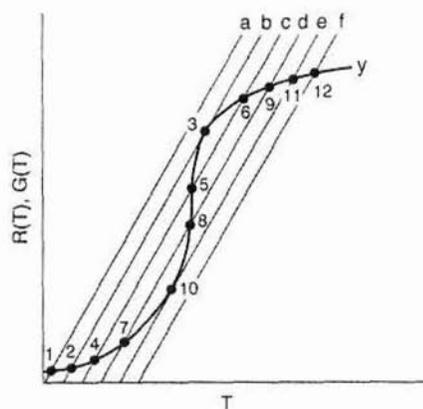


Figure 8-19 Finding multiple steady states with T_0 varied.

TABLE 8-5. MULTIPLE STEADY-STATE TEMPERATURES

Entering Temperature	Reactor Temperatures		
T_{01}		T_{s1}	
T_{02}		T_{s2}	T_{s3}
T_{03}	T_{s4}	T_{s5}	T_{s6}
T_{04}	T_{s7}	T_{s8}	T_{s9}
T_{05}	T_{s10}		T_{s11}
T_{06}		T_{s12}	

We must exceed a certain feed temperature to operate at the upper steady state where the temperature and conversion are higher.

this jump occurs is called the *ignition temperature*. If a reactor were operating at T_{s12} and we began to cool the entering temperature down from T_{06} , the steady-state reactor temperature T_{s3} would eventually be reached, corresponding to an entering temperature T_{02} . Any slight decrease below T_{02} would drop the steady-state reactor temperature to T_{s2} . Consequently, T_{02} is called the *extinction temperature*.

The middle points 5 and 8 in Figures 8-19 and 8-20 represent unstable steady-state temperatures. Consider the heat removal line d in Figure 8-19 along with the heat-generated curve which is replotted in Figure 8-21.

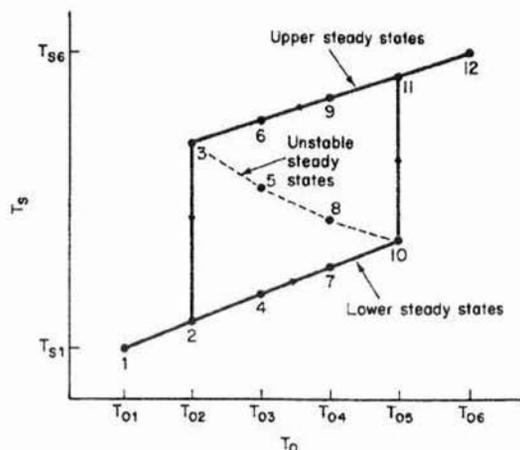


Figure 8-20 Temperature ignition-extinction curve.

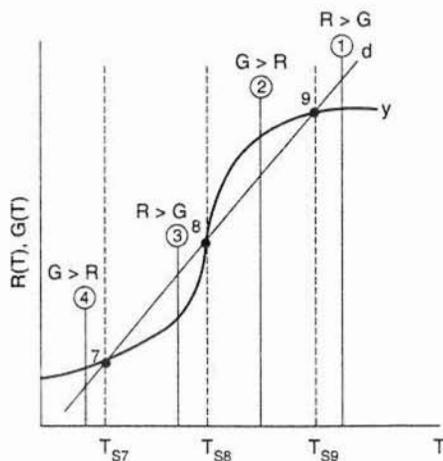


Figure 8-21 Stability on multiple state temperatures.

If we were operating at T_{s8} , for example, and a pulse increase in reactor temperature occurred, we would find ourselves at the temperature shown by vertical line ② between points 8 and 9. We see along this vertical line ② the heat-generated curve, G , is greater than the heat-removed line R ($G > R$). Consequently, the temperature in the reactor would continue to increase until point 9 is reached at the upper steady state. On the other hand, if we had a pulse decrease in temperature from point 8, we would find ourselves a vertical line ③ between

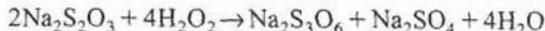
points 7 and 8. Here we see the heat-removed curve is greater than the heat-generated curve so the temperature will continue to decrease until the lower steady state is reached. That is a small change in temperature either above or below the middle steady-state temperature, T_{s8} will cause the reactor temperature to move away from this middle steady state. Steady states that behave in the manner are said to be unstable.

