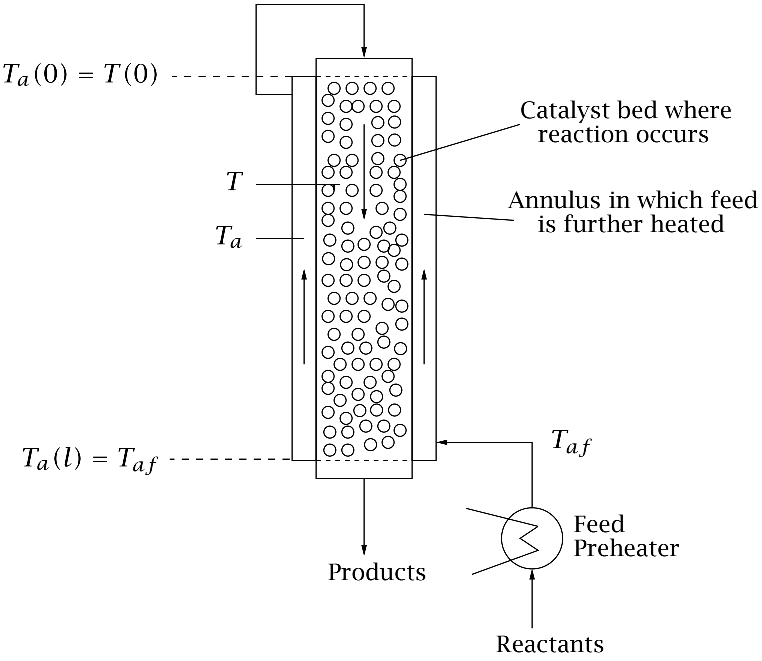

Figure 6.37: Autothermal plug-flow reactor; the heat released by the exothermic reaction is used to preheat the feed.

feed temperatures and feed o-xylene mole fractions, which increases the production rate. □

6.5.2 The Autothermal Plug-Flow Reactor

In many applications, it is necessary to heat a feed stream to achieve a reactor inlet temperature having a high reaction rate. If the reaction also is exothermic, we have the possibility to lower the reactor operating cost by heat integration. The essential idea is to use the heat released by the reaction to heat the feed stream. As a simple example of this concept, consider the heat integration scheme depicted in Figure 6.37 [1]. This reactor configuration is known as an autothermal plug-flow reactor. The reactor system is an annular tube. The feed passes through the outer region and is heated through contact with the hot reactor wall. The feed then enters the inner reaction region, which is filled with the catalyst, and flows countercurrently to the feed stream. The heat released due to reaction in the inner region is used to heat the feed in the outer region. When the reactor is operating at steady state, no external heat is required to preheat the feed. Of course, during the reactor start up, external heat must be supplied to ignite the reactor.

Although recycle of energy can offer greatly lower operating costs, the dynamics and control of these reactors may be complex. We next examine an ammonia synthesis example to show that multiple steady states are possible. Ammonia synthesis is also interesting because of its large impact on the early development of the chemical engineering discipline. Quoting Aftalion [2, p. 101]

> While physicists and chemists were linking up to understand the structure of matter and giving birth to *physical chemistry*, another discipline was emerging, particularly in the United States, at the beginning of the twentieth century, that of *chemical engineering* ... it was undoubtedly the synthesis of ammonia by BASF, successfully achieved in 1913 in Oppau, which forged the linking of chemistry with physics and engineering as it required knowledge in areas of analysis, equilibrium reactions, high pressures, catalysis, resistance of materials, and design of large-scale apparatus.

Example 6.6: Ammonia synthesis

Calculate the steady-state conversion for the synthesis of ammonia using the autothermal process shown in Figure 6.37 [25]. A rate expression for the reaction

$$\mathrm{N_2} + 3\mathrm{H_2} \underset{\mathrm{k_{-1}}}{\overset{\mathrm{k_1}}{\rightleftharpoons}} 2\mathrm{NH_3} \tag{6.54}$$

over an iron catalyst at 300 atm pressure is suggested by Temkin [21]

$$r = k_{-1}/RT\left[K^2(T)\frac{P_N P_H^{3/2}}{P_A} - \frac{P_A}{P_H^{3/2}}\right] \tag{6.55}$$

in which P_N, P_H, P_A are the partial pressures of nitrogen, hydrogen, and ammonia, respectively, and K is the equilibrium constant for the reaction forming one mole of ammonia. For illustration, we assume the thermochemical properties are constant and the gases form an ideal-gas mixture. More accurate thermochemical properties and a more accurate equation of state do not affect the fundamental behavior predicted by the reactor model.

