Chemical Reactor Modelling and Analysis

The chemical reactor is one of the most important unit operations considered by chemical engineers; thus, proper modelling and analysis are essential. The engineer should be able to derive the basic balances for typical reactor designs and to anticipate the range of likely dynamic behavior. This appendix is provided to complement and extend the coverage in Chapters 3 through 5 by deriving the energy balance, demonstrating linear analysis, and addressing more complex dynamic behavior. Sections C.1 to C.3 apply standard modelling and analysis methods to this important chemical process and should be understood by all students. The material in Sections C.4 and C.5 presents more complex behavior that occurs in some chemical reactors and can be covered as enrichment material.

C.1 □ ENERGY BALANCE

Material balances for reacting systems were derived in Chapter 3 and applied throughout the book. The energy balance for a continuous-flow chemical reactor is used, but not derived, in Section 3.5. The reactor energy balance is derived here, beginning with the general energy balance in equation (3.5), with the following assumptions:

1. The system volume is constant.
2. The heat capacity and density are constant.
3. $\Delta PE = \Delta KE = 0$.
4. The tank is well mixed.
5. One chemical reaction is occurring.

In this derivation the partial molar enthalpy of component i in a stream of n components, h_i, is assumed to be a function of temperature only.

$$\frac{\partial H}{\partial C_i} = h_i(T) = \text{partial molar enthalpy} \tag{C.1}$$

The symbol C_i is (moles/volume) of component i. The individual terms in equation (3.5) can be expressed as

$$\text{Accumulation:} \quad \frac{dU}{dt} \approx \frac{dH}{dt} = V \sum_{i=1}^{n} \frac{d[C_i h_i(T)]}{dt} \tag{C.2}$$

$$\text{Flow in:} \quad F H_0 = F \sum_{i=1}^{n} C_{i0} h_i(T_0) \tag{C.3}$$

$$\text{Flow out:} \quad F H = F \sum_{i=1}^{n} C_i h_i(T) \tag{C.4}$$

The accumulation term can be expanded to give

$$V \sum_{i=1}^{n} \frac{d[C_i h_i(T)]}{dt} = V \left[\sum_{i=1}^{n} h_i \frac{dC_i}{dt} + \sum_{i=1}^{n} C_i \left(\frac{\partial h_i}{\partial T} \frac{dT}{dt} \right) \right] \tag{C.5}$$

The second term of the right-hand side of equation (C.5) can be simplified by noting that $\sum C_i (\partial h_i/\partial T) = \rho c_p$ (cal/[volume K]). Also, the first term on the right-hand side can be expanded by substituting the dynamic component material balance from equation (3.75) for dC_i/dt to give

$$\sum_{i=1}^{n} h_i \left[V \frac{dC_i}{dt} \right] = \sum_{i=1}^{n} h_i [F C_{i0} - F C_i + V \mu_i r]$$

$$= F \sum_{i=1}^{n} C_{i0} h_i(T) - F \sum_{i=1}^{n} C_i h_i(T) + V \Delta H_{rxn} r \tag{C.6}$$

The coefficients μ_i represent the amount of the component i generated from the extent of reaction r; for the example of a single reaction A $\rightarrow$ B; the coefficients are -1 for component A and $+1$ for component B. The sum of the products of these coefficients times their component enthalpies is commonly called the *heat of reaction* and is available in references. Combining the results gives

$$\rho V C_p \frac{dT}{dt} = F \sum_{i=1}^{n} C_{i0} [h_i(T_0) - h_i(T)]$$

$$+ F \sum_{i=1}^{n} C_i [h_i(T) \overset{0}{\cancel{- h_i(T)}}] + V(-\Delta H_{rxn}) r + Q - W_s \tag{C.7}$$

Clearly, the second term on the right is zero. Also, the first term can be simplified, because partial molar enthalpy is assumed independent of composition, by expressing the total enthalpy of a stream as a function of its temperature to give

$$V \rho C_p \frac{dT}{dt} = F \rho C_p (T_0 - T) + V(-\Delta H_{rxn}) r + Q - W_s \tag{C.8}$$

Equation (C.8) is the basic energy balance for a well-mixed, continuous-flow, liquid-phase chemical reactor. The second term on the right-hand side can be

thought of as "generation due to reaction," but it is important to recognize that no generation term exists in the basic energy balance in equation (3.5). Also, it is important to recognize that many approximations have been employed that are not general. This equation is usually valid for liquid-phase systems but contains assumptions often not valid for gas-phase reactors. For alternative presentations and cogent discussion of reactor modelling, see Aris (1989) and Denn (1986).