In contrast to these unstable operating points, there are stable operating points. Consider what would happen if a reactor operating at T_{s9} were subjected to a pulse increase in reactor temperature indicated by line ① in Figure 8-21. We see that the heat-removed line (d) is greater than the heat-generated curve (y), so that the reactor temperature will decrease and return to T_{s9} . On the other hand, if there is a sudden drop in temperature below T_{s9} as indicated by line ②, we see the heat-generated curve (y) is greater than the heat-removed line (d) and the reactor temperature will increase and return to the upper steady state at T_{s9} .

Next let's look at what happens when the lower steady-state temperature at T_{s7} is subjected to pulse increase to the temperature shown as line ③ in Figure 8-21. Here we again see that the heat removed, R , is greater than the heat generated, G , so that the reactor temperature will drop and return to T_{s7} . If there is a sudden decrease in temperature below T_{s7} to the temperature indicated by line ④, we see that the heat generated is greater than the heat removed, $G > R$, and that the reactor temperature will increase until it returns to T_{s7} . A similar analysis could be carried out for temperature T_{s1} , T_{s2} , T_{s4} , T_{s6} , T_{s11} , and T_{s12} and one would find that reactor temperatures would always return to *local steady-state values*, when subjected to both positive and negative fluctuations.

While these points are locally stable, they are not necessarily globally stable. That is, a perturbation in temperature or concentration, while small, may be sufficient to cause the reactor to fall from the upper steady state (corresponding to high conversion and temperature such as point 9 in Figure 8-21) to the lower steady state (corresponding to low temperature and conversion, point 7). We will examine this case in detail in Section 9.4 and in Problem P9-16B.

An excellent experimental investigation that demonstrates the multiplicity of steady states was carried out by Vejtasa and Schmitz (Figure 8-22). They studied the reaction between sodium thiosulfate and hydrogen peroxide:



in a CSTR operated adiabatically. The multiple steady-state temperatures were examined by varying the flow rate over a range of space times, τ , as shown in Figure 8-23. One observes from this figure that at a space-time of 12 s, steady-state reaction temperatures of 4, 33, and 80°C are possible. If one were operating on the higher steady-state temperature line and the volumetric flow rates were steadily increased (i.e., the space-time decreased), one notes that if the space velocity dropped below about 7 s, the reaction temperature would drop from 70°C to 2°C. The flow rate at which this drop occurs is referred to as the *blowout velocity*.

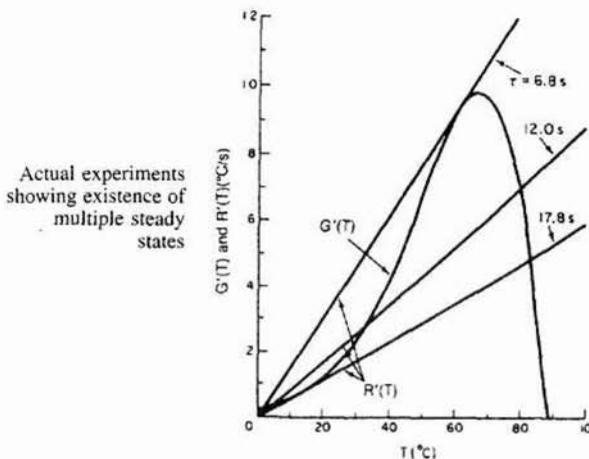


Figure 8-22 Heat generation and removal functions for feed mixture of 0.8 M $\text{Na}_2\text{S}_2\text{O}_3$ and 1.2 M H_2O_2 at 0°C.

By S. A. Vejtasa and R. A. Schmitz, *AIChE J.*, 16 (3), 415 (1970). (Reproduced by permission of the American Institute of Chemical Engineers. Copyright © 1970 AIChE. All right reserved.) See Journal Critique Problem P8C-4.

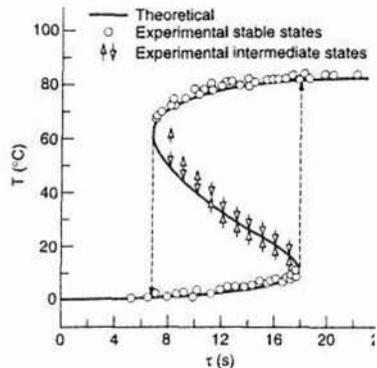


Figure 8-23 Multiple steady states.