The steady-state material balance for the ammonia is

$$\frac{dN_A}{dV} = R_A = 2r$$
$$N_A(0) = N_{Af}$$

and the other molar flows are calculated from

$$N_N = N_{Nf} - 1/2(N_A - N_{Af})$$
$$N_H = N_{Hf} - 3/2(N_A - N_{Af})$$

If we assume an ideal gas in this temperature and pressure range, the volumetric flowrate is given by

$$Q = \frac{RT}{P}(N_A + N_N + N_H)$$

The energy balance for the reactor is the usual

$$Q\rho\hat{C}_P\frac{dT}{dV} = -\Delta H_R r + \dot{q} \tag{6.56}$$

in which $\dot{q}$ is the heat transfer taking place between the reacting fluid and the cold feed

$$\dot{q} = \frac{2}{R}U^o(T_a - T)$$

The material balances for the feed-heating section are simple because reaction does not take place without the catalyst. Without reaction, the molar flow of all species are constant and equal to their feed values and the energy balance for the feed-heating section is

$$Q_a\rho_a\hat{C}_{Pa}\frac{dT_a}{dV_a} = -\dot{q} \tag{6.57}$$
$$T_a(0) = T_{af}$$

in which the subscript a represents the fluid in the feed-heating section. Notice the heat terms are of opposite signs in Equations 6.57 and 6.56. If we assume the fluid properties do not change significantly over the temperature range of interest, and switch the direction of integration in Equation 6.57 using $dV_a = -dV$, we obtain

$$Q\rho\hat{C}_P\frac{dT_a}{dV} = \dot{q} \tag{6.58}$$
$$T_a(V_R) = T_{af} \tag{6.59}$$

Parameter	Value	Units
P	300	atm
Q_0	0.16	m^3/s
A_c	1	m^2
l	12	m
T_{af}	323	K
$\gamma = \dfrac{2\pi R U^o}{Q\rho \hat{C}_P}$	0.5	1/m
$\beta = \dfrac{\Delta H_R A_c}{Q\rho \hat{C}_P}$	−2.342	m^2 s K/mol
ΔG°	4250	cal/mol
ΔH°	-1.2×10^4	cal/mol
k_{-10}	7.794×10^{11}	
E_{-1}/R	2×10^4	K

Table 6.6: Parameter values for Example 6.6; heat of reaction and mixture heat capacity assumed constant.

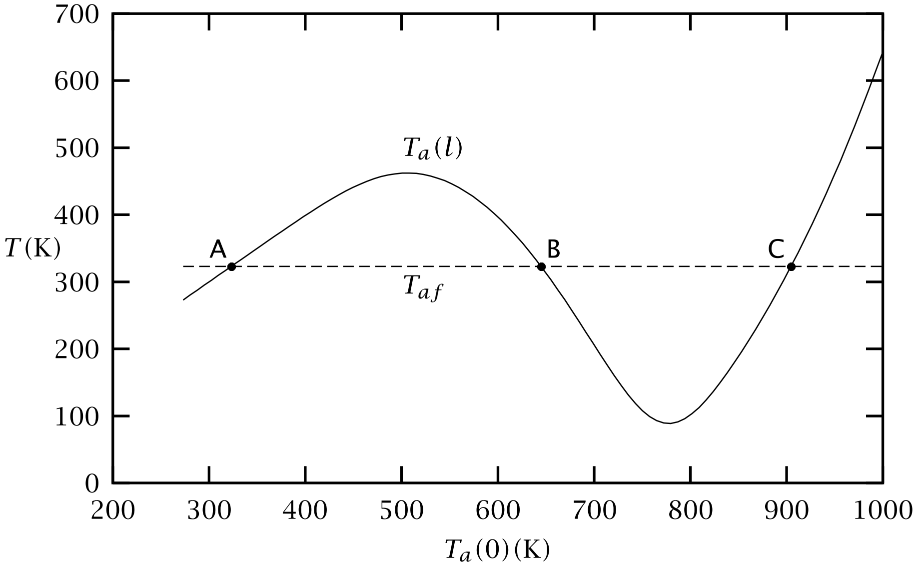

Figure 6.38: Coolant temperature at reactor outlet versus temperature at reactor inlet, $T_a(l)$ versus $T_a(0)$; intersection with coolant feed temperature T_{af} indicates three steady-state solutions (A,B,C).