C.2 □ MODELLING OF AN EXAMPLE NONISOTHERMAL CSTR

In this section, the basic material and energy balances are applied to the nonisothermal CSTR shown in Figure C.1. Also, these equations are linearized, so that the linearized model can be used to determine important properties of the process, such as stability.

GOAL. The temperature of a chemical reactor is to be raised to 395.3 K, without exceeding 395.3 K, by adjusting the coolant flow. How should the coolant flow be adjusted? A more fundamental question is the shape of the dynamic response; is it monotonic or oscillatory, and what design parameters and external variables influence this response?

FIGURE C.1

Nonisothermal CSTR process.

INFORMATION. The process is shown in Figure C.1, and the system is taken to be the liquid in the tank. The chemical reaction is first-order with Arrhenius temperature dependence.

ASSUMPTIONS.

1. The tank is well mixed.
2. Physical properties are constant.
3. The shaft work is negligible.
4. The irreversible, elementary reaction is A → B.

DATA.

1. $F = 1$ m³/min; $V = 1$ m³; $C_{A0} = 2.0$ kmole/m³; $T_0 = 323$ K; $C_p = 1$ cal/(g K); $\rho = 10^6$ g/m³; $k_0 = 1.0 \times 10^{10}$ min⁻¹; $E/R = 8330.1$ K; $-\Delta H_{rxn} = 130 \times 10^6$ cal/(kmole); $T_{cin} = 365$ K; $(F_c)_s = 15$ m³/min; $C_{pc} = 1$ cal/(g K); $\rho_c = 10^6$ g/m³; $a = 1.678 \times 10^6$ (cal/min)/(K); $b = 0.5$.
2. For this data, the steady-state values of the dependent variables are $T_s = 394$ K and $C_{As} = 0.265$ kmole/m³.
3. The change in coolant flow is a step of -1 m³/min.

FORMULATION. The system is the liquid in the tank. The overall material balance, as in several previous examples, demonstrates that the mass in the tank is approximately constant; thus, $F_0 = F_1 = F$. The component material balance on the reactant gives

$$V \frac{dC_A}{dt} = F(C_{A0} - C_A) - V k_0 e^{-E/RT} C_A \qquad (C.9)$$

The energy balance for this system is

$$V\rho C_p \frac{dT}{dt} = \rho C_p F(T_0 - T) - \frac{aF_c^{b+1}}{F_c + \frac{aF_c^b}{2\rho_c C_{pc}}}(T - T_{cin})$$

$$+(-\Delta H_{rxn})Vk_0 e^{-E/RT}C_A \tag{C.10}$$

These two nonlinear differential equations cannot be solved analytically. The linearized equations in deviation variables are as follows:

$$\frac{dC_A'}{dt} = a_{11}C_A' + a_{12}T' + a_{13}C_{A0}' + a_{14}F_c' + a_{15}T_0' + a_{16}'F' \tag{C.11}$$

$$\frac{dT'}{dt} = a_{21}C_A' + a_{22}T' + a_{23}C_{A0}' + a_{24}F_c' + a_{25}T_0' + a_{26}F' \tag{C.12}$$

where $\quad a_{11} = -\frac{F}{V} - k_0 e^{-E/RT_s}$

$$a_{12} = -\frac{E}{RT_s^2}k_0 e^{-E/RT_s}C_{As}$$

$$a_{13} = \frac{F}{V}$$

$$a_{14} = 0$$

$$a_{15} = 0$$

$$a_{16} = \frac{(C_{A0} - C_A)_s}{V}$$

$$a_{21} = \frac{-\Delta H_{rxn}k_0 e^{-E/RT_s}}{\rho C_p}$$

$$\tag{C.13}$$

$$a_{22} = -\frac{F}{V} - \frac{UA_s^*}{V\rho C_p} + (-\Delta H_{rxn})\frac{\frac{E}{RT_s^2}}{\rho C_p}k_0 e^{-E/RT_s}C_{As}$$

$$a_{23} = 0$$

$$a_{24} = \frac{-abF_{cs}^b\left(F_{cs} + \frac{a}{b}\frac{F_{cs}^b}{2\rho_c C_{pc}}\right)[T_s - (T_{cin})_s]}{(V\rho C_p)\left(F_{cs} + \frac{aF_{cs}^b}{2\rho_c C_{pc}}\right)^2}$$

