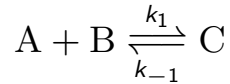


- To specify the rates of reactions in a nonisothermal reactor, we require a model to determine the temperature of the reactor, i.e. for the reaction

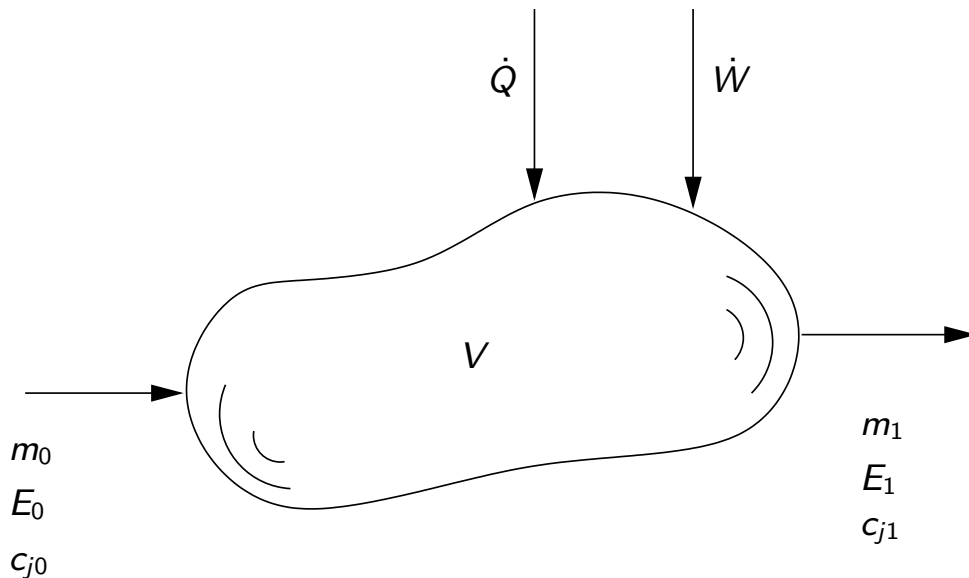


$$r = k_1(T) c_A c_B - k_{-1}(T) c_C$$

- The temperature is determined by the energy balance for the reactor.
- We derive the energy balance by considering an arbitrary reactor volume element, shown in Figure 6.1

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General Energy Balance



The statement of conservation of energy for this system takes the form,

$$\left\{ \begin{array}{l} \text{rate of energy} \\ \text{accumulation} \end{array} \right\} = \left\{ \begin{array}{l} \text{rate of energy} \\ \text{entering system} \\ \text{by inflow} \end{array} \right\} - \left\{ \begin{array}{l} \text{rate of energy} \\ \text{leaving system} \\ \text{by outflow} \end{array} \right\} + \left\{ \begin{array}{l} \text{rate of heat} \\ \text{added to system} \end{array} \right\} + \left\{ \begin{array}{l} \text{rate of work} \\ \text{done on system} \end{array} \right\} \quad (1)$$

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In terms of the defined variables, we can write Equation 6.1 as,

$$\frac{dE}{dt} = m_0 \hat{E}_0 - m_1 \hat{E}_1 + \dot{Q} + \dot{W} \quad (6.2)$$

in which the hat indicates an energy per unit mass.

It is convenient to split the work term into three parts: \dot{W}_f , the work done by the flow streams while moving material into and out of the reactor, \dot{W}_s , the shaft work being done by stirrers, compressors, etc., and \dot{W}_b , the work done when moving the system boundary.

$$\underbrace{\dot{W}}_{\text{total work}} = \underbrace{\dot{W}_f}_{\text{flow streams}} + \underbrace{\dot{W}_s}_{\text{shaft work}} + \underbrace{\dot{W}_b}_{\text{boundary work}} \quad (6.3)$$

Work done by the flow streams

$$\dot{W}_f = v_0 A_0 P_0 - v_1 A_1 P_1 = Q_0 P_0 - Q_1 P_1$$

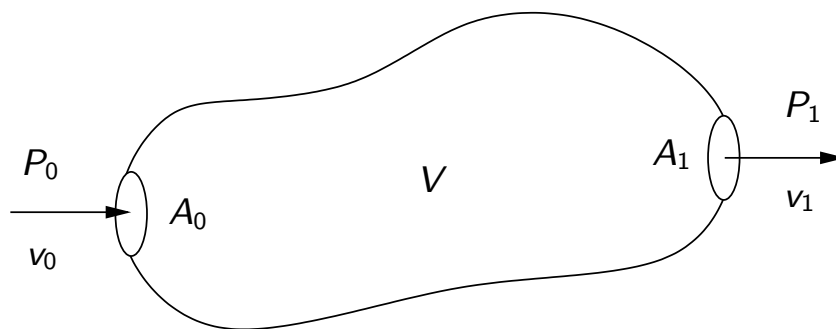


Figure 6.2: Flow streams entering and leaving the volume element.

We also can express the volumetric flowrate as a mass flowrate divided by the density, $Q = m/\rho$

$$\dot{W}_f = m_0 \frac{P_0}{\rho_0} - m_1 \frac{P_1}{\rho_1}$$

The overall rate of work can then be expressed as

$$\dot{W} = \dot{W}_f + \dot{W}_s + \dot{W}_b = m_0 \frac{P_0}{\rho_0} - m_1 \frac{P_1}{\rho_1} + \dot{W}_s + \dot{W}_b \quad (6.4)$$

The total energy may be regarded as composed of many forms. Obvious contributions to the total energy arise from the internal, kinetic and potential energies.¹

$$\hat{E} = \hat{U} + \hat{K} + \hat{\Phi} + \dots$$

For our purposes in this chapter, we consider only these forms of energy. Recalling the definition of enthalpy, $H = U + PV$, or expressed on a per-unit mass basis, $\hat{H} = \hat{U} + P/\rho$, allows us to rewrite Equation 6.2 as

$$\frac{d}{dt}(U + K + \Phi) = m_0(\hat{H} + \hat{K} + \hat{\Phi})_0 - m_1(\hat{H} + \hat{K} + \hat{\Phi})_1 + \dot{Q} + \dot{W}_s + \dot{W}_b \quad (6.5)$$

¹In some cases one might need to consider also electrical and magnetic energies. For example, we might consider the motion of charged ionic species between the plates in a battery cell.

The Batch Reactor

Since the batch reactor has no flow streams Equation 6.5 reduces to

$$\frac{d}{dt}(U + K + \Phi) = \dot{Q} + \dot{W}_s + \dot{W}_b \quad (6.6)$$

In chemical reactors, we normally assume the internal energy is the dominant contribution and neglect the kinetic and potential energies. Normally we neglect the work done by the stirrer, unless the mixture is highly viscous and the stirring operation draws significant power [3]. Neglecting kinetic and potential energies and shaft work yields

$$\frac{dU}{dt} + P \frac{dV_R}{dt} = \dot{Q} \quad (6.7)$$

in which $\dot{W}_b = -PdV_R/dt$.

It is convenient to use enthalpy rather than internal energy in the subsequent development. Taking the differential of the definition of enthalpy gives for $V = V_R$

$$dH = dU + PdV_R + V_R dP$$

Forming the time derivatives and substitution into Equation 6.7 gives

$$\frac{dH}{dt} - V_R \frac{dP}{dt} = \dot{Q} \quad (6.8)$$

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Effect of changing T, P, n_j

For *single-phase systems*, we consider the enthalpy as a function of temperature, pressure and number of moles, and express its differential as

$$dH = \left(\frac{\partial H}{\partial T} \right)_{P, n_j} dT + \left(\frac{\partial H}{\partial P} \right)_{T, n_j} dP + \sum_j \left(\frac{\partial H}{\partial n_j} \right)_{T, P, n_k} dn_j \quad (6.9)$$

The first partial derivative is the definition of the heat capacity, C_P .

$$C_P = V_R \rho \hat{C}_P$$

The second partial derivative can be expressed as

$$\left(\frac{\partial H}{\partial P} \right)_{T, n_j} = V - T \left(\frac{\partial V}{\partial T} \right)_{P, n_j} = V(1 - \alpha T)$$

in which $\alpha = (1/V)(\partial V/\partial T)_{P, n_j}$ is the coefficient of expansion of the mixture.

The final partial derivatives are the partial molar enthalpies, \bar{H}_j

$$\left(\frac{\partial H}{\partial n_j} \right)_{T, P, n_k} = \bar{H}_j$$

so Equation 6.9 can be written compactly as

$$dH = V_R \rho \hat{C}_P dT + (1 - \alpha T) V_R dP + \sum_j \bar{H}_j dn_j \quad (6.10)$$

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Forming the time derivatives from this expression and substituting into Equation 6.8 gives

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha T V_R \frac{dP}{dt} + \sum_j \bar{H}_j \frac{dn_j}{dt} = \dot{Q} \quad (6.11)$$

We note that the material balance for the batch reactor is

$$\frac{dn_j}{dt} = R_j V_R = \sum_{i=1}^{n_r} \nu_{ij} r_i V_R, \quad j = 1, \dots, n_s \quad (6.12)$$

which upon substitution into Equation 6.11 yields

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha T V_R \frac{dP}{dt} = - \sum_i \Delta H_{Ri} r_i V_R + \dot{Q} \quad (6.13)$$

in which ΔH_{Ri} is the heat of reaction

$$\Delta H_{Ri} = \sum_j \nu_{ij} \bar{H}_j \quad (6.14)$$

A plethora of special cases—incompressible

We now consider several special cases. If the reactor operates at constant pressure ($dP/dt = 0$) or the fluid is incompressible ($\alpha = 0$), then Equation 6.13 reduces to

Incompressible-fluid or constant-pressure reactor.

$$\boxed{V_R \rho \hat{C}_P \frac{dT}{dt} = - \sum_i \Delta H_{Ri} r_i V_R + \dot{Q}} \quad (6.15)$$

A plethora of special cases – constant volume

Change from T, P, n_j to T, V, n_j by considering P to be a function of $T, V (V = V_R), n_j$

$$dP = \left(\frac{\partial P}{\partial T} \right)_{V, n_j} dT + \left(\frac{\partial P}{\partial V} \right)_{T, n_j} dV + \sum_j \left(\frac{\partial P}{\partial n_j} \right)_{T, V, n_k} dn_j$$

For reactor operation at constant volume, $dV = 0$, and forming time derivatives and substituting into Equation 6.11 gives

$$\left[V_R \rho \hat{C}_P - \alpha T V_R \left(\frac{\partial P}{\partial T} \right)_{V, n_j} \right] \frac{dT}{dt} + \sum_j \left[\bar{H}_j - \alpha T V_R \left(\frac{\partial P}{\partial n_j} \right)_{T, V, n_k} \right] \frac{dn_j}{dt} = \dot{Q}$$

We note that the first term in brackets is $C_V = V_R \rho \hat{C}_V$ (see Exercise 6.23)

$$V_R \rho \hat{C}_V = V_R \rho \hat{C}_P - \alpha T V_R \left(\frac{\partial P}{\partial T} \right)_{V, n_j}$$

The pressure derivative with respect to the moles can be shown to be (see Exercise 6.23)

$$\left(\frac{\partial P}{\partial n_j} \right)_{T, V, n_{k \neq j}} = \frac{\bar{V}_j}{V \kappa_T}$$

in which $\kappa_T = -(1/V)(\partial V / \partial P)_{T, n_j}$ is the isothermal compressibility of the mixture, and \bar{V}_j is the partial molar volume.

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Constant volume

Substitution of these two thermodynamic relations and the material balance yields the energy balance for the constant-volume batch reactor

Constant-volume reactor.

$$V_R \rho \hat{C}_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - \frac{\alpha}{\kappa_T} T \Delta V_{Ri}) r_i V_R + \dot{Q} \quad (6.16)$$

If we consider an ideal gas, it is straightforward to calculate $\alpha T = 1$, $\kappa_T P = 1$, and $\Delta V_{Ri} = \bar{v}_i (RT/P)$, where $\bar{v}_i = \sum_j \nu_{ij}$. Substitution into the constant-volume energy balance gives

Constant-volume reactor, ideal gas.