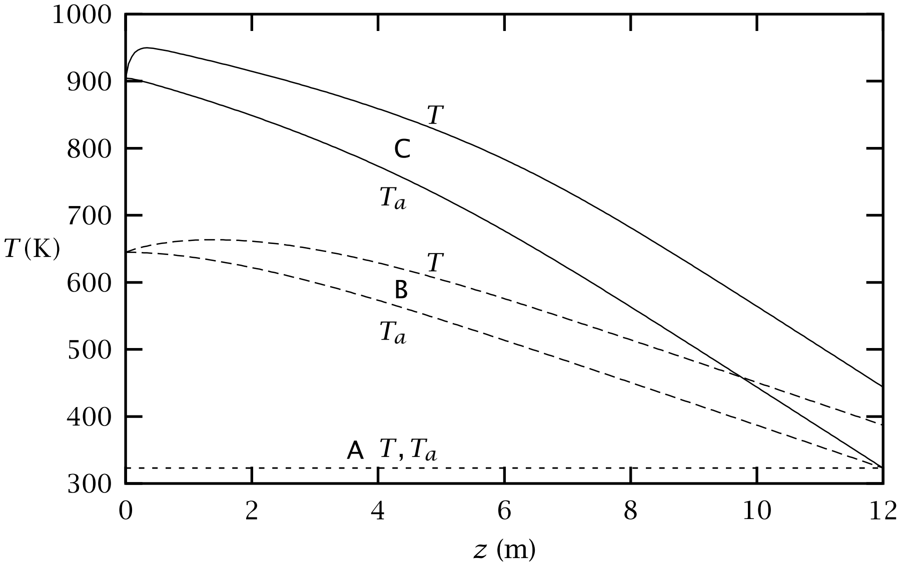

Figure 6.39: Reactor and coolant temperature profiles versus reactor length; lower (A), unstable middle (B), and upper (C) steady states.

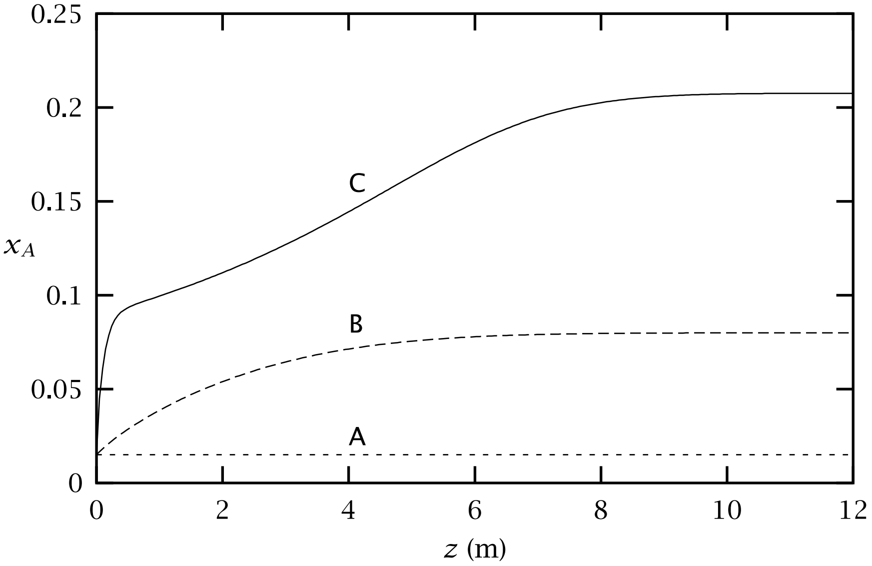

Figure 6.40: Ammonia mole fraction versus reactor length; lower (A), unstable middle (B), and upper (C) steady states.

Finally we require a boundary condition for the reactor energy balance, which we have from the fact that the heating fluid enters the reactor at $z = 0, T(0) = T_a(0)$. Combining these balances and boundary conditions and converting to reactor length in place of volume gives the model

$$\boxed{\begin{aligned} \frac{dN_A}{dz} &= 2A_c r & N_A(0) &= N_{Af} \\ \frac{dT}{dz} &= -\beta r + \gamma(T_a - T) & T(0) &= T_a(0) \\ \frac{dT_a}{dz} &= \gamma(T_a - T) & T_a(l) &= T_{af} \end{aligned}} \tag{6.60}$$

in which

$$\beta = \frac{\Delta H_R A_c}{Q\rho \hat{C}_P} \qquad \gamma = \frac{2\pi R U^o}{Q\rho \hat{C}_P}$$

Equation 6.60 is a boundary-value problem, rather than an initial-value problem, because T_a is specified at the exit of the reactor. A simple solution strategy is to guess the reactor inlet temperature, solve the model to the exit of the reactor, and then compare the computed feed preheat temperature to the specified value T_{af}. This strategy is known as a shooting method. We guess the missing values required to produce an initial-value problem. We solve the initial-value problem, and then iterate on the guessed values until we match the specified boundary conditions. We will see more about boundary-value problems and shooting methods when we treat diffusion in Chapter 7.