8.7.4 Runaway Reactions in a CSTR

In many reacting systems, the temperature of the upper steady state may be sufficiently high that it is undesirable or even dangerous to operate at this condition. For example, at the higher temperatures, secondary reactions can take place, or as in the case of propylene glycol in Examples 8-8 and 8-9, evaporation of the reacting materials can occur.

We saw in Figure 8-20, that we operated at the upper steady state; if we exceeded the ignition temperature. For a CSTR, we shall consider runaway (ignition) to occur when we move from the lower steady state to the upper steady state. The ignition temperature occurs at the point of tangency of the heat removed curve to the heat-generated curve. If we move slightly off this point of tangency as shown in Figure 8-24, then runaway is said to have occurred.

At this point of tangency, T^* , we have not only

$$R(T^*) = G(T^*)$$

$$C_{p_o}(1 + \kappa)(T^* - T_c) = (-\Delta H_{rx})X^* = (-\Delta H_{rx})\frac{(-r_A^*V)}{F_{A0}} \quad (8)$$

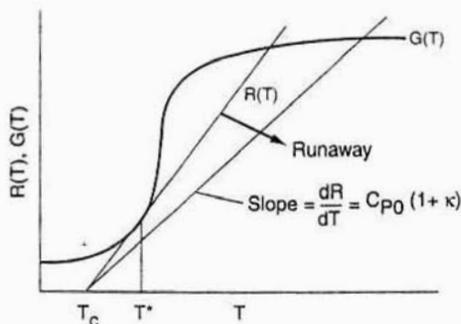


Figure 8-24 Runaway in a CSTR.

but also the slopes of the $R(T)$ and $G(T)$ curves are also equal. For the heat-removed curve, the slope is

$$\left. \frac{dR(T)}{dT} \right|_{T^*} = C_{P_0}(1 + \kappa) \quad (8-66)$$

and for the heat-generated curve, the slope is

$$\left. \frac{dG(T)}{dT} \right|_{T^*} = \frac{d \left[\frac{(-\Delta H_{R_x}) (-r_A) V}{F_{A0}} \right]}{dT} \bigg|_{T^*} = \left(\frac{(-\Delta H_{R_x}) V}{F_{A0}} \right) \left. \frac{d(-r_A)}{dT} \right|_{T^*} \quad (8-67)$$

Assuming that the reaction is irreversible and follows a power law model and that the concentrations of the reacting species are weak functions of temperature,

$$-r_A = (Ae^{-E/RT}) \text{fn}(C_i) \quad (8-68)$$

then

$$\left. \frac{d(-r_A)}{dT} \right|_{T^*} = \frac{E}{RT^{*2}} A e^{-E/RT^*} \text{fn}(C_i) = \frac{E}{RT^{*2}} (-r_A^*)$$

Substituting for the derivative of $(-r_A)$ wrt T in Equation (8-67)

$$\left. \frac{dG(T)}{dT} \right|_{T^*} = \left(\frac{(-\Delta H_{R_x}) (-r_A^*) V}{F_{A0}} \right) \frac{E}{RT^{*2}} = G(T^*) \frac{E}{RT^{*2}} \quad (8-69)$$

$$\left. \frac{dG(T)}{dT} \right|_{T^*} = S^*$$

where

$$S^* = G(T^*) \frac{E}{RT^{*2}}$$

Equating Equations (8-66) and (8-69) yields

$$C_{P0}(1 + \kappa) = \frac{E}{RT^{*2}} \overbrace{(-r_A^* V) \frac{(-\Delta H_{Rx}^o)}{F_{A0}}}^{G(T^*)} = S^* \quad (8-70)$$

$$S^* = \frac{E}{RT^{*2}} G(T^*)$$

Next, we divide Equation (8-65) by Equation (8-70) to obtain the following ΔT value for a CSTR operating at $T = T^*$:

$$\Delta T_{rc} = T^* - T_c = \frac{RT^{*2}}{E} \quad (8-71)$$

If this difference between the reactor temperature and T_c , ΔT_{rc} , is exceeded, transition to the upper steady state will occur. For many industrial reactions, E/RT is typically between 16 and 24, and the reaction temperatures may be between 300 to 500 K. Consequently, this critical temperature difference ΔT_{rc} will be somewhere around 15 to 30°C.