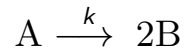
$$V_R \rho \hat{C}_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - RT \bar{v}_i) r_i V_R + \dot{Q} \quad (6.17)$$

where $\bar{v}_i = \sum_j \nu_{ij}$.

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Example 6.1: Constant-pressure versus constant-volume reactors

Consider the following two well-mixed, adiabatic, *gas-phase* batch reactors for the elementary and irreversible decomposition of A to B,



Reactor 1: The reactor volume is held constant (reactor pressure therefore changes).

Reactor 2: The reactor pressure is held constant (reactor volume therefore changes).

Both reactors are charged with pure A at 1.0 atm and k has the usual Arrhenius activation energy dependence on temperature,

$$k(T) = k_0 \exp(-E/T)$$

The heat of reaction, ΔH_R , and heat capacity of the mixture, \hat{C}_P , may be assumed constant over the composition and temperature range expected.

Write the material and energy balances for these two reactors. Which reactor converts the reactant more quickly? □

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Solution — Material balance

The material balance is

$$\frac{d(c_A V_R)}{dt} = R_A V_R$$

Substituting in the reaction-rate expression, $r = k(T)c_A$, and using the number of moles of A, $n_A = c_A V_R$ yields

$$\frac{dn_A}{dt} = -k(T)n_A \quad (6.20)$$

Notice the temperature dependence of $k(T)$ prevents us from solving this differential equation immediately.

We must solve it simultaneously with the energy balance, which provides the information for how the temperature changes.

The energy balances for the two reactors are *not* the same. We consider first the constant-volume reactor. For the $A \rightarrow 2B$ stoichiometry, we substitute the rate expression and $\bar{\nu} = 1$ into Equation 6.17 to obtain

$$C_V \frac{dT}{dt} = -(\Delta H_R - RT) kn_A$$

in which $C_V = V_R \rho \hat{C}_V$ is the total constant-volume heat capacity.

The energy balance for the constant-pressure case follows from Equation 6.15

$$C_P \frac{dT}{dt} = -\Delta H_R kn_A$$

in which $C_P = V_R \rho \hat{C}_P$ is the total constant-pressure heat capacity. For an ideal gas, we know from thermodynamics that the two total heat capacities are simply related,

$$C_V = C_P - nR \quad (6.21)$$

Comparing the production rates of A and B produces

$$2n_A + n_B = 2n_{A0} + n_{B0}$$

Because there is no B in the reactor initially, subtracting n_A from both sides yields for the total number of moles

$$n = n_A + n_B = 2n_{A0} - n_A$$

The two energy balances

Substitution of the above and Equation 6.21 into the constant-volume case yields

$$\frac{dT}{dt} = -\frac{(\Delta H_R - RT)kn_A}{C_P - (2n_{A0} - n_A)R} \quad \text{constant volume} \quad (6.22)$$

and the temperature differential equation for the constant-pressure case is

$$\frac{dT}{dt} = -\frac{\Delta H_R kn_A}{C_P} \quad \text{constant pressure} \quad (6.23)$$

We see by comparing Equations 6.22 and 6.23 that the numerator in the constant-volume case is larger because ΔH_R is negative and the positive RT is subtracted.

We also see the denominator is smaller because C_P is positive and the positive nR is subtracted.

Therefore the time derivative of the temperature is larger for the constant-volume case. The reaction proceeds more quickly in the constant-volume case. The constant-pressure reactor is expending work to increase the reactor size, and this work results in a lower temperature and slower reaction rate compared to the constant-volume case.

Liquid-phase batch reactor

Example 6.2: Liquid-phase batch reactor

The exothermic elementary *liquid-phase* reaction



is carried out in a batch reactor with a cooling coil to keep the reactor isothermal at 27°C . The reactor is initially charged with equal concentrations of A and B and no C, $c_{A0} = c_{B0} = 2.0 \text{ mol/L}$, $c_{C0} = 0$.

- ① How long does it take to reach 95% conversion?
- ② What is the total amount of heat (kcal) that must be removed by the cooling coil when this conversion is reached?
- ③ What is the maximum *rate* at which heat must be removed by the cooling coil (kcal/min) and at what time does this maximum occur?
- ④ What is the adiabatic temperature rise for this reactor and what is its significance?

Additional data:

Rate constant, $k = 0.01725 \text{ L/mol}\cdot\text{min}$, at 27°C

Heat of reaction, $\Delta H_R = -10 \text{ kcal/mol A}$, at 27°C

Partial molar heat capacities, $\bar{C}_{PA} = \bar{C}_{PB} = 20 \text{ cal/mol}\cdot\text{K}$, $\bar{C}_{PC} = 40 \text{ cal/mol}\cdot\text{K}$

Reactor volume, $V_R = 1200 \text{ L}$

- ① Assuming constant density, the material balance for component A is

$$\frac{dc_A}{dt} = -k c_A c_B$$

The stoichiometry of the reaction, and the material balance for B gives

$$c_A - c_B = c_{A0} - c_{B0} = 0$$

or $c_A = c_B$. Substitution into the material balance for species A gives

$$\frac{dc_A}{dt} = -k c_A^2$$

Separation of variables and integration gives

$$t = \frac{1}{k} \left[\frac{1}{c_A} - \frac{1}{c_{A0}} \right]$$

Substituting $c_A = 0.05 c_{A0}$ and the values for k and c_{A0} gives

$$t = 551 \text{ min}$$

- ② We assume the incompressible-fluid energy balance is accurate for this liquid-phase reactor. If the heat removal is manipulated to maintain constant reactor temperature, the time derivative in Equation 6.15 vanishes leaving

$$\dot{Q} = \Delta H_R r V_R \quad (6.24)$$

Substituting $dc_A/dt = -r$ and multiplying through by dt gives

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The CSTR — Dynamic Operation

$$\frac{d}{dt} (U + K + \Phi) = m_0 \left(\hat{H} + \hat{K} + \hat{\Phi} \right)_0 - m_1 \left(\hat{H} + \hat{K} + \hat{\Phi} \right)_1 + \dot{Q} + \dot{W}_s + \dot{W}_b$$

We assume that the internal energy is the dominant contribution to the total energy and take the entire reactor contents as the volume element.

We denote the feed stream with flowrate Q_f , density ρ_f , enthalpy \hat{H}_f , and component j concentration c_{jf} .

The outflow stream is flowing out of a well-mixed reactor and its intensive properties are therefore assumed the same as the reactor contents.

Its flowrate is denoted Q . Writing Equation 6.5 for this reactor gives,

$$\frac{dU}{dt} = Q_f \rho_f \hat{H}_f - Q \rho \hat{H} + \dot{Q} + \dot{W}_s + \dot{W}_b \quad (6.26)$$

If we neglect the shaft work

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

or if we use the enthalpy rather than internal energy ($H = U + PV$)

$$\frac{dH}{dt} - V_R \frac{dP}{dt} = Q_f \rho_f \hat{H}_f - Q \rho \hat{H} + \dot{Q} \quad (6.28)$$

The Enthalpy change

For a single-phase system we consider the change in H due to changes in T, P, n_j

$$dH = V_R \rho \hat{C}_P dT + (1 - \alpha T) V_R dP + \sum_j \bar{H}_j dn_j$$

Substitution into Equation 6.28 gives

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha T V_R \frac{dP}{dt} + \sum_j \bar{H}_j \frac{dn_j}{dt} = Q_f \rho_f \hat{H}_f - Q \rho \hat{H} + \dot{Q} \quad (6.29)$$

The material balance for the CSTR is

$$\frac{dn_j}{dt} = Q_f c_{jf} - Q c_j + \sum_i \nu_{ij} r_i V_R \quad (6.30)$$

Substitution into Equation 6.29 and rearrangement yields

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha T V_R \frac{dP}{dt} = - \sum_i \Delta H_{Ri} r_i V_R + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j) + \dot{Q} \quad (6.31)$$

Again, a variety of important special cases may be considered. These are listed in Table 6.8 in the chapter summary. A common case is the liquid-phase reaction, which usually is well approximated by the incompressible-fluid equation,

$$V_R \rho \hat{C}_P \frac{dT}{dt} = - \sum_i \Delta H_{Ri} r_i V_R + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j) + \dot{Q} \quad (6.32)$$

In the next section we consider further simplifying assumptions that require less thermodynamic data and yield useful approximations.

CSTR — Summary of energy balances

Neglect kinetic and potential energies

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

Neglect shaft work

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

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

Single phase

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha TV_R \frac{dP}{dt} + \sum_j \bar{H}_j \frac{dn_j}{dt} = Q_f \rho_f \hat{H}_f - Q \rho \hat{H} + \dot{Q}$$

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha TV_R \frac{dP}{dt} = - \sum_i \Delta H_{Ri} r_i V_R + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j) + \dot{Q}$$

a. Incompressible-fluid or constant-pressure reactor

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

b. Constant-volume reactor

$$V_R \rho \hat{C}_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - \alpha TV_R \sum_j \nu_{ij} P_{nj}) r_i V_R + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j) + \alpha TV_R \sum_j P_{nj} (c_{jf} Q_f - c_j Q) + \dot{Q}$$

b.1 Constant-volume reactor, ideal gas

If the CSTR is at steady state, the time derivatives in Equations 6.30 and 6.31 can be set to zero yielding,

$$Q_f c_{jf} - Q c_j + \sum_i \nu_{ij} r_i V_R = 0 \quad (6.33)$$

$$- \sum_i \Delta H_{Ri} r_i V_R + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j) + \dot{Q} = 0 \quad (6.34)$$

Equations 6.33 and 6.34 provide $n_s + 1$ algebraic equations that can be solved simultaneously to obtain the steady-state concentrations and temperature in the CSTR. Note that the heats of reaction ΔH_{Ri} are evaluated at the reactor temperature and composition.

Liquid phase, Steady-State Operation

If the heat capacity of the liquid phase does not change significantly with composition or temperature, possibly because of the presence of a large excess of a nonreacting solvent, and we neglect the pressure effect on enthalpy, which is normally small for a liquid, we obtain

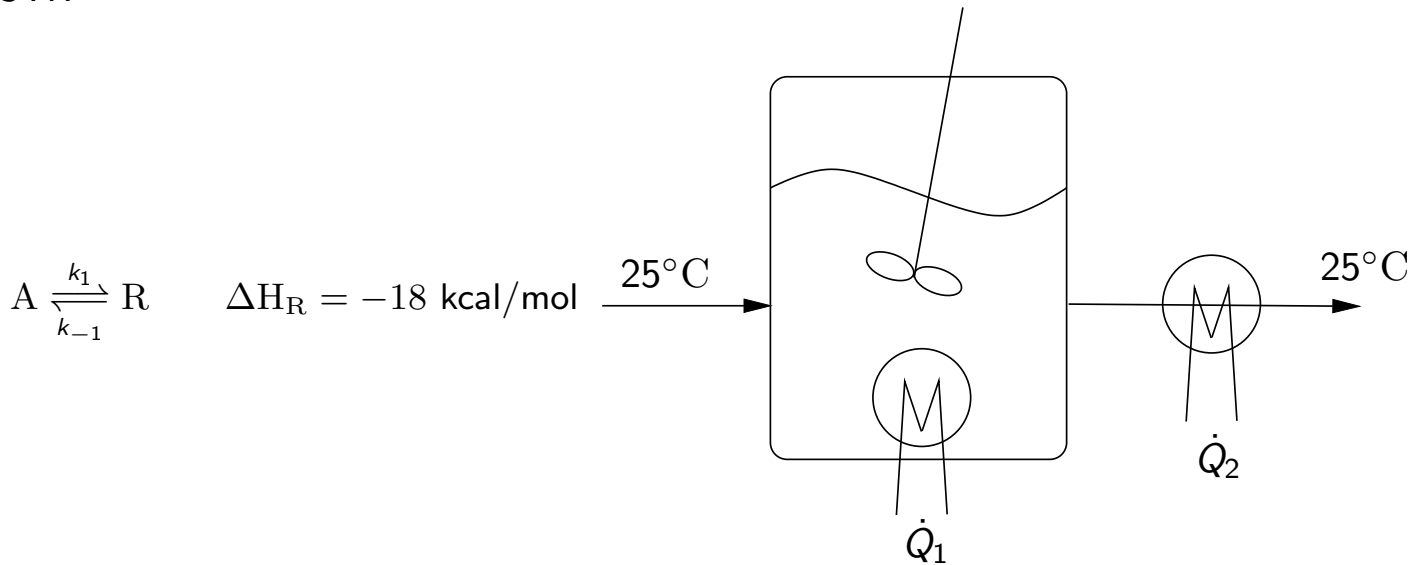
$$\bar{H}_{jf} - \bar{H}_j = \bar{C}_{Pj} (T_f - T)$$

Substitution into Equation 6.34 gives

$$- \sum_i r_i \Delta H_{Ri} V_R + Q_f \rho_f \hat{C}_P (T_f - T) + \dot{Q} = 0 \quad (6.35)$$

Example 6.3: Temperature control in a CSTR

An aqueous solution of species A undergoes the following elementary reaction in a 2000 L CSTR



The feed concentration, C_{Af} , is 4 mol/L and feed flowrate, Q_f , is 250 L/min. □

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The reaction-rate constants have been determined experimentally

$$k_1 = 3 \times 10^7 e^{-5838/T} \text{ min}^{-1}$$

$$K_1 = 1.9 \times 10^{-11} e^{9059/T}$$

- ① At what temperature must the reactor be operated to achieve 80% conversion?
- ② What are the heat duties of the two heat exchangers if the feed enters at 25°C and the product is to be withdrawn at this temperature? The heat capacity of feed and product streams can be approximated by the heat capacity of water, $\hat{C}_P = 1 \text{ cal/g K}$.