Solution

Figure 6.38 shows the results for the parameter values listed in Table 6.6, which are based on those used by van Heerden [25]. For given values of $T_a(0)$, we solve the initial-value problem, Equation 6.60, and plot the resulting $T_a(V_R)$ as the solid line in Figure 6.38. The intersection of that line with the feed temperature $T_{af} = 323$ K indicates a steady-state solution. Notice three steady-state solutions are indicated in Figure 6.38 for these values of parameters. The profiles in the reactor for these three steady states are shown in Figures 6.39 and 6.40. It is important to operate at the upper steady state so that a reasonably large production of ammonia is achieved. □

Neglect kinetic and potential energies

$$\frac{dU}{dt} = \dot{Q} + \dot{W}_s + \dot{W}_b \tag{6.61}$$

Neglect shaft work

$$\frac{dU}{dt} + P\frac{dV_R}{dt} = \dot{Q} \tag{6.62}$$

$$\frac{dH}{dt} - V_R\frac{dP}{dt} = \dot{Q} \tag{6.63}$$

Single phase

$$V_R\rho\hat{C}_P\frac{dT}{dt} - \alpha T V_R\frac{dP}{dt} + \sum_j H_j\frac{dn_j}{dt} = \dot{Q} \tag{6.64}$$

$$V_R\rho\hat{C}_P\frac{dT}{dt} - \alpha T V\frac{dP}{dt} = -\sum_i \Delta H_{Ri} r_i V_R + \dot{Q} \tag{6.65}$$

a. Incompressible-fluid or constant-pressure reactor

$$V_R\rho\hat{C}_P\frac{dT}{dt} = -\sum_i \Delta H_{Ri} r_i V_R + \dot{Q} \tag{6.66}$$

b. Constant-volume reactor

$$V_R\rho\hat{C}_V\frac{dT}{dt} = -\sum_i\left[\Delta H_{Ri} - \alpha T V_R\sum_j \nu_{ij}\left(\frac{\partial P}{\partial n_j}\right)_{T,V,n_k}\right] r_i V_R + \dot{Q} \tag{6.67}$$

b.1 Constant-volume reactor, ideal gas

$$V_R\rho\hat{C}_V\frac{dT}{dt} = -\sum_i\left(\Delta H_{Ri} - RT\bar{\nu}_i\right) r_i V_R + \dot{Q} \tag{6.68}$$

Table 6.7: Energy balances for the batch reactor.

6.6 Summary

Tables 6.7–6.10 summarize the important energy balances for the batch, continuous-stirred-tank, semi-batch, and plug-flow reactors. In contrast to the material balance, which is reasonably straightforward, choosing the proper energy balance requires some care. It is unwise to select an energy balance from a book without carefully considering the assumptions that have been made in the derivation of that particular

Neglect kinetic and potential energies

$$\frac{dU}{dt} = Q_f \rho_f \hat{H}_f - Q\rho\hat{H} + \dot{Q} + \dot{W}_s + \dot{W}_b \tag{6.69}$$

Neglect shaft work

$$\frac{dU}{dt} + P\frac{dV_R}{dt} = Q_f \rho_f \hat{H}_f - Q\rho\hat{H} + \dot{Q} \tag{6.70}$$

$$\frac{dH}{dt} - V_R\frac{dP}{dt} = Q_f \rho_f \hat{H}_f - Q\rho\hat{H} + \dot{Q} \tag{6.71}$$

Single phase

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha T V_R \frac{dP}{dt} + \sum_j H_j \frac{dn_j}{dt} = Q_f \rho_f \hat{H}_f - Q\rho\hat{H} + \dot{Q} \tag{6.72}$$

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha T V_R \frac{dP}{dt} = -\sum_i \Delta H_{Ri} r_i V_R + \sum_j c_{jf} Q_f (H_{jf} - H_j) + \dot{Q} \tag{6.73}$$

---

a. Incompressible-fluid or constant-pressure reactor

$$V_R \rho \hat{C}_P \frac{dT}{dt} = -\sum_i \Delta H_{Ri} r_i V_R + \sum_j c_{jf} Q_f (H_{jf} - H_j) + \dot{Q} \tag{6.74}$$

---

b. Constant-volume reactor

$$V_R \rho \hat{C}_V \frac{dT}{dt} = -\sum_i \left[\Delta H_{Ri} - \alpha V_R \sum_j \nu_{ij} \left(\frac{\partial P}{\partial n_j} \right)_{T,V,n_k} \right] r_i V_R + \sum_j c_{jf} Q_f (H_{jf} - H_j) + \dot{Q} \tag{6.75}$$