Stability Diagram. We now want to develop a stability diagram that will show regions of stable operation and unstable operation. One such diagram would be a plot of S^* as a function of T_c . To construct this plot, we first solve Equation (8-71) for T^* , the reactor temperature at the point of tangency,

$$T^* = \frac{E}{2R} \left[1 - \sqrt{1 - 4 \frac{T_c R}{E}} \right] \quad (8-72)$$

and recalling

$$T_c = \frac{\kappa T_a + T_0}{1 + \kappa}$$

We can now vary T_c , then calculate T^* [Equation (8-72)], calculate k^* ($k^* = Ae^{-E/RT^*}$), calculate $-r_A^*$ at T^* from rate law, calculate $G(T^*)$ [Equation (8-59)], and then finally calculate S^* to make a plot of S^* as a function of T_c as shown in Figure 8-25. We see that any deviation to the right or below the intersection of $C_{P0}(1 + \kappa)$ and S^* will result in runaway.

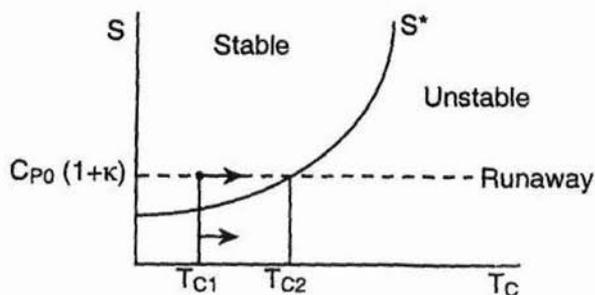


Figure 8-25 CSTR stability diagram.

For example, for a first-order reaction, the equation for S^* is

$$S^* = \left(\frac{\tau A e^{-E/RT^*}}{1 + \tau A e^{-E/RT^*}} \right) (-\Delta H_{\text{Rx}}) \frac{E}{RT^{*2}} \quad (8-73)$$

We simply combine Equation (8-72) and the equation for T_c and then substitute the result into Equation (8-73) and plot S^* as a function of T_0 . From Figure 8-25, we see that for a given value of $[C_{p0}(1+\kappa)]$, if we were to increase the entering temperature T_0 from some low-value T_{01} (T_{c1}) to a higher entering temperature value T_{02} (T_{c2}), we would reach a point at which runaway would occur. Further discussions are given on the CD-ROM professional reference shelf R8.2. Referring to Equation (8-70), we can infer

$$C_{p0}(1 + \kappa) > S^* \quad (8-74)$$

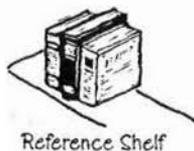
we will not move to the upper steady state, and runaway will not occur. However, if

$$C_{p0}(1 + \kappa) < S^* \quad (8-75)$$

runaway will occur.

8.8 Nonisothermal Multiple Chemical Reactions

Most reacting systems involve more than one reaction and do not operate isothermally. **This section is one of the most important sections of the book.** It ties together all the previous chapters to analyze multiple reactions that do not take place isothermally.



Reference Shelf

8.8.1 Energy Balance for Multiple Reactions in Plug-Flow Reactor

In this section we give the energy balance for multiple reactions. We begin by recalling the energy balance for a single reaction taking place in a PFR which is given by Equation (8-35),

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)[- \Delta H_{Rx}(T)]}{\sum_{i=1}^m F_i C_{P_i}} \quad (8-35)$$

When q multiple reactions are taking place in the PFR and there are m species, it is easily shown that Equation (8-35) can be generalized to

Energy balance for multiple reactions

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + \sum_{i=1}^q (-r_{ij})[- \Delta H_{R_{xij}}(T)]}{\sum_{j=1}^m F_j C_{P_j}} \quad (8-36)$$

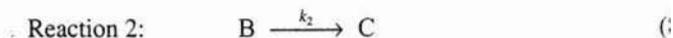
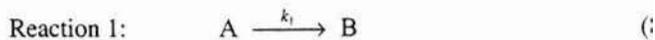
i = Reaction number
 j = Species

The heat of reaction for reaction i must be referenced to the same species j as the rate, r_{ij} , by which $\Delta H_{R_{xij}}$ is multiplied, that is,

$$\begin{aligned} [-r_{ij}][-\Delta H_{R_{xij}}] &= \left[\frac{\text{Moles of } j \text{ reacted in reaction } i}{\text{Volume} \cdot \text{time}} \right] \times \left[\frac{\text{Joules "released" in reaction } i}{\text{Moles of } j \text{ reacted in reaction } i} \right] \\ &= \left[\frac{\text{Joules "released" in reaction } i}{\text{Volume} \cdot \text{time}} \right] \end{aligned}$$

where the subscript j refers to the species, the subscript i refers to the particular reaction, q is the number of **independent** reactions, and m is the number of species.