$$a_{25} = \frac{F}{V}$$

$$a_{26} = \frac{(T_0 - T)_s}{V}$$

where $\quad UA_s^* = a(F_c)_s^{b+1}/[(F_c)_s + a(F_c)_s^b/2\rho_c C_{pc}]$

The approximate model is derived about the steady-state operating point for the reactor. Note that the inlet concentration C_{A0}', the coolant flow rate F_c', the inlet temperature T_0', and the feed flow rate F' are input variables in the foregoing linearized equations, although only the coolant flow varies in this example; this is done because changes in other input variables will be considered elsewhere.
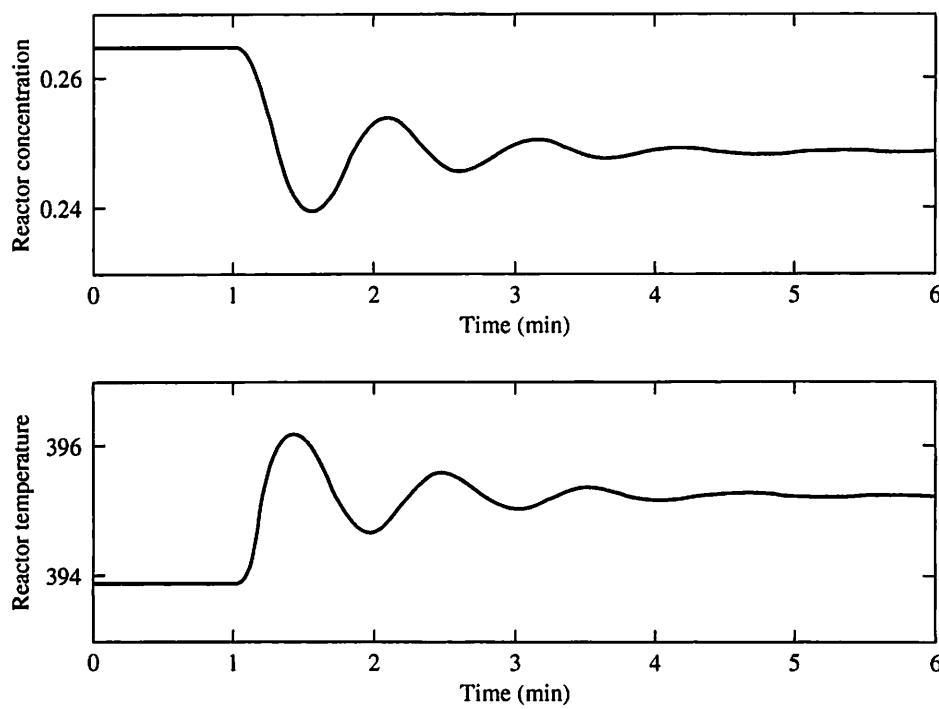
FIGURE C.2

Dynamic response for CSTR for step in cooling flow of $-1\text{m}^3/\text{min}$ at time $= 1$.

SOLUTION. The analytical solution to the linearized model requires the simultaneous solution of equations (C.11) and (C.12), because C'_A and T' appear in both equations. Since the integrating factor method cannot be applied to this problem, the analytical solution to the linearized equations can be determined using Laplace transforms. To determine the behavior of the process and answer the specific question posed in this example, the solution of the nonlinear model will be determined via a numerical solution using an explicit method; the result for the Euler method with a step size of 0.005 minute is given in Figure C.2. The solution is underdamped (i.e., oscillatory) for this model and set of design parameters and operating conditions. As a result, a single step in the coolant flow large enough to raise the temperature to its desired final value of 395.3 K leads to a response that exceeds this maximum value during the transient. Thus, it is not possible with one adjustment of the cooling flow to achieve the temperature specifications, although the temperature could be increased very close to, without exceeding, 395.3 K through a series of smaller adjustments to the coolant flow.