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- ① The steady-state material balances for components A and R in a constant-density CSTR are

$$Q(c_{Af} - c_A) - rV_R = 0$$

$$Q(c_{Rf} - c_R) + rV_R = 0$$

Adding these equations and noting $c_{Rf} = 0$ gives

$$c_R = c_{Af} - c_A$$

Substituting this result into the rate expression gives

$$r = k_1(c_A - \frac{1}{K_1}(c_{Af} - c_A))$$

Substitution into the material balance for A gives

$$Q(c_{Af} - c_A) - k_1(c_A - \frac{1}{K_1}(c_{Af} - c_A))V_R = 0 \quad (6.36)$$

If we set $c_A = 0.2c_{Af}$ to achieve 80% conversion, we have one equation and one unknown, T , because k_1 and K_1 are given functions of temperature. Solving this equation numerically gives

$$T = 334 \text{ K}$$

Watch out

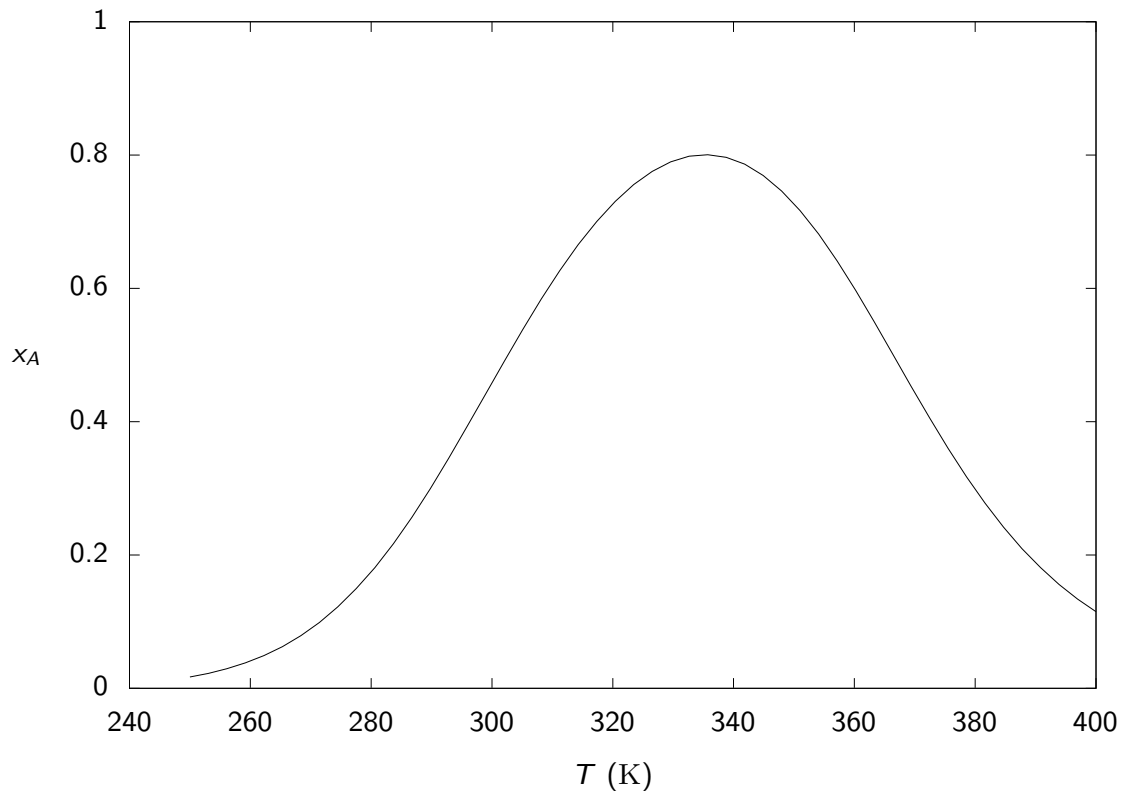
Because the reaction is reversible, we do not know if 80% conversion is achievable for *any* temperature when we attempt to solve Equation 6.36.

It may be valuable to first make a plot of the conversion as a function of reactor temperature. If we solve Equation 6.36 for c_A , we have

$$c_A = \frac{Q/V_R + k_1/K_1}{Q/V_R + k_1(1 + 1/K_1)} c_{Af}$$

or for $x_A = 1 - c_A/c_{Af}$

$$x_A = \frac{k_1}{Q/V_R + k_1(1 + 1/K_1)} = \frac{k_1\tau}{1 + k_1\tau(1 + 1/K_1)}$$



We see that the conversion 80% is just reachable at 334 K, and that for any conversion lower than this value, there are two solutions.

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Heat removal rate

- ① A simple calculation for the heat-removal rate required to bring the reactor outflow stream from 334 K to 298 K gives

$$\begin{aligned}\dot{Q}_2 &= Q_f \rho \hat{C}_P \Delta T \\ &= (250 \text{ L/min})(1000 \text{ g/L})(1 \text{ cal/g K})(298 - 334 \text{ K}) \\ &= -9 \times 10^3 \text{ kcal/min}\end{aligned}$$

Applying Equation 6.35 to this reactor gives

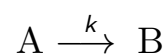
$$\begin{aligned}\dot{Q}_1 &= k_1 \left(c_A - \frac{1}{K_1} (c_{Af} - c_A) \right) \Delta H_R V_R - Q_f \rho \hat{C}_P (T_f - T) \\ &= -5.4 \times 10^3 \text{ kcal/min}\end{aligned}$$

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- The coupling of the material and energy balances for the CSTR can give rise to some surprisingly complex and interesting behavior.
- Even the steady-state solution of the material and energy balances holds some surprises.
- In this section we explore the fact that the steady state of the CSTR is not necessarily unique.
- As many as three steady-state solutions to the material and energy balances may exist for even the simplest kinetic mechanisms.
- This phenomenon is known as steady-state multiplicity.

An Example

We introduce this topic with a simple example [5]. Consider an adiabatic, constant-volume CSTR with the following elementary reaction taking place in the liquid phase



We wish to compute the steady-state reactor conversion and temperature. The data and parameters are listed in Table 6.1.

Parameter	Value	Units
T_f	298	K
T_m	298	K
\hat{C}_P	4.0	kJ/kg K
c_{Af}	2.0	kmol/m ³
k_m	0.001	min ⁻¹
E	8.0×10^3	K
ρ	10^3	kg/m ³
ΔH_R	-3.0×10^5	kJ/kmol
U^o	0	

Table 6.1: Parameter values for multiple steady states.

Material Balance

The material balance for component A is

$$\frac{d(c_A V_R)}{dt} = Q_f c_{Af} - Q c_A + R_A V_R$$

The production rate is given by

$$R_A = -k(T)c_A$$

For the steady-state reactor with constant-density, liquid-phase streams, the material balance simplifies to

$$0 = c_{Af} - (1 + k\tau)c_A \quad (6.37)$$

Equation 6.37 is one nonlinear algebraic equation in two unknowns: c_A and T . The temperature appears in the rate-constant function,

$$k(T) = k_m e^{-E(1/T - 1/T_m)}$$

Now we write the energy balance. We assume the heat capacity of the mixture is constant and independent of composition and temperature.

Energy balance

b. Constant-volume reactor

$$V_R \rho \hat{C}_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - \alpha TV_R \sum_j \nu_{ij} P_{nj}) r_i V_R + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j) + \alpha TV_R \sum_j P_{nj} (c_{jf} Q_f - c_j Q) + \dot{Q}$$

b.1 Constant-volume reactor, ideal gas

$$V_R \rho \hat{C}_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - RT \bar{\nu}_i) r_i V_R + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j) + RT \sum_j (c_{jf} Q_f - c_j Q) + \dot{Q}$$

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

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

Table: Energy balances for the CSTR.

We assume the heat capacity of the mixture is constant and independent of composition and temperature.

With these assumptions, the steady-state energy balance reduces to

$$0 = -k_{CA}\Delta H_R V_R + Q_f \rho_f \hat{C}_P (T_f - T) + U^o A (T_a - T)$$

Dividing through by V_R and noting $U^o = 0$ for the adiabatic reactor gives

$$0 = -k_{CA}\Delta H_R + \frac{C_{Ps}}{\tau} (T_f - T) \quad (6.38)$$

in which $C_{Ps} = \rho_f \hat{C}_P$, a heat capacity per volume.

Two algebraic equations, two unknowns

$$0 = c_{Af} - (1 + k(T)\tau)c_A$$

$$0 = -k(T)c_A\Delta H_R + \frac{C_{Ps}}{\tau}(T_f - T)$$

The solution of these two equations for c_A and T provide the steady-state CSTR solution. The parameters appearing in the problem are: c_{Af} , T_f , τ , C_{Ps} , k_m , T_m , E , ΔH_R . We wish to study this solution as a function of one of these parameters, τ , the reactor residence time.

- Set $\Delta H_R = 0$ to model the isothermal case. Find $c_A(\tau)$ and $T(\tau)$ as you vary τ , $0 \leq \tau \leq 1000$ min.
- We will need the following trick later. Switch the roles of c_A and τ and find $\tau(c_A)$ and $T(c_A)$ versus c_A for $0 \leq c_A \leq c_{Af}$.
- It doesn't matter which is the parameter and which is the unknown, you can still plot $c_A(\tau)$ and $T(\tau)$. Check that both approaches give the same plot.
- For the isothermal reactor, we already have shown that

$$c_A = \frac{c_{Af}}{1 + k\tau}, \quad x = \frac{k\tau}{1 + k\tau}$$

Exothermic (and endothermic) cases

- Set $\Delta H_R = -3 \times 10^5$ kJ/kmol and solve again. What has happened?
- Fill in a few more ΔH_R values and compare to Figures 6.5–6.6.
- Set $\Delta H_R = +5 \times 10^4$ kJ/kmol and try an endothermic case.