Consider the following reaction sequence carried out in a PFR:



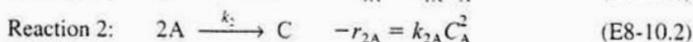
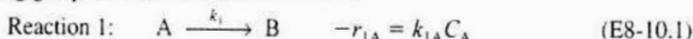
The PFR energy balance becomes

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_{1A})(-\Delta H_{R_{x1A}}) + (-r_{2B})(-\Delta H_{R_{x2B}})}{F_A C_{PA} + F_B C_{PB} + F_C C_{PC}} \quad (8-39)$$

where $\Delta H_{R_{x1A}} = [\text{kJ/mol of A reacted in reaction 1}]$ and $\Delta H_{R_{x2B}} = [\text{kJ/mol of B reacted in reaction 2}]$.

Example 8-10 Parallel Reactions in a PFR with Heat Effects

The following gas-phase reactions occur in a PFR:



Pure A is fed at a rate of 100 mol/s, a temperature of 150°C, and a concentration of 0.1 mol/dm³. Determine the temperature and flow rate profiles down the reactor.

Additional information:

$$\Delta H_{R_{X1A}} = -20,000 \text{ J/(mol of A reacted in reaction 1)}$$

$$\Delta H_{R_{X2A}} = -60,000 \text{ J/(mol of A reacted in reaction 2)}$$

$$C_{pA} = 90 \text{ J/mol} \cdot ^\circ\text{C} \quad k_{1A} = 10 \exp\left[\frac{E_1}{R}\left(\frac{1}{300} - \frac{1}{T}\right)\right] \text{ s}^{-1}$$

$$C_{pB} = 90 \text{ J/mol} \cdot ^\circ\text{C} \quad E_1/R = 4000 \text{ K}$$

$$C_{pC} = 180 \text{ J/mol} \cdot ^\circ\text{C} \quad k_{2A} = 0.09 \exp\left[\frac{E_2}{R}\left(\frac{1}{300} - \frac{1}{T}\right)\right] \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}$$

$$Ua = 4000 \text{ J/m}^3 \cdot \text{s} \cdot ^\circ\text{C} \quad E_2/R = 9000 \text{ K}$$

$$T_a = 100^\circ\text{C}$$

Solution

The PFR energy balance becomes [cf. Equation (8-76)]

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_{1A})(-\Delta H_{R_{X1A}}) + (-r_{2A})(-\Delta H_{R_{X2A}})}{F_A C_{pA} + F_B C_{pB} + F_C C_{pC}} \quad (\text{E8-10.3})$$

Mole balances:

$$\frac{dF_A}{dV} = r_A \quad (\text{E8-10.4})$$

$$\frac{dF_B}{dV} = r_B \quad (\text{E8-10.5})$$

$$\frac{dF_C}{dV} = r_C \quad (\text{E8-10.6})$$

Rate laws, relative rates, and net rates:*Rate laws*

$$r_{1A} = -k_{1A}C_A \quad (\text{E8-10.1})$$

$$r_{2A} = -k_{2A}C_A^2 \quad (\text{E8-10.2})$$



Living Example Problem

One of the major goals of this text is that the reader will be able to solve multiple reactions with heat effects.