C.3 ▢ THE REACTOR TRANSFER FUNCTIONS

The numerical solution of the nonlinear equations provides an excellent estimate of the behavior for a specific situation, but it does not provide important analysis of the effects of parameters on key aspects of the reactor's dynamic behavior. These insights can be determined by analyzing the linearized dynamic model in transfer function form. For example, the transfer function for the temperature-coolant flow relationship can be determined by taking the Laplace transforms of equations (C.11) and (C.12), setting the deviation variables of all but one of the inputs (F'_c) to zero, and combining equations. The resulting transfer function for

902

▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓

APPENDIX C
Chemical Reactor
Modelling and
Analysis

this example is (C.14)

$$\frac{T(s)}{F_c(s)} = \frac{a_{24}s + (a_{21}\,a_{14} - a_{24}a_{11})}{s^2 - (a_{11} + a_{22})s + (a_{11}a_{22} - a_{12}a_{21})} \tag{C.14}$$

When the numerical values of the data in Section C.2 are substituted, the result is

$$a_{11} = -7.55 \qquad a_{12} = -0.093 \qquad a_{14} = 0.0$$
$$a_{21} = 852.02 \qquad a_{22} = 5.77 \qquad a_{24} = -6.07$$

$$\frac{T(s)}{F_c(s)} = \frac{(-6.07s - 45.83)}{(s^2 + 1.79s + 35.80)} \tag{C.15}$$

For the design parameters introduced in Section C.2, the roots of the denominator, i.e., the characteristic polynomial, are $-0.894 \pm 5.92j$. The following important aspects of the reactor behavior can be determined from the transfer function:

1. Since the roots of the denominator have negative real parts, the system is stable.
2. Since the roots of the denominator have complex parts, the system is underdamped.

The dynamic behavior of the linearized model can be determined by substituting the step input $F_c(s) = \Delta F_c/s = -1/s$ into equation (C.15) and inverting the Laplace transform. This transform does not appear in Table 4.1 but could be found in more complete tables. (Alternatively, the partial fractions method could be applied, as shown in Example H.1 in Appendix H.) The resulting expression for the temperature response to a step in coolant flow is given in the following equation.

$$T'(t) = 1.28 + 2e^{-0.894}[-0.64\cos(5.92t) + 0.42\sin(5.92t)] \tag{C.16}$$

The temperature is stable and oscillatory, results consistent with the analysis based on the roots of the characteristic polynomial. The validity of this analysis is confirmed by the nonlinear simulation results in Figure C.2, which also show damped oscillations in the temperature dynamics.

More complex behaviors, which occur occasionally in chemical reactors, are introduced in the next sections.

C.4 ▨ MULTIPLE STEADY STATES

Some physical processes exhibit multiple steady states, a behavior that is not obvious without careful analysis. Recall that a steady state is defined as a condition in which all relevant balances are satisfied when the accumulation terms are zero. For linear equations, this situation would occur at only one (if any) set of operating conditions. However, the equations describing most chemical processes are nonlinear, and multiple solutions are possible, although they do not always, or even often, occur.

The steady-state material balance for the system with a single reaction A → B is determined from equation (C.9) to be

$$C_A = \left[\frac{F}{F + Vk_0e^{-E/RT}}\right]C_{A0} \tag{C.17}$$

The second equation, the steady-state energy balance, can be separated into two terms: Q_T for energy transfer and Q_R for release due to reaction, which sum to zero at steady state.

$$0 = Q_T + Q_R \qquad (C.18)$$

where $\quad Q_T = F\rho C_P(T_0 - T) - \dfrac{a F_c^{b+1}}{F_c + \dfrac{a F_c^b}{2\rho_c C_{pc}}}(T - T_{cin})$

$$Q_R = (-\Delta H_{rxn})Vk_0e^{-E/RT}C_A$$

The steady-state solution is achieved when the two terms, $-Q_T$ and Q_R, are equal. However, more than one solution can exist for this system. To check for multiple solutions, it is convenient to graph the two terms versus temperature, remembering that the concentration value used at each temperature is determined from equation (C.17) at the appropriate temperature.

This procedure has been carried out for three cases of reactor designs, which are described in Table C.1. Note that most parameters, including the chemical reaction, are the same in all cases; they differ in only the feed temperature and the coolant system. In addition to the design input variable values, the table presents the steady-state output variables, C_{As} and T_s. Also, the linearized stability analysis, in the form of the poles of the system (without control) at each steady state, is presented; the poles are the roots of the denominator of equation (C.14).
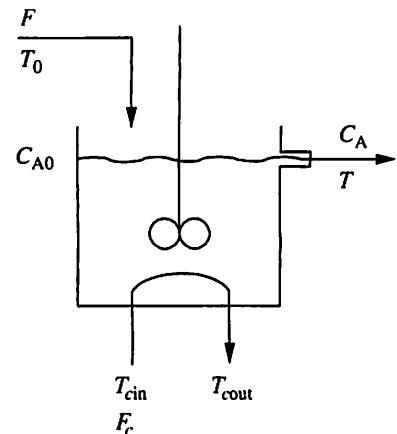
DATA