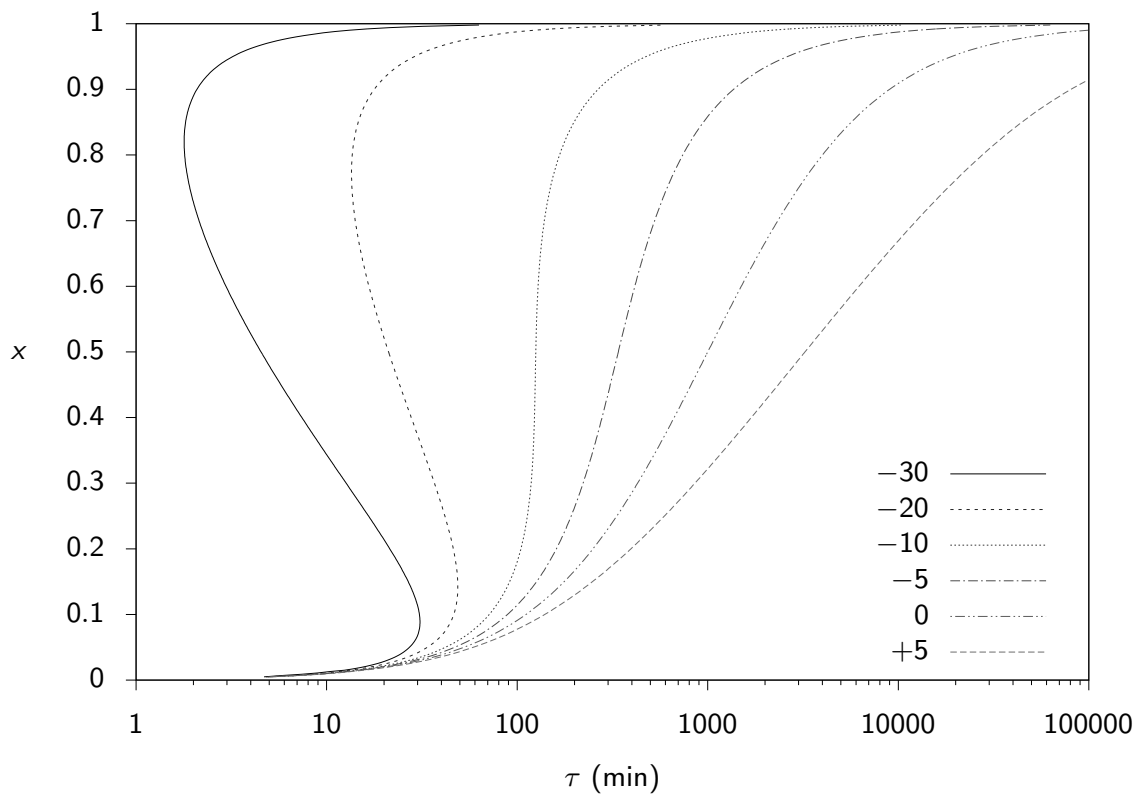


Figure 6.5: Steady-state conversion versus residence time for different values of the heat of reaction ($\Delta H_R \times 10^{-4}$ kJ/kmol).

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Steady-state multiplicity, ignition, extinction

- Note that if the heat of reaction is more exothermic than -10 kJ/kmol, there is a range of residence times in which there is not one but several steady-state solutions, three solutions in this case.
- The reactor is said to exhibit **steady-state multiplicity** for these values of residence time.
- The points at which the steady-state curves turn are known as **ignition** and **extinction** points.

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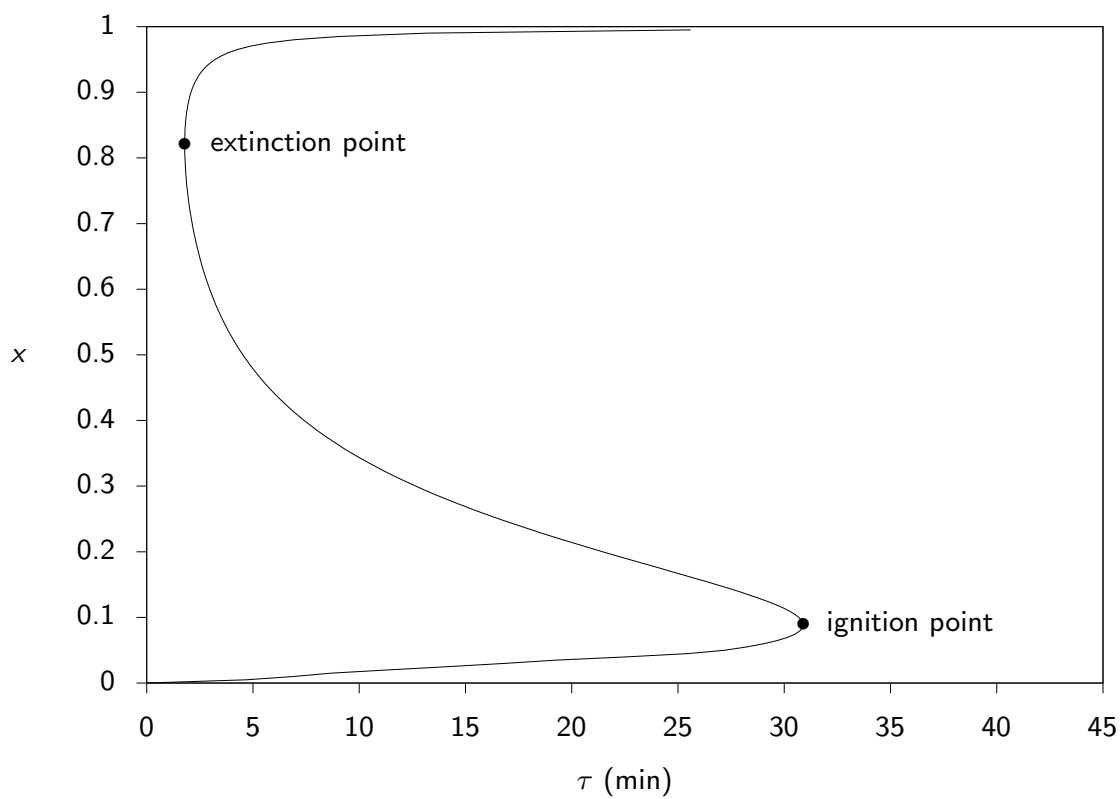


Figure 6.7: Steady-state conversion versus residence time for $\Delta H_R = -3 \times 10^5$ kJ/kmol; ignition and extinction points.

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Hysteresis at the ignition and extinction points

- Consider a small value of residence time, 10 min, at low conversion of A and low temperature. If the feed flowrate were decreased slightly (τ increased), there would be a small upset and the reactor would increase in conversion and temperature as it approached the new steady state at the new residence time.
- Consider the situation at the ignition point, however, $\tau = 30.9$ min at $x = 0.09$ and $T = 311$ K. If there is a small decrease in feed flowrate there is no steady state near the temperature and concentration of the reactor. A large release of heat occurs and the reactor ignites and moves to the steady state near $x = 1$ and $T = 448$ K.
- A reactor operating near the extinction point can exhibit the opposite phenomenon. A small increase in feed flowrate causes the residence time to decrease enough so that no steady-state solution exists near the current temperature and concentration. A rapid drop in temperature and increase in concentration of A occurs as the reactor approaches the new steady state.

We next discuss why some steady states are stable and others are unstable. This discussion comes in two parts. First we present a plausibility argument and develop some physical intuition by constructing and examining van Heerden diagrams [6].

The text also presents a rigorous mathematical argument, which has wide applicability in analyzing the stability of any system described by differential equations.

Dynamic Model

We examine the stability numerically by solving the dynamic model.

$$\begin{aligned}\frac{dc_A}{dt} &= \frac{c_{Af} - c_A}{\tau} - k_{CA} \\ \frac{dT}{dt} &= \frac{U^o A}{V_R C_{Ps}} (T_a - T) + \frac{T_f - T}{\tau} - \frac{\Delta H_R}{C_{Ps}} k_{CA}\end{aligned}\tag{6.40}$$

Steady-state temperature versus residence time

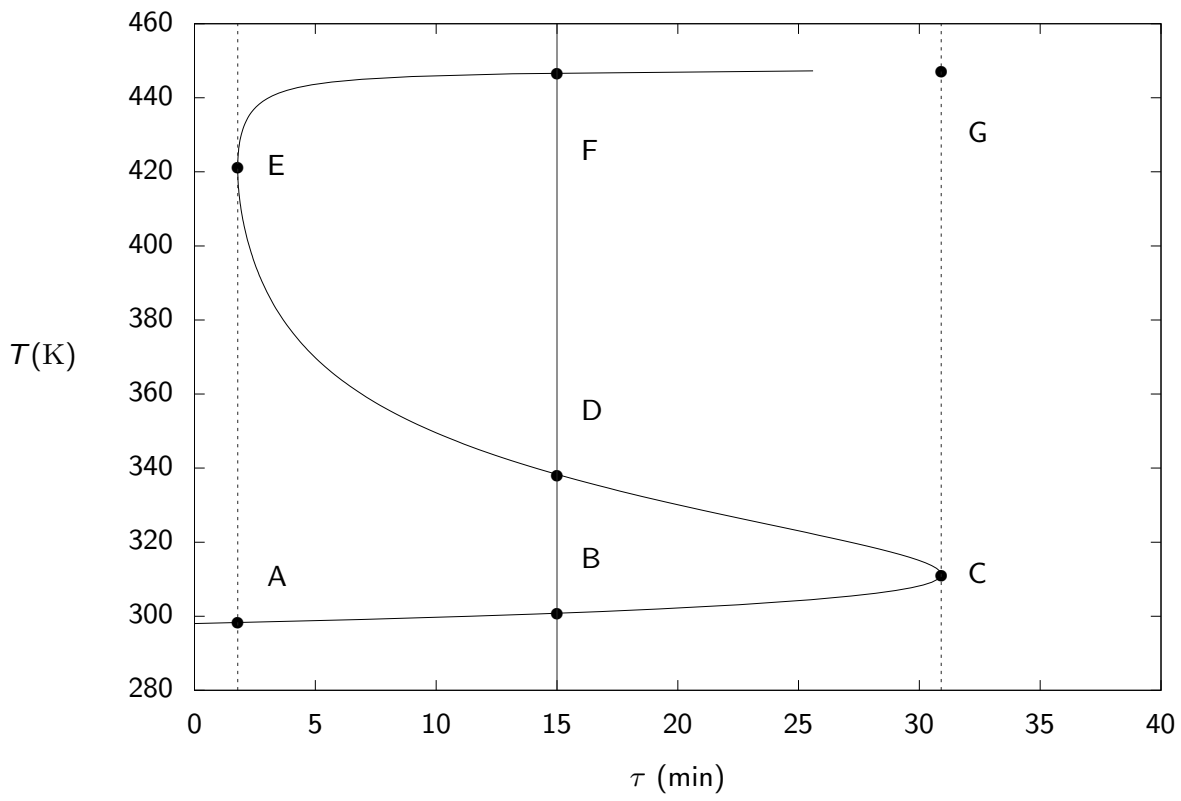


Figure 6.9: Steady-state temperature versus residence time for $\Delta H_R = -3 \times 10^5$ kJ/kmol.

If we substitute the the mass balance for c_A into the energy balance, we obtain one equation for one unknown, T ,

$$0 = \underbrace{-\frac{k}{1+k\tau} c_{Af} \Delta H_R}_{\dot{Q}_g} + \underbrace{\frac{C_{Ps}}{\tau} (T_f - T)}_{\dot{Q}_r} \quad (6.39)$$

We call the first term the heat-generation rate, \dot{Q}_g . We call the second term the heat-removal rate, \dot{Q}_r ,

$$\dot{Q}_g = -\frac{k(T)}{1+k(T)\tau} c_{Af} \Delta H_R, \quad \dot{Q}_r = \frac{C_{Ps}}{\tau} (T - T_f)$$

in which we emphasize the temperature dependence of the rate constant,

$$k(T) = k_m e^{-E(1/T - 1/T_m)}$$

Graphical solution

Obviously we have a steady-state solution when these two quantities are equal.

Consider plotting these two functions as T varies.

The heat-removal rate is simply a straight line with slope C_{Ps}/τ .

The heat-generation rate is a nonlinear function that is asymptotically constant at low temperatures ($k(T)$ much less than one) and high temperatures ($k(T)$ much greater than one).

These two functions are plotted next for $\tau = 1.79$ min.