Relative rates

$$\text{Reaction 1:} \quad \frac{r_{1A}}{-1} = \frac{r_{1B}}{1}; \quad r_{1B} = -r_{1A} = k_{1A}C_A$$

$$\text{Reaction 2:} \quad \frac{r_{2A}}{-2} = \frac{r_{2C}}{1}; \quad r_{2C} = -\frac{1}{2} r_{2A} = \frac{k_{2A}}{2} C_A^2$$

Net rates:

$$r_A = r_{1A} + r_{2A} = -k_{1A}C_A - k_{2A}C_A^2 \quad (\text{E8-10.7})$$

$$r_B = r_{1B} = k_{1A}C_A \quad (\text{E8-10.8})$$

$$r_C = r_{2C} = \frac{1}{2} k_{2A}C_A^2 \quad (\text{E8-10.9})$$

Stoichiometry (gas phase $\Delta P = 0$):

$$C_A = C_{T0} \left(\frac{F_A}{F_T} \right) \left(\frac{T_0}{T} \right) \quad (\text{E8-10.10})$$

$$C_B = C_{T0} \left(\frac{F_B}{F_T} \right) \left(\frac{T_0}{T} \right) \quad (\text{E8-10.11})$$

$$C_C = C_{T0} \left(\frac{F_C}{F_T} \right) \left(\frac{T_0}{T} \right) \quad (\text{E8-10.12})$$

$$F_T = F_A + F_B + F_C \quad (\text{E8-10.13})$$

$$k_{1A} = 10 \exp \left[3000 \left(\frac{1}{300} - \frac{1}{T} \right) \right] \text{s}^{-1} \quad (T \text{ in K})$$

$$k_{2A} = 0.09 \exp \left[9000 \left(\frac{1}{300} - \frac{1}{T} \right) \right] \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}$$

Energy balance:

$$\frac{dT}{dV} = \frac{4000(373 - T) + (-r_{1A})(20,000) + (-r_{2A})(60,000)}{.90F_A + 90F_B + 180F_C} \quad (\text{E8-10.14})$$

The Polymath program and its graphical outputs are shown in Table E8-10.1 and Figures E8-10.1 and E8-10.2.

The algorithm for multiple reactions with heat effects

TABLE E8-10.1. POLYMATH PROGRAM

Equations:

POLYMATH Results

Example 8-10 Parallel Reaction in a PFR with Heat Effects 08-13-2004, Rev.5.1.232

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	1	1
Fa	100	2.738E-06	100	2.738E-06
Fb	0	0	55.04326	55.04326
Fc	0	0	22.478369	22.478369
T	423	423	812.19122	722.08816
k1a	482.8247	482.8247	4.484E+04	2.426E+04
k2a	553.05566	553.05566	1.48E+07	3.716E+06
Cto	0.1	0.1	0.1	0.1
Ft	100	77.521631	100	77.521631
To	423	423	423	423
Ca	0.1	2.069E-09	0.1	2.069E-09
Cb	0	0	0.0415941	0.0415941
Cc	0	0	0.016986	0.016986
r1a	-48.28247	-373.39077	-5.019E-05	-5.019E-05
r2a	-5.5305566	-848.11153	-1.591E-11	-1.591E-11

ODE Report (RK45)

Differential equations as entered by the user

- $d(Fa)/d(V) = r1a+r2a$
- $d(Fb)/d(V) = -r1a$
- $d(Fc)/d(V) = -r2a/2$
- $d(T)/d(V) = (4000*(373-T)+(-r1a)*20000+(-r2a)*60000)/(90*Fa+90*Fb+180*Fc)$

Explicit equations as entered by the user

- $k1a = 10*\exp(4000*(1/300-1/T))$
- $k2a = 0.09*\exp(9000*(1/300-1/T))$
- $Cto = 0.1$
- $Ft = Fa+Fb+Fc$
- $To = 423$
- $Ca = Cto*(Fa/Ft)*(To/T)$
- $Cb = Cto*(Fb/Ft)*(To/T)$
- $Cc = Cto*(Fc/Ft)*(To/T)$
- $r1a = -k1a*Ca$
- $r2a = -k2a*Ca^2$

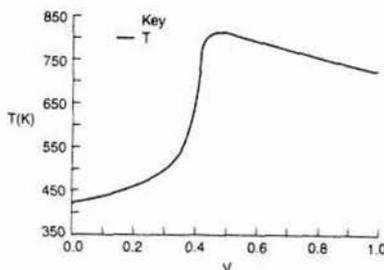
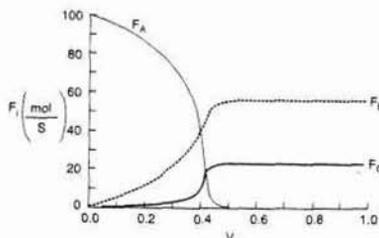


Figure E8-10.1 Temperature profile.