$F = 1 \text{ m}^3/\text{min}$, $V = 1 \text{ m}^3$, $C_{A0} = 2.0 \text{ kmole/m}^3$, $C_p = 1 \text{ cal}/(\text{g}^\circ\text{C})$, $\rho = 10^6\text{g/m}^3$,

$k_o = 1.0 \times 10^{10} \text{ min}^{-1}$, $E/R = 8330.1\text{K}^{-1}$, $-\Delta H_{rxn} = 130 \times 10^6 \text{ cal}/(\text{kmole})$

$(F_c)_s = 15 \text{ m}^3/\text{min}$, $C_{pc} = 1 \text{ cal}/(\text{g K})$, $\rho_c = 10^6 \text{ g/m}^3$, $b = 0.5$

Case I is identical to the reactor introduced in Section C.2. The system has a single steady state, because a graph of the terms $-Q_T$ and Q_R in equation (C.18) has only one intersection. This steady state is stable, because the real parts of the poles are negative, and the behavior is underdamped, because the poles are complex.

Case II has multiple steady states, as is demonstrated in Figure C.3, where the (negative of the) "energy transfer" and "release due to reaction" terms are equal

TABLE C.1

Data for continuous-flow stirred-tank reactors

Variables	Case I	Case II			Case III
T_0(K)	323	343			323
T_{cin}(K)	365	310			340
a (cal/min K)/(m³/min)	1.678×10^6	0.516×10^6			1.291×10^6
Steady-state C_A(kmole/m³)	0.26	1.79	1.37	0.16	1.06
Steady-state T(K)	393.9	330.9	350	404.7	360
Poles (min⁻¹)	$-0.89 \pm 5.92j$	$-0.96 \pm 0.47j$	$1.94, -0.71$	$-1.6 \pm 4.6j$	$0.34 \pm 1.41j$

at three temperatures! Thus, this chemical reactor can operate at three distinct sets of concentration and temperature for the *same values of all input variables and parameters*. Next, the stability in a small region about each steady state is evaluated, using linearized models about each steady state to determine whether the reactor would operate at the conditions without feedback control. The results in Table C.1 indicate that two steady states are stable, whereas the steady state with the intermediate temperature is (locally) unstable, because it has a pole that is real and positive. This result indicates that only the two stable steady states can be achieved in practice without control. Any slight deviation from the *exact* values in the inputs in the table would result in the reactor dynamic response moving away from the unstable steady state toward one of the stable steady states. The final steady state achieved depends on the initial conditions of the reactor. For example, if the initial conditions are taken (arbitrarily) as 393.9 K and 0.26 kmole/m^3 (the values from Case I), the Case II reactor does not approach the unstable steady state, but rather approaches the steady state at the higher temperature, as shown in Figure C.4.

The instability of the intermediate temperature in Case II can be understood from steady-state arguments. It can be determined from Figure C.3 that as the temperature increases slightly from the intermediate steady state, the magnitude of the heat release increases faster than the magnitude of the heat transfer; that is, $d(-Q_T)/dT < d(Q_R)/dT$. Thus, any small positive deviation from the intermediate temperature will create a tendency to increase the temperature further. A similar conclusion can be determined for a small negative deviation in temperature. Thus, the intermediate temperature is unstable in the region about the intermediate steady state, as confirmed by the linearized stability analysis.