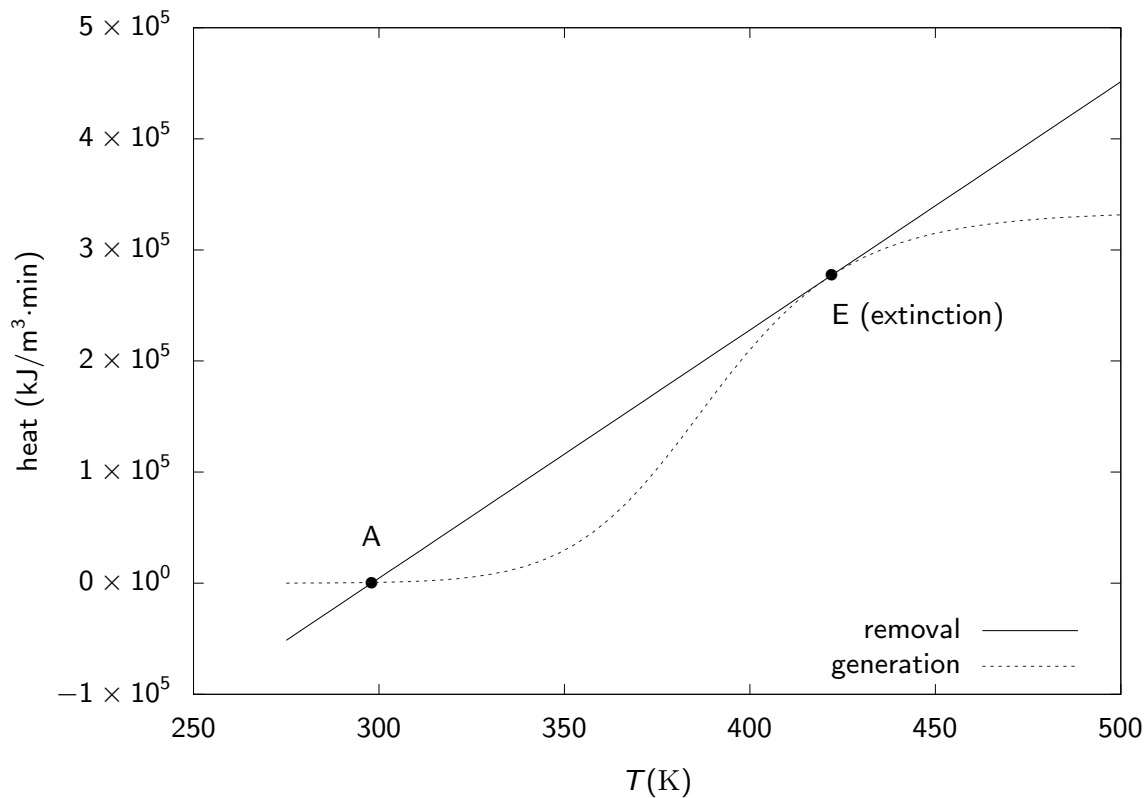


Figure 6.10: Rates of heat generation and removal for $\tau = 1.79$ min.

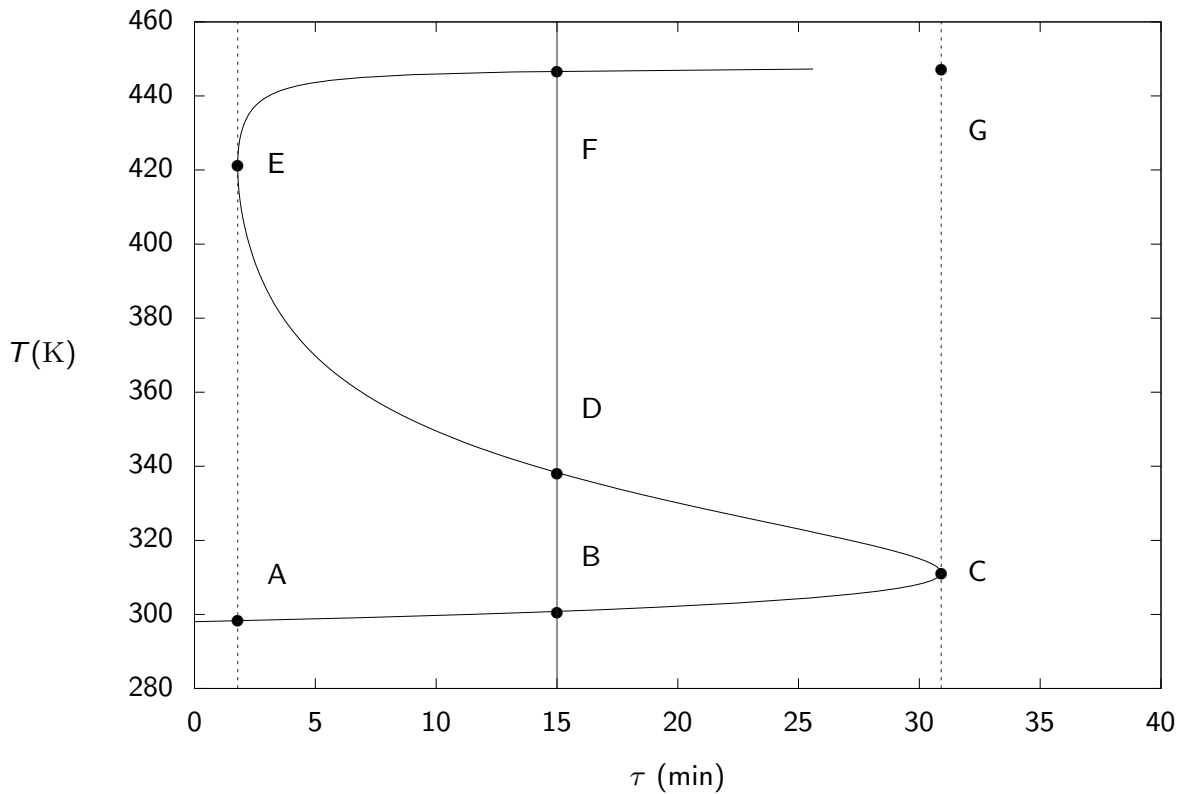
Changing the residence time

Notice the two intersections of the heat-generation and heat-removal functions corresponding to steady states A and E.

If we decrease the residence time slightly, the slope of the heat-removal line increases and the intersection corresponding to point A shifts slightly.

Because the two curves are just tangent at point E, however, the solution at point E disappears, another indicator that point E is an extinction point.

The other view of changing the residence time.



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Stability — small residence time

If we were to increase the reactor temperature slightly, we would be to the right of point A in Figure 6.10.

To the right of A we notice that the heat-removal rate is larger than the heat-generation rate. That causes the reactor to cool, which moves the temperature back to the left. In other words, the system responds by resisting our applied perturbation.

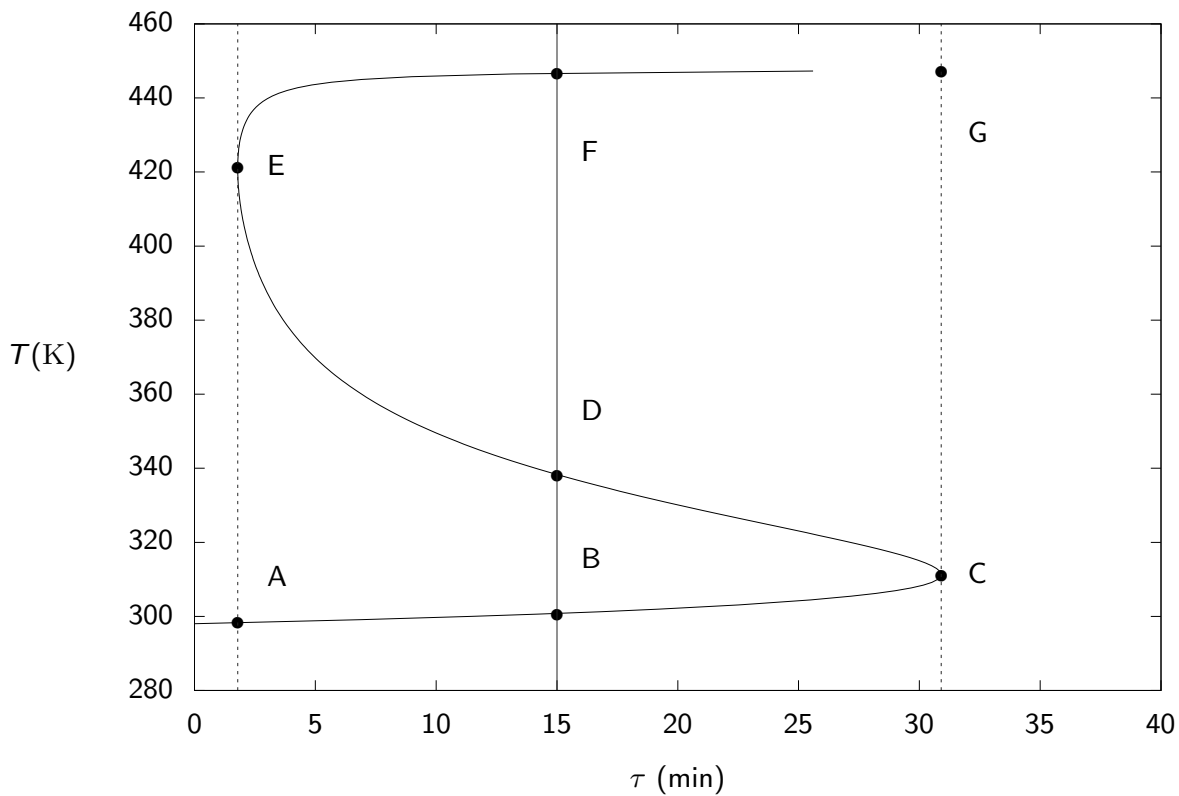
Similarly, consider a decrease to the reactor temperature. To the left of point A, the heat-generation rate is larger than the heat-removal rate causing the reactor to heat up and move back to the right.

Point A is a stable steady state because small perturbations are rejected by the system.

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Intermediate residence time

Consider next the points on the middle branch. Figure 6.11 displays the heat-generation and heat-removal rates for points B, D and F, $\tau = 15$ min.



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Intermediate residence time

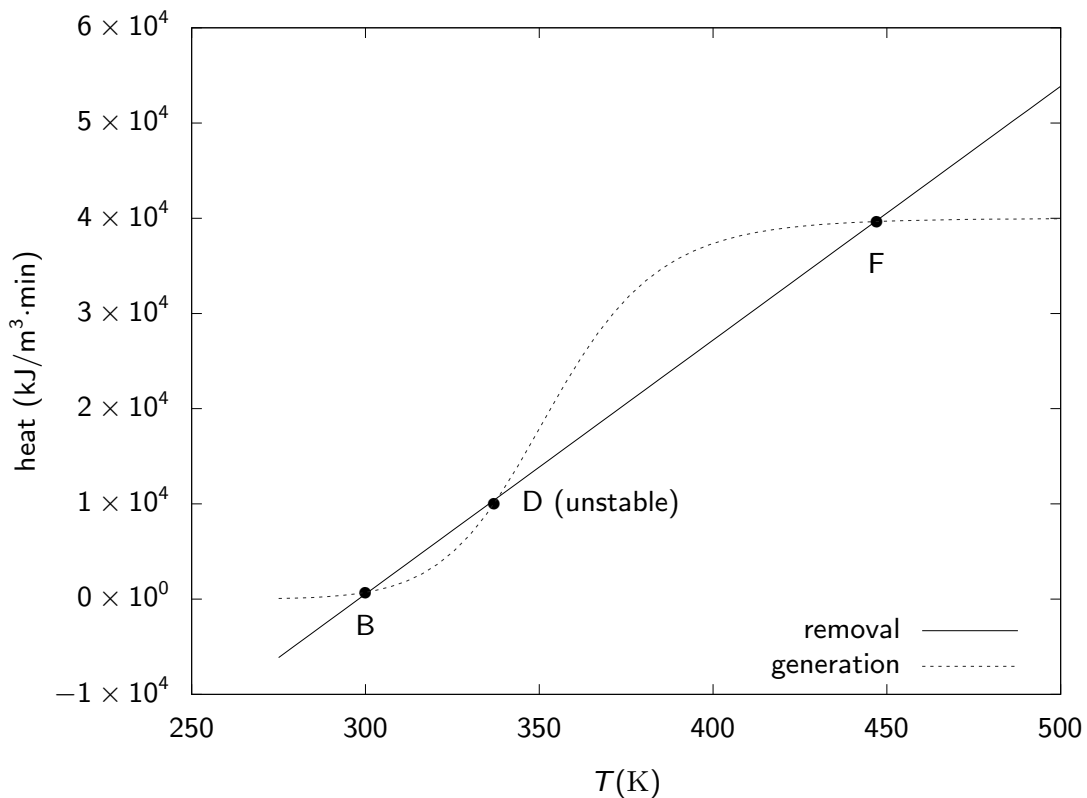


Figure 6.11: Rates of heat generation and removal for $\tau = 15$ min.