---

b.1 Constant-volume reactor, ideal gas

$$V_R \rho \hat{C}_V \frac{dT}{dt} = -\sum_i \left(\Delta H_{Ri} - RT\bar{\nu}_i \right) r_i V_R + \sum_j c_{jf} Q_f (H_{jf} - H_j) + \dot{Q} \tag{6.76}$$

---

c. Steady state, constant $\hat{C}_P$, $P = P_f$

$$-\sum_i \Delta H_{Ri} r_i V_R + Q_f \rho_f \hat{C}_P (T_f - T) + \dot{Q} = 0 \tag{6.77}$$

Table 6.8: Energy balances for the CSTR.

Neglect kinetic and potential energies

$$\frac{dU}{dt} = Q_f \rho_f \hat{H}_f + \dot{Q} + \dot{W}_s + \dot{W}_b \tag{6.78}$$

Neglect shaft work

$$\frac{dU}{dt} + P\frac{dV_R}{dt} = Q_f \rho_f \hat{H}_f + \dot{Q} \tag{6.79}$$

$$\frac{dH}{dt} - V_R\frac{dP}{dt} = Q_f \rho_f \hat{H}_f + \dot{Q} \tag{6.80}$$

Single phase[t]

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha T V_R \frac{dP}{dt} + \sum_j H_j \frac{dn_j}{dt} = Q_f \rho_f \hat{H}_f + \dot{Q} \tag{6.81}$$

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha T V_R \frac{dP}{dt} = -\sum_i \Delta H_{Ri} r_i V_R + \sum_j c_{jf} Q_f (H_{jf} - H_j) + \dot{Q} \tag{6.82}$$

---

a. Incompressible-fluid or constant-pressure reactor

$$V_R \rho \hat{C}_P \frac{dT}{dt} = -\sum_i \Delta H_{Ri} r_i V_R + \sum_j c_{jf} Q_f (H_{jf} - H_j) + \dot{Q} \tag{6.83}$$

---

a.1 Constant $\hat{C}_P$

$$V_R \rho \hat{C}_P \frac{dT}{dt} = -\sum_i \Delta H_{Ri} r_i V_R + Q_f \rho_f \hat{C}_P (T_f - T) + \dot{Q} \tag{6.84}$$

Table 6.9: Energy balances for the semi-batch reactor.

energy balance. Adding to the confusion, many books do not state clearly what assumptions have been made in deriving various energy balances, and some books list energy balances that are simply incorrect. See Denn [9] for a thorough discussion of common errors in energy balances and a list of books containing incorrect energy balances.

Nonisothermal reactor design requires the simultaneous solution of the appropriate energy balance and the species material balances. For the batch, semi-batch, and steady-state plug-flow reactors, these balances are sets of initial-value ODEs that must be solved numerically. In very limited situations (constant thermodynamic properties, single

Neglect kinetic and potential energies and shaft work

$$\frac{\partial}{\partial t}(\rho \hat{U}) = -\frac{1}{A_c}\frac{\partial}{\partial z}(Q\rho \hat{H}) + \dot{q} \tag{6.85}$$

Heat transfer with an overall heat-transfer coefficient

$$\dot{q} = \frac{2}{R}U^o(T_a - T) \tag{6.86}$$

Steady state

$$\frac{d}{dV}(Q\rho \hat{H}) = \dot{q} \tag{6.87}$$

Single phase

$$Q\rho \hat{C}_P \frac{dT}{dV} + Q(1-\alpha T)\frac{dP}{dV} = -\sum_i \Delta H_{Ri} r_i + \dot{q} \tag{6.88}$$

a. Neglect pressure drop, or ideal gas

$$Q\rho \hat{C}_P \frac{dT}{dV} = -\sum_i \Delta H_{Ri} r_i + \dot{q} \tag{6.89}$$

b. Incompressible fluid

$$Q\rho \hat{C}_P \frac{dT}{dV} + Q\frac{dP}{dV} = -\sum_i \Delta H_{Ri} r_i + \dot{q} \tag{6.90}$$

Table 6.10: Energy balances for the plug-flow reactor.

reaction, adiabatic), one can solve the energy balance to get an algebraic relation between temperature and concentration or molar flowrate.

The nonlinear nature of the energy and material balances can lead to multiple steady-state solutions. Steady-state solutions may be unstable, and the reactor can exhibit sustained oscillations. These reactor behaviors were illustrated with exothermic CSTRs and autothermal tubular reactors.