Figure E8-10.2 Profile of molar flow rates F_A , F_B , and F_C .

Why does the temperature go through a maximum value?



Living Example Problem

8.8.2 Energy Balance for Multiple Reactions in CSTR

Recall that $-F_{A0}X = r_A V$ for a CSTR and that $\Delta H_{R_x}(T) = \Delta H_{R_x}^\circ + \Delta C_p(T - T_0)$ so that Equation (8-27) for the steady-state energy balance for a single reaction may be written as

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_i \Theta_i C_{p_i} (T - T_0) + [\Delta H_{R_x}(T)] [r_A V] = 0 \quad (8-80)$$

For q multiple reactions and m species, the CSTR energy balance becomes

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_{i=1}^m \Theta_i C_{p_i} (T - T_0) + V \sum_{j=1}^q r_{ij} \Delta H_{R_{xij}}(T) = 0 \quad (8-81)$$

Energy balance for multiple reactions in a CSTR

Substituting Equation (8-50) for \dot{Q} , neglecting the work term, and assuming constant heat capacities, Equation (8-80) becomes

$$UA(T_a - T) - F_{A0} \sum_{i=1}^m C_{p_i} \Theta_i (T - T_0) + V \sum_{j=1}^q r_{ij} \Delta H_{R_{xij}}(T) = 0 \quad (8-82)$$

For the two parallel reactions described in Example 8-10, the CSTR energy balance is

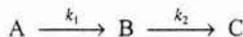
$$UA(T_a - T) - F_{A0} \sum_{i=1}^m \Theta_i C_{p_i} (T - T_0) + V r_{1A} \Delta H_{R_{x1A}}(T) + V r_{2A} \Delta H_{R_{x2A}}(T) = 0 \quad (8-83)$$

Major goal of CRE

One of the major goals of this text is to have the reader solve problems involving multiple reactions with heat effects (cf. Problem P8-26C).

Example 8-11 Multiple Reactions in a CSTR

The elementary liquid-phase reactions



take place in a 10-dm³ CSTR. What are the effluent concentrations for a volume feed rate of 1000 dm³/min at a concentration of A of 0.3 mol/dm³?

The inlet temperature is 283 K.

Additional information:

$$C_{p_A} = C_{p_B} = C_{p_C} = 200 \text{ J/mol} \cdot \text{K}$$

$$k_1 = 3.3 \text{ min}^{-1} \text{ at } 300 \text{ K, with } E_1 = 9900 \text{ cal/mol}$$

$$k_2 = 4.58 \text{ min}^{-1} \text{ at } 500 \text{ K, with } E_2 = 27,000 \text{ cal/mol}$$

$$\Delta H_{R_{x1A}} = -55,000 \text{ J/mol A} \quad UA = 40,000 \text{ J/min} \cdot \text{K with } T_a = 57^\circ\text{C}$$

$$\Delta H_{R_{x2B}} = -71,500 \text{ J/mol B}$$

Solution

The reactions follow elementary rate laws

$$r_{1A} = -k_{1A}C_A$$

$$r_{2B} = -k_{2B}C_B$$

1. Mole Balance on Every Species

A: Combined mole balance and rate law for A:

$$V = \frac{F_{A0} - F_A}{-r_A} = \frac{v_0[C_{A0} - C_A]}{-r_{1A}} = \frac{v_0[C_{A0} - C_A]}{k_1 C_A} \quad (\text{E8-11.1})$$

Solving for C_A gives us

$$C_A = \frac{C_{A0}}{1 + \tau k_1} \quad (\text{E8-11.2})$$

B: Combined mole balance and rate law for B:

$$V = \frac{0 - C_B v_0}{-r_B} = \frac{C_B v_0}{(r_{1B} + r_{2B})} = \frac{C_B v_0}{k_1 C_A - k_2 C_B} \quad (\text{E8-11.3})$$

Solving for C_B yields

$$C_B = \frac{\tau k_1 C_A}{1 + \tau k_2} = \frac{\tau k_1 C_{A0}}{(1 + \tau k_1)(1 + \tau k_2)} \quad (\text{E8-11.4})$$