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The middle branch

Consider next the points on the middle branch. Figure 6.11 displays the heat-generation and heat-removal rates for points B, D and F, $\tau = 15$ min.

Point B on the lower branch is stable as was point A. Point F on the upper branch also is stable because the slope of the heat-generation rate is smaller than the heat-removal rate at point F.

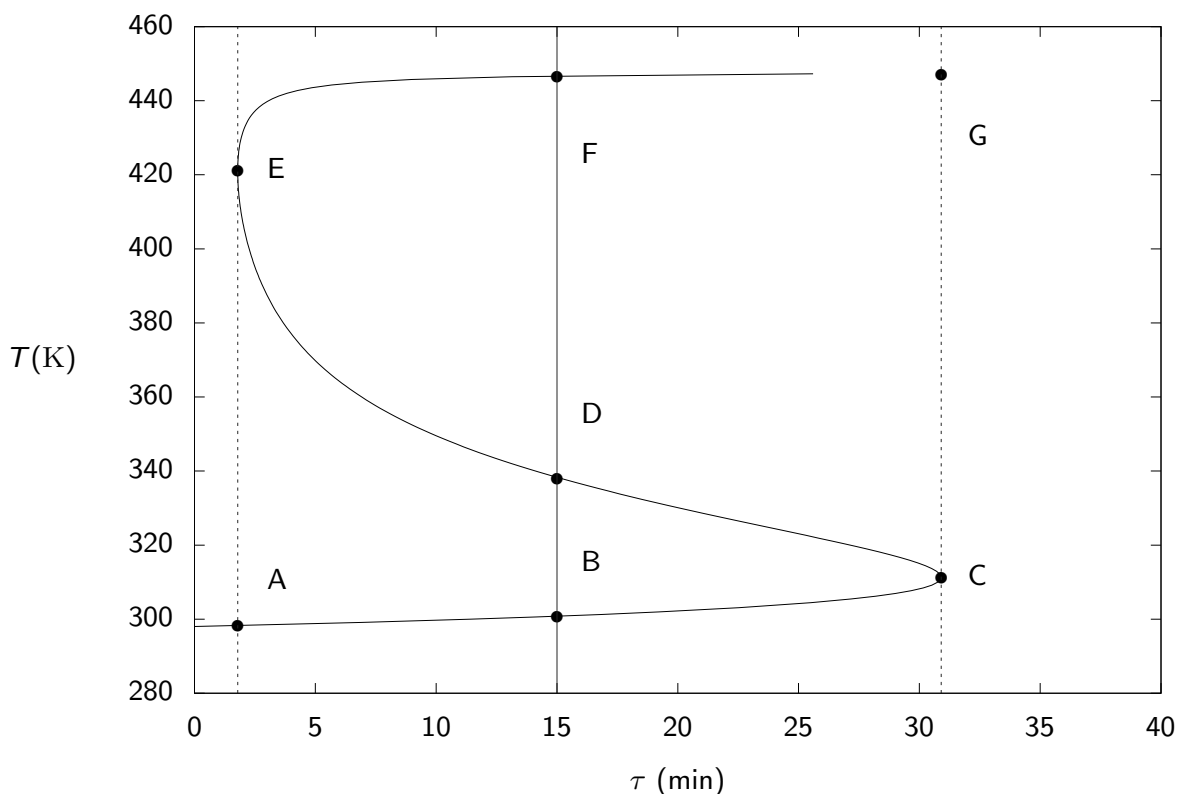
At point D, however, the slope of the heat-generation rate is larger than the heat-removal rate.

For point D, increasing temperature causes heat generation to be larger than heat removal, and decreasing temperature causes heat generation to be smaller than heat removal. Both of these perturbations are amplified by the system at point D, and this solution is unstable.

All points on the middle branch are similar to point D.

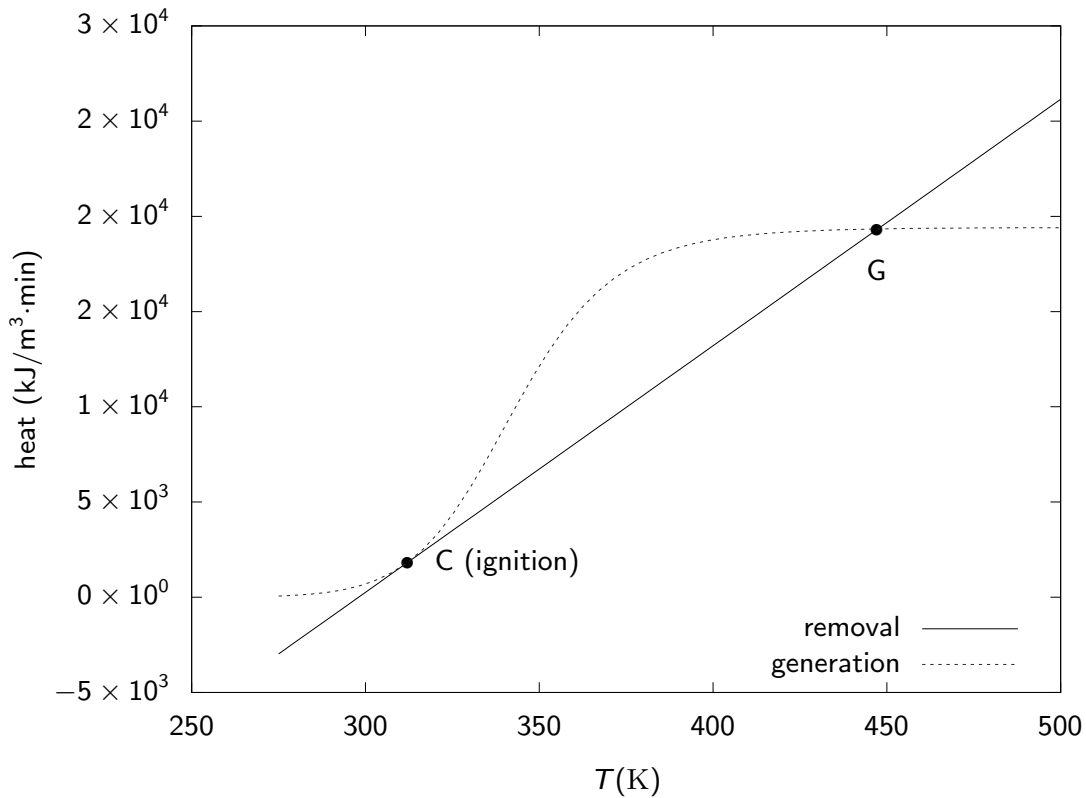
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Large residence time



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Next observe the heat-generation and heat-removal rates for $\tau = 30.9$ min.



Notice that point G on the upper branch is stable and point C, the ignition point, is similar to extinction point E, perturbations in one direction are rejected, but in the other direction they are amplified.

I will not cover this section in lecture. Please read the text.

A simple mechanical analogy

You may find it helpful to draw an analogy between the chemical reactor with multiple steady states and simple mechanical systems that exhibit the same behavior. Consider a marble on a track in a gravitational field as depicted in Figure 6.15.

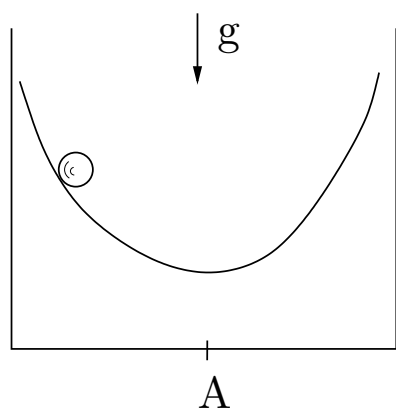


Figure 6.15: Marble on a track in a gravitational field; point A is the unique, stable steady state.

Single steady state

Based on our physical experience with such systems we conclude immediately that the system has a single steady state, position A, which is asymptotically stable.

If we expressed Newton's laws of motion for this system, and linearized the model at point A, we would expect to see eigenvalues with negative real part and nonzero imaginary part because the system exhibits a decaying oscillation back to the steady-state position after a perturbation.

The oscillation decays because of the friction between the marble and the track.

Now consider the track depicted in Figure 6.16.

A simple mechanical analogy

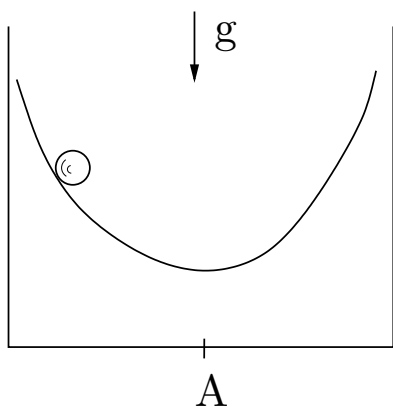


Figure: Marble on a track in a gravitational field; point A is the unique, stable steady state.

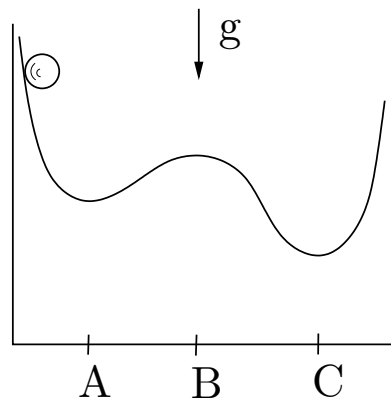


Figure 6.16: Marble on a track with three steady states; points A and C are stable, and point B is unstable.

Here we have three steady states, the three positions where the tangent curve to the track has zero slope. This situation is analogous to the chemical reactor with multiple steady states.

The steady states A and C are obviously stable and B is unstable. Perturbations from point B to the right are attracted to steady-state C and perturbations to the left are attracted to steady-state A.

The significant difference between the reactor and marble systems is that the marble decays to steady state in an oscillatory fashion, and the reactor, with its zero imaginary eigenvalues, returns to the steady state without overshoot or oscillation.

Now consider the track depicted in Figure 6.17.

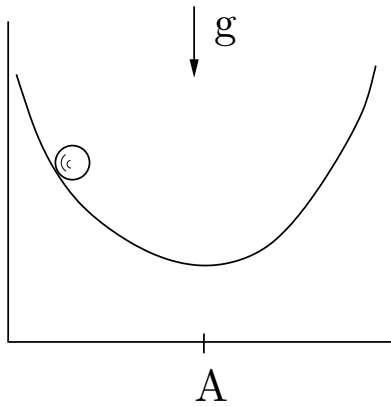


Figure: Marble on a track in a gravitational field; point A is the unique, stable steady state.

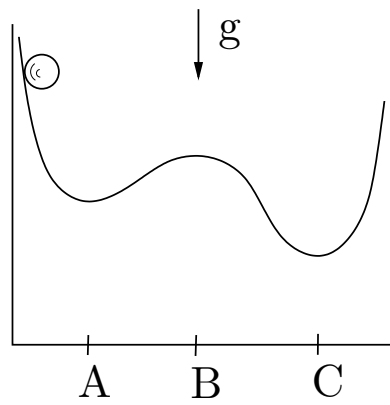


Figure: Marble on a track with three steady states; points A and C are stable, and point B is unstable.

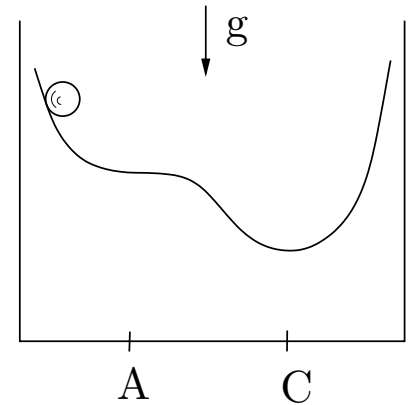


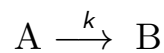
Figure 6.17: Marble on a track with an ignition point (A) and a stable steady state (C).