The previous analysis demonstrated that the intermediate steady state satisfies the steady-state balances but is not locally stable. However, these operating conditions can be achieved by stabilizing the system through feedback control. Thus, if a feedback PI controller is implemented to maintain temperature at 350 K by adjusting the coolant flow rate, the system reaches the intermediate steady state stabilized by feedback control at exactly the operating conditions given in Table C.1; the dynamic response is given in Figure C.5 for this example. The occurrence
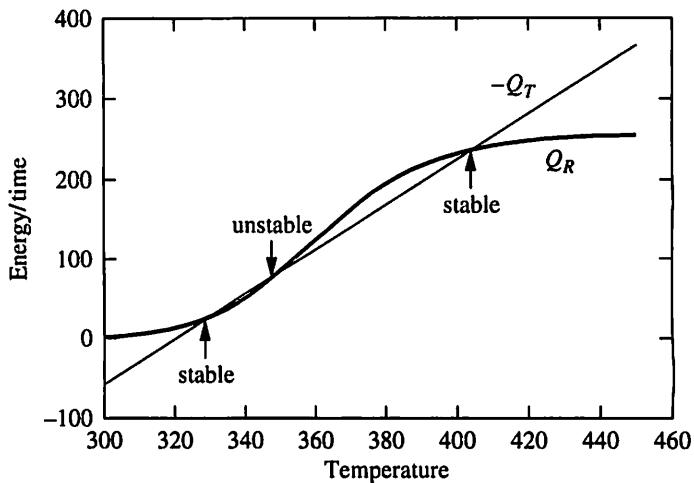
FIGURE C.3

Steady-state analysis of Case II showing three steady states.
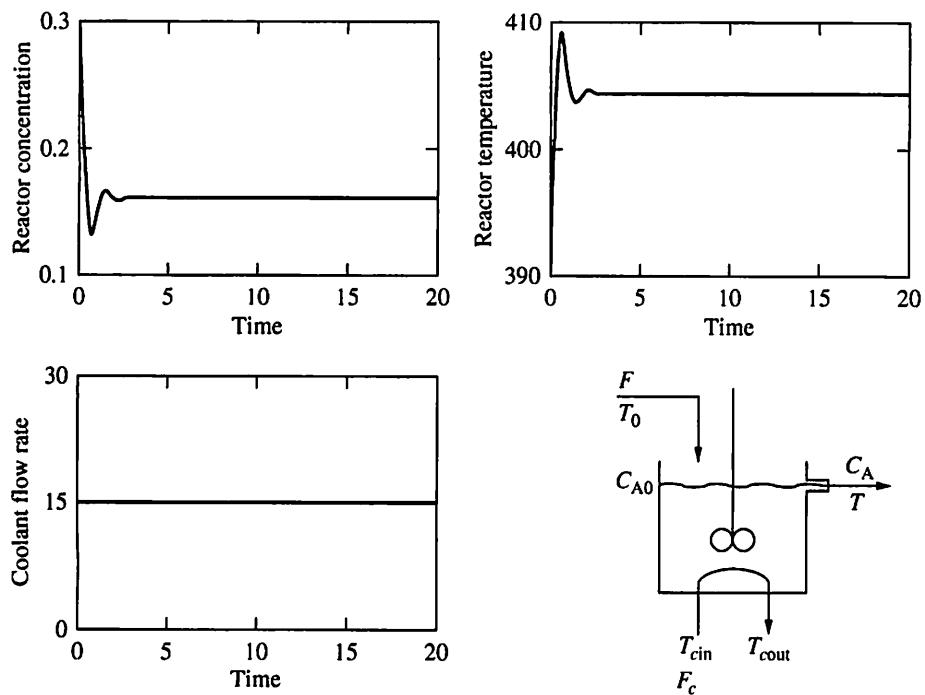
FIGURE C.4

Dynamic response of Case II without control.
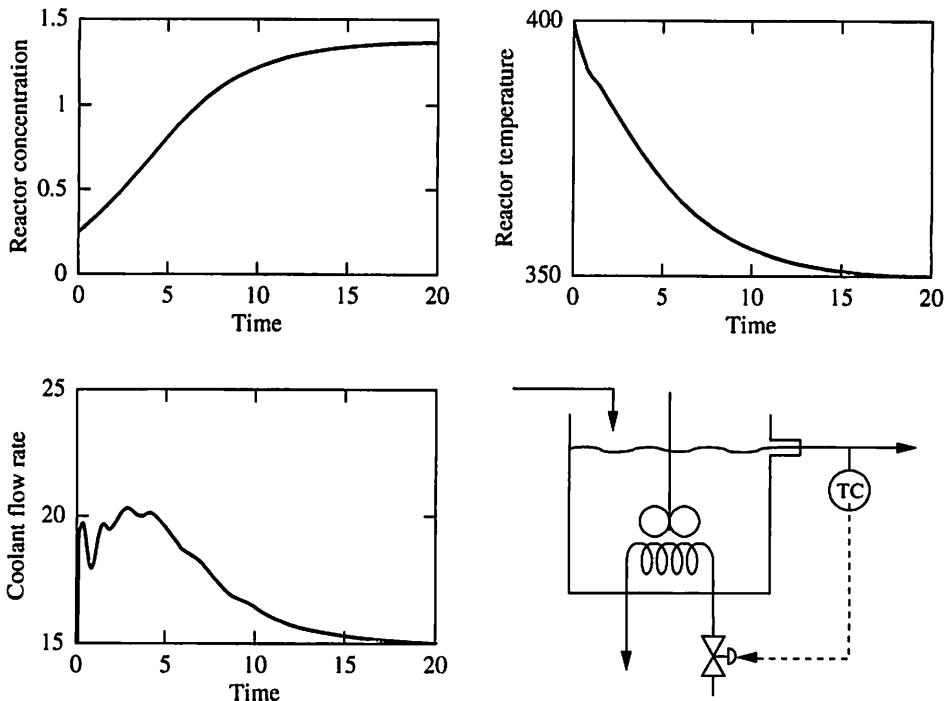
FIGURE C.5