2. Rate Laws:

$$-r_{1A} = k_1 C_A = \frac{k_1 C_{A0}}{1 + \tau k_1} \quad (\text{E8-11.5})$$

$$-r_{2B} = k_2 C_B = \frac{k_2 \tau k_1 C_{A0}}{(1 + \tau k_1)(1 + \tau k_2)} \quad (\text{E8-11.6})$$

3. Energy Balances:

Applying Equation (8-82) to this system gives

$$UA(T_a - T) - F_{A0} C_{pA} (T - T_0) + V[r_{1A} \Delta H_{R_{x1A}} + r_{2B} \Delta H_{R_{x2B}}] = 0 \quad (\text{E8-11.7})$$

Substituting for r_{1A} and r_{2B} and rearranging, we have

$$\underbrace{\left[-\frac{\Delta H_{R_{x1A}} \tau k_1}{1 + \tau k_1} - \frac{\tau k_1 \tau k_2 \Delta H_{R_{x2B}}}{(1 + \tau k_1)(1 + \tau k_2)} \right]}_{G(T)} = \underbrace{\frac{R(T)}{C_p(1 + \kappa)[T - T_c]}}_{R(T)} \quad (\text{E8-11.8})$$

$$\kappa = \frac{UA}{F_{A0} C_{pA}} = \frac{40,000 \text{ J/min} \cdot \text{K}}{(0.3 \text{ mol/dm}^3)(1000 \text{ dm}^3/\text{min}) 200 \text{ J/mol} \cdot \text{K}} = 0.667$$

$$T_c = \frac{T_0 + \kappa T_d}{1 + \kappa} = \frac{283 + (0.666)(330)}{1 + 0.667} = 301.8 \text{ K} \quad (\text{E8-11.9})$$

$$G(T) = \left[-\frac{\Delta H_{R1A} \tau k_1}{1 + \tau k_1} - \frac{\tau k_1 \tau k_2 \Delta H_{R2B}}{(1 + \tau k_1)(1 + \tau k_2)} \right] \quad (\text{E8-11.10})$$

$$R(T) = C_p(1 + \kappa)[T - T_c] \quad (\text{E8-11.11})$$

We are now going to write a Polymath program to increment temperature to obtain $G(T)$ and $R(T)$. The Polymath program to plot $R(T)$ and $G(T)$ vs. T is shown in Table E8-11.1, and the resulting graph is shown in Figure E8-11.1.

TABLE E8-11.1. POLYMATH

Equations:

POLYMATH Results**Example 8-11 Multiple Reactions in a CSTR** 08-13-2004, Rev5.1.232**ODE Report (RKF45)**

Differential equations as entered by the user

[1] $d(T)/d(t) = 2$

Explicit equations as entered by the user

[1] $C_p = 200$

[2] $C_{a0} = 0.3$

[3] $T_0 = 283$

[4] $\tau = .01$

[5] $DH1 = -55000$

[6] $DH2 = -71500$

[7] $v_0 = 1000$

[8] $E2 = 27000$

[9] $E1 = 9900$

[10] $UA = 40000$

[11] $T_a = 330$

[12] $k_2 = 4.58 \cdot \exp((E2/1.987) \cdot (1/500 - 1/T))$

[13] $k_1 = 3.3 \cdot \exp((E1/1.987) \cdot (1/300 - 1/T))$

[14] $C_a = C_{a0}/(1 + \tau k_1)$

[15] $\kappa = UA/(v_0 \cdot C_{a0})/C_p$

[16] $G = -\tau k_1/(1 + \tau k_1) \cdot DH1 - k_1 \tau k_2 \tau \cdot DH2/((1 + \tau k_1)(1 + \tau k_2))$

[17] $T_c = (T_0 + \kappa T_a)/(1 + \kappa)$

[18] $C_b = \tau k_1 \cdot C_a/(1 + \tau k_2)$

[19] $R = C_p(1 + \kappa)(T - T_c)$

[20] $C_c = C_{a0} - C_a - C_b$

[21] $F = G - R$

Incrementing temperature in this manner is an easy way to generate $R(T)$ and $G(T)$ plots



Living Example Problem

When $F = 0$
 $G(T) = R(T)$ and
the steady states
can be found.

We see that five steady states (SS) exist. The exit concentrations and temperatures listed in Table E8-11.2 were interpreted from the tabular output of the Polymath program.