Ignition and extinction

We have flattened the track between points A and B in Figure 6.16 so there is just a single point of zero slope, now marked point A. Point A now corresponds to a reactor ignition point as shown in Figures 6.7 and 6.8. Small perturbations push the marble over to the only remaining steady state, point C, which remains stable.

The dynamic behavior of the CSTR can be more complicated than multiple steady states with ignition, extinction and hysteresis.

In fact, at a given operating condition, all steady states may be unstable and the reactor may exhibit sustained oscillations or limit cycles. Consider the same simple kinetic scheme as in the previous section,



but with the following parameter values.

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Param.	Value	Units
T_f	298	K
T_m	298	K
\hat{C}_P	4.0	kJ/kg K
c_{Af}	2.0	kmol/m ³
$k_m(T_m)$	0.004	min ⁻¹
E	1.5×10^4	K
ρ	10^3	kg/m ³
ΔH_R	-2.2×10^5	kJ/kmol
$U^\circ A/V_R$	340	kJ/(m ³ min K)

Table 6.3: Parameter values for limit cycles.

Note: the last line of this table is missing in the first printing!

Notice that the activation energy in Table 6.3 is significantly larger than in Table 6.1.

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If we compute the solutions to the steady-state mass and energy balances with these new values of parameters, we obtain the results displayed in the next Figures.

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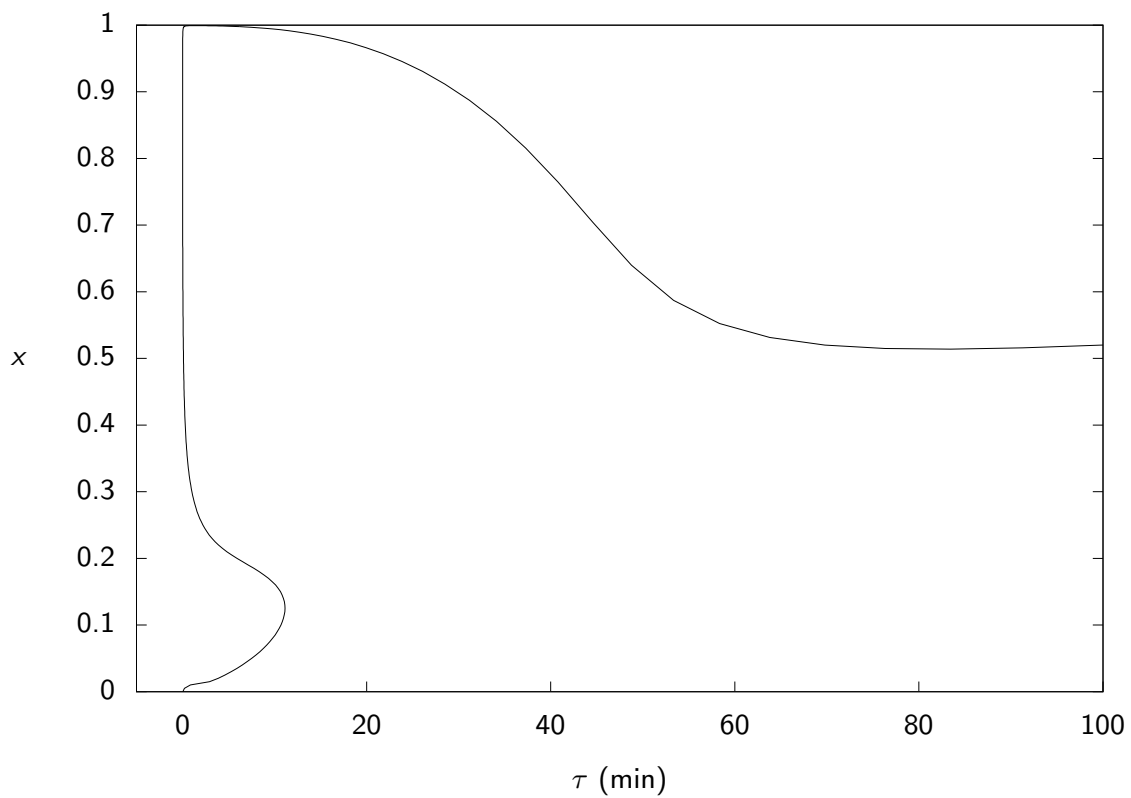


Figure 6.18: Steady-state conversion versus residence time.

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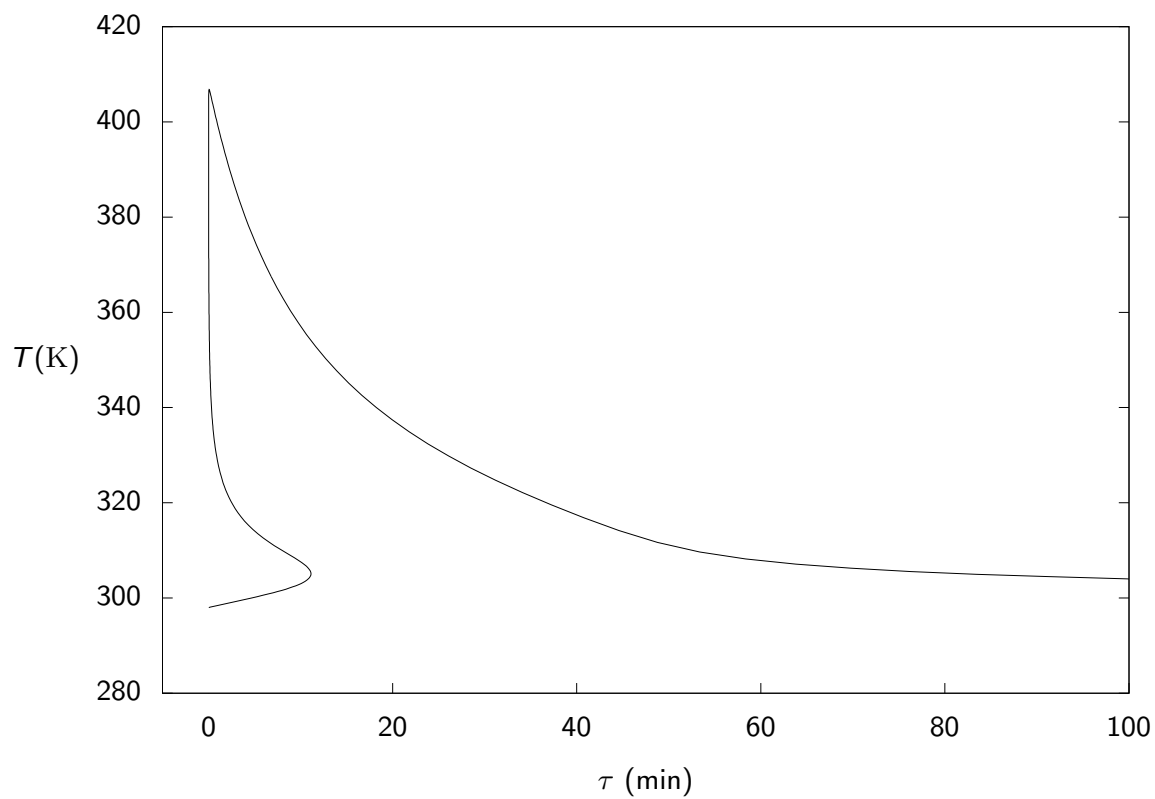


Figure 6.19: Steady-state temperature versus residence time.

If we replot these results using a log scaling to stretch out the x axis, we obtain the results in Figures 6.20 and 6.21.

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We have labeled points A–F on the steady-state curves. Table 6.4 summarizes the locations of these points in terms of the residence times, the steady-state conversions and temperatures, and the eigenvalue of the Jacobian with largest real part.

Point	$\tau(\text{min})$	x	$T(\text{K})$	$\text{Re}(\lambda)(\text{min}^{-1})$	$\text{Im}(\lambda)(\text{min}^{-1})$
A	11.1	0.125	305	0	0
B	0.008	0.893	396	0	0
C	19.2	0.970	339	-0.218	0
D	20.7	0.962	336	-0.373	0
E	29.3	0.905	327	0	0.159
F	71.2	0.519	306	0	0.0330

Table 6.4: Steady state and eigenvalue with largest real part at selected points in Figures 6.20 and 6.21.

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Now we take a walk along the steady-state solution curve and examine the dynamic behavior of the system.

What can simulations can show us. A residence time of $\tau = 35$ min is between points E and F as shown in Table 6.4. Solving the dynamic mass and energy balances with this value of residence time produces

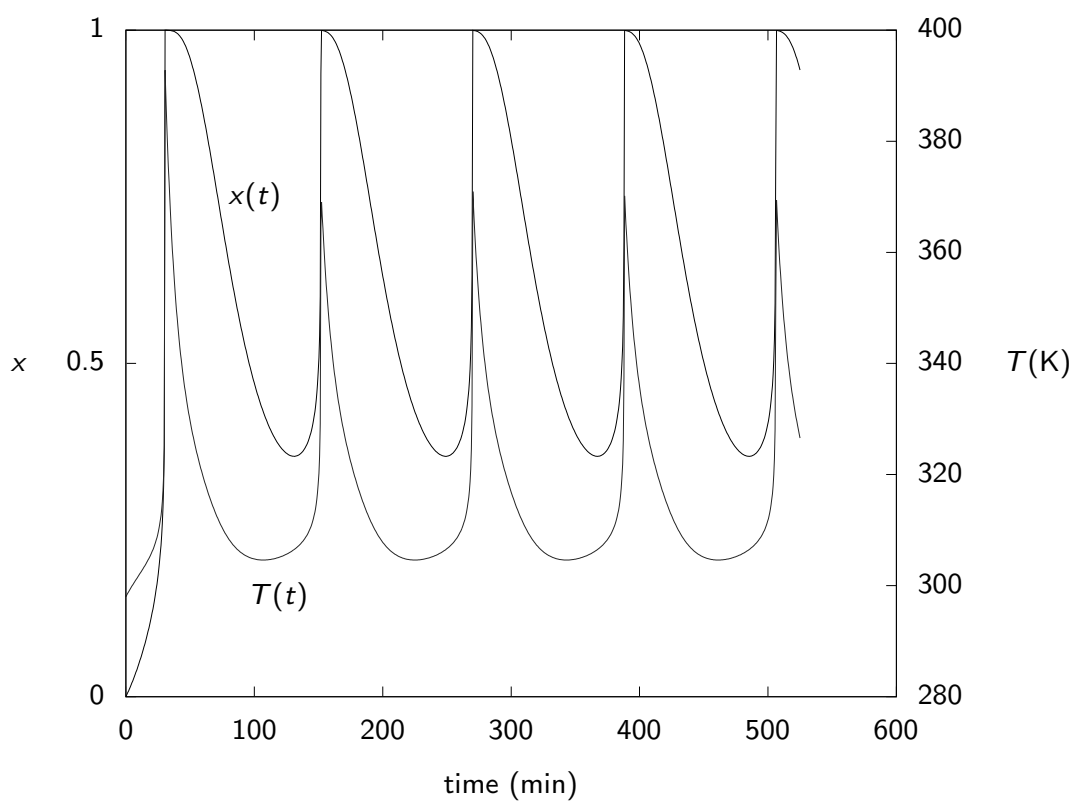


Figure 6.25: Conversion and temperature vs. time for $\tau = 35$ min.

We see that the solution does not approach the steady state but oscillates continuously. These oscillations are sustained; they do not damp out at large times. Notice also that the amplitude of the oscillation is large, more than 80 K in temperature and 50% in conversion.