Closed-loop dynamic response of Case II with PI feedback control
(SP = 350 K, $K_c = -1(\text{m}^3/\text{min})/\text{K}$, $T_I = 5$ min).

of multiple steady states and the stabilization of an open-loop unstable steady state via feedback has been verified empirically for a stirred-tank reactor (e.g., Chang and Schmitz, 1975b).

Most models of processes used in design and analysis in chemical engineering do not exhibit multiple steady states. Typically, systems that are known to have multiple steady states are analyzed by ad hoc methods such as the one employed in this section, although some general correlations are available for CSTRs with simple kinetics (Perlmutter, 1972).

C.5 ⊠ CONTINUOUS OSCILLATIONS DUE TO LIMIT CYCLES

Some strongly nonlinear systems can exhibit dynamic behavior that is quite surprising when first encountered: continuous oscillations in the output variables although the input variables are absolutely constant! Case III in Table C.1 is an example of a process with this behavior, which is termed a *limit cycle*. Notice that this system has a single steady state that is locally unstable, as demonstrated by the positive real part of its poles. This is a puzzle, because the only conditions for which the steady-state balances are satisfied cannot be approached stably; thus, how does the reactor behave? The answer is given in Figure C.6, which gives the results from the dynamic simulation of Case III. Clearly, the concentration and temperature never achieve their steady-state values, because they have periodic behavior that continues indefinitely without damping. This is "stable" periodic behavior, because the system will return to the same limit cycle after a pulse perturbation.

This behavior is not common but has occurred, to the surprise and consternation of practicing engineers in commercial situations (Bush, 1969). The behavior has also been analyzed mathematically (Aris and Amundson, 1958) and produced experimentally (Chang and Schmitz, 1975a). Some systems that experience limit cycles can be stabilized through feedback control (e.g., Chang and
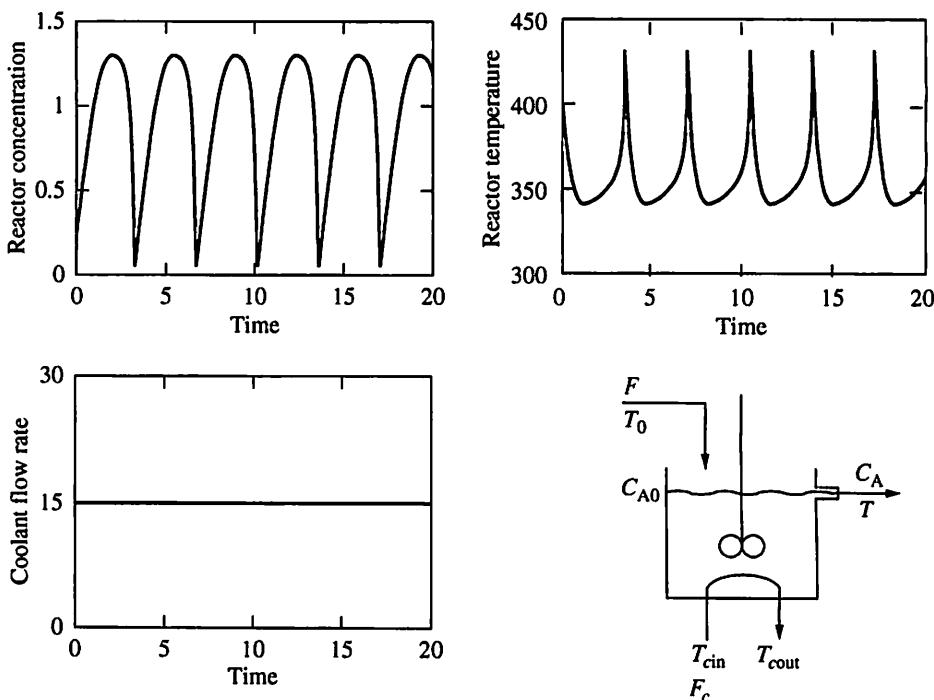
FIGURE C.6

Dynamic response of Case III without control, showing a limit cycle.