We can obtain another nice view of this result if we plot the conversion versus the temperature rather than both of them versus time. This kind of plot is known as a phase plot or phase portrait

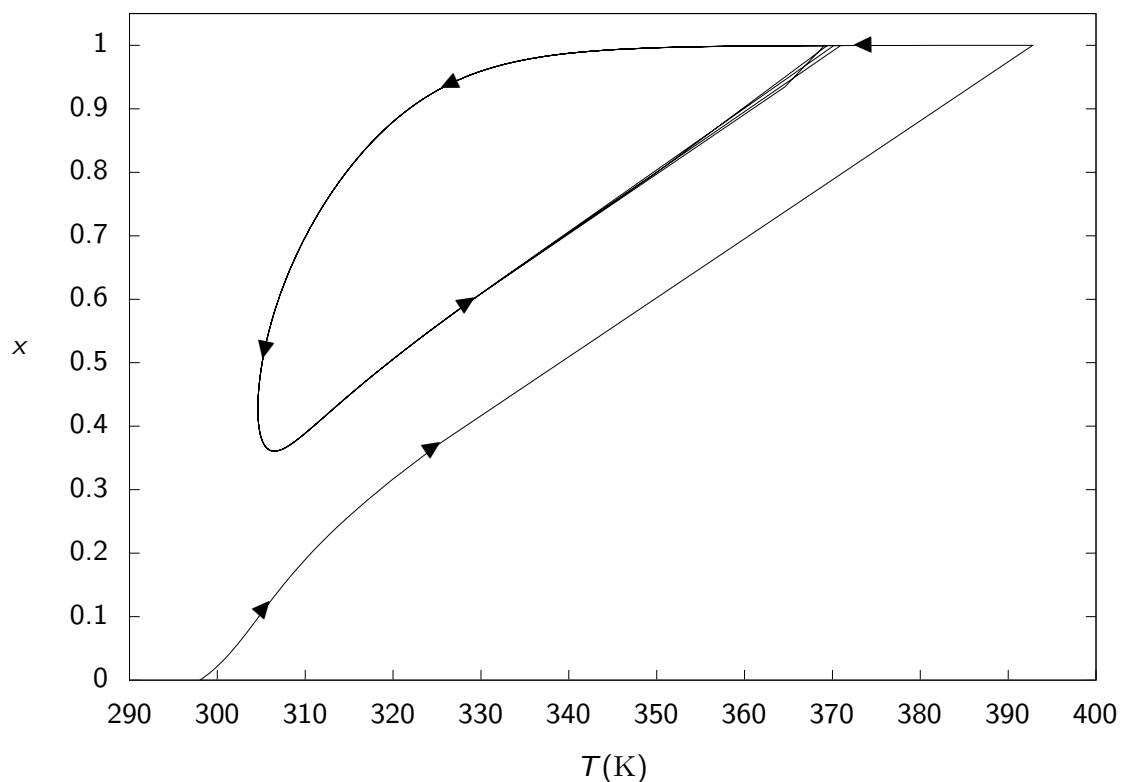


Figure 6.26: Phase portrait of conversion versus temperature for feed initial condition; $\tau = 35$ min.

Time increases as we walk along the phase plot; the reactor ignites, then slowly decays, ignites again, and eventually winds onto the steady limit cycle shown in the figure. The next figure explores the effect of initial conditions.

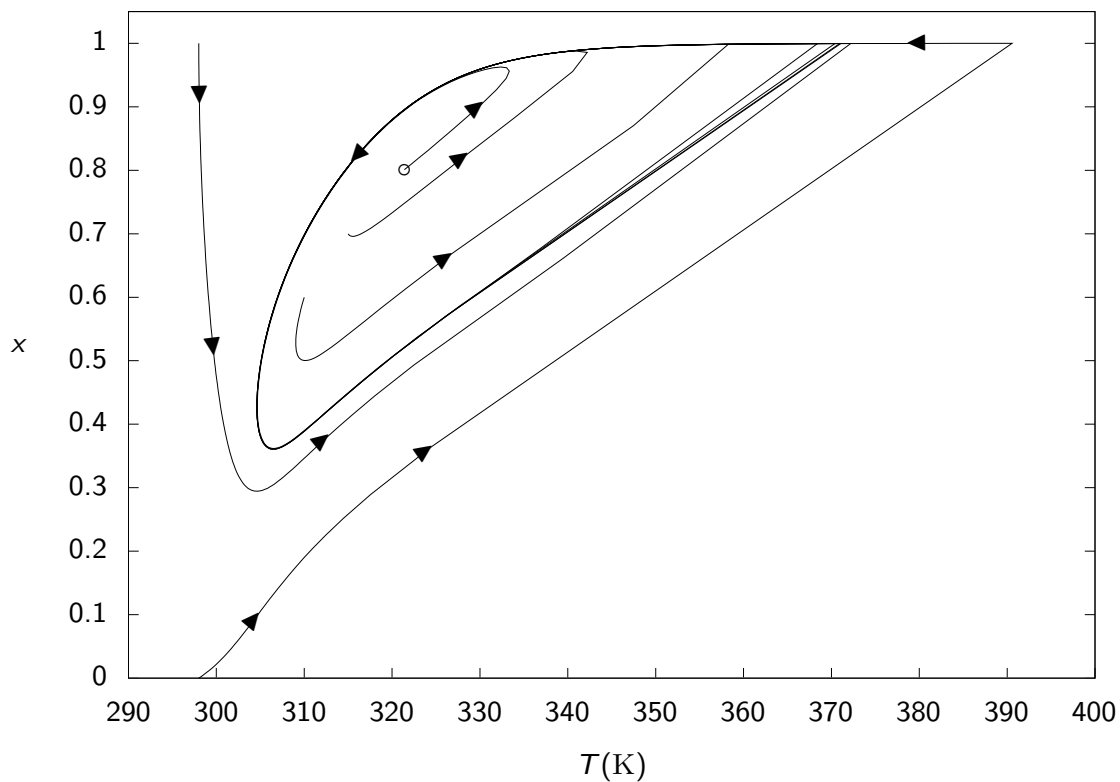


Figure 6.27: Phase portrait of conversion versus temperature for several initial conditions; $\tau = 35$ min.

The trajectory starting with the feed temperature and concentration is shown again. The trajectory starting in the upper left of the figure has the feed temperature and zero A concentration as its initial condition. Several other initial conditions inside the limit cycle are shown also, including starting the reactor at the unstable steady state. All of these initial conditions wind onto the same final limit cycle. We say that the limit cycle is a global *attractor* because all initial conditions wind onto this same solution.

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Decrease residence time

If we decrease the residence time to $\tau = 30$ min, we are close to point E, where the stability of the upper steady state changes. A simulation at this residence time is shown in the next figure.

Notice the amplitude of these oscillations is much smaller, and the shape is more like a pure sine wave.

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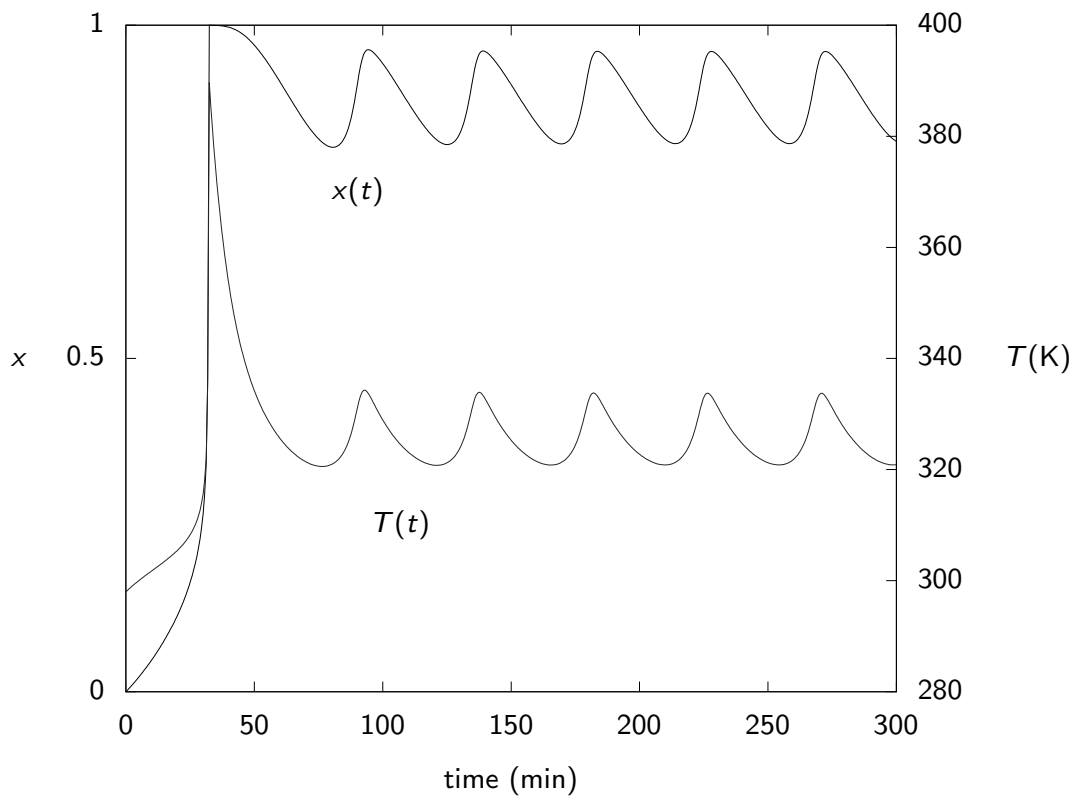


Figure 6.28: Conversion and temperature vs. time for $\tau = 30$ min.

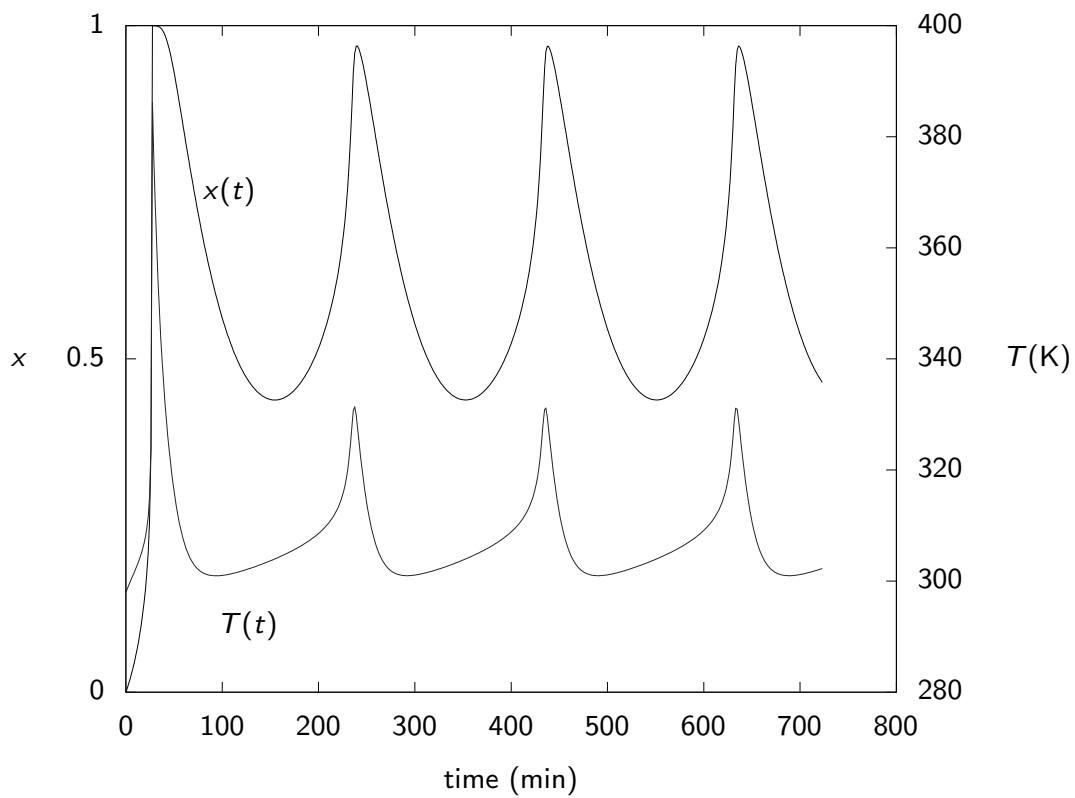


Figure 6.29: Conversion and temperature vs. time for $\tau = 72.3$ min.

As we pass point F, the steady state is again stable. A simulation near point F is shown in Figure 6.29. Notice, in contrast to point E, the amplitude of the oscillations is not small near point F.

To see how limit cycles can remain after the steady state regains its stability, consider the next figure, constructed for $\tau = 73.1$ min.