Schmitz, 1975a), but sometimes process design changes are required to obtain acceptable performance (e.g., Penlidis et al., 1989).

C.6 ◻ CONCLUSIONS

This appendix has provided the derivation of the energy balance for chemically reacting systems and samples of complex behavior that can be exhibited by such nonisothermal reactors. Note that all of the examples in this section involved the same chemical kinetics; thus, a wide array of behaviors can be achieved by changing the process design parameters. Generally, the occurrence of multiple steady states and unstable steady states results from some type of positive feedback in the system. In the examples in this appendix, the positive feedback is provided by the exothermic chemical reaction. The analysis of steady-state multiplicity and stability is covered in greater detail in Perlmutter (1972), and the influence of these phenomena on design and control is reviewed by Seider et al. (1991) and Silverstein and Shinnar (1982).

REFERENCES

Aris, R., *Elementary Chemical Reactor Analysis*, Butterworth, Boston, 1989.

Aris, R., and N. Amundson, "An Analysis of Chemical Reactor Stability and Control," *CES, 7, 3*, 121–131 (1958).

Bush, S., *Proc. Royal Soc., 309A*, 1–26 (1969).

Chang, M., and R. Schmitz, "An Experimental Study of Oscillatory States in a Stirred Reactor," *CES, 30*, 21–34 (1975a).

Chang, M., and R. Schmitz, "Feedback Control of Unstable States in a Laboratory Reactor," *CES, 30*, 837–846 (1975b).

Denn, M., *Process Modeling*, Pitman Publishing, Marshfield, MA, 1986.

Penlidis, A., J. MacGregor, and A. Hamielec, "Continuous Emulsion Polymerization: Design and Control Considerations for CSTR Trains," *CES, 44*, 273–281 (1989).

Perlmutter, D., *Stability of Chemical Reactors*, Prentice-Hall, Englewood Cliffs, NJ, 1972.

Seider, W., D. Brengel, and S. Widagdo, "Nonlinear Analysis in Process Control," *AIChE J, 37*, 1–38 (1991).

Silverstein, J. and R. Shinnar, "Effect of Design on Stability and Control of Fixed Bed Catalytic Reactors with Heat Feedback," *IEC Proc. Des. Devel., 21*, 241–256 (1982).

QUESTIONS

C.1. A slightly modified version of the CSTR described and modelled in Section C.2 is to be considered in this question. The system is the same except for the heat of reaction, ΔH_{rxn}, which is 0.0. You may use all of the results in the example, specifically equations (C.11) to (C.13) without deriving, and simply modify the results as appropriate. You do not have to substitute numerical values to answer this question.

   (a) The coolant flow experiences a single step change of magnitude ΔF_c. Derive a model that describes the response of the concentration of

component A, $C_A'(t)$. The result should be in terms of the parameters of the process and can be expressed in terms of the a_{ij} coefficients in equations (C.11) and (C.12).

(b) Determine whether the response in part (a) of this question is stable or under what conditions it can be unstable.

(c) Describe the shape of the response to the step input for the case in which the system is stable. Under what conditions can it be periodic (underdamped) like the response in Figure C.2?

C.2. For the nonisothermal CSTR in Section C.2, determine the transfer functions relating $C_A(s)/F_c(s)$ and $C_A(s)/C_{A0}(s)$. These should be in terms of the a_{ij} coefficients in the linearized model. Compare the results with the numerators and denominators in equation (C.14) and comment.

C.3. Calculate the (open-loop) frequency response of the reactor temperature in Section C.2 for a sine input in the coolant flow rate, and discuss its important features. [Hint: You can use the transfer function in equation (C.15)].

C.4. Discuss the use of empirical identification of linear models for the CSTR in Section C.2. Be sure to address experimental design and the proper selection of parameter estimation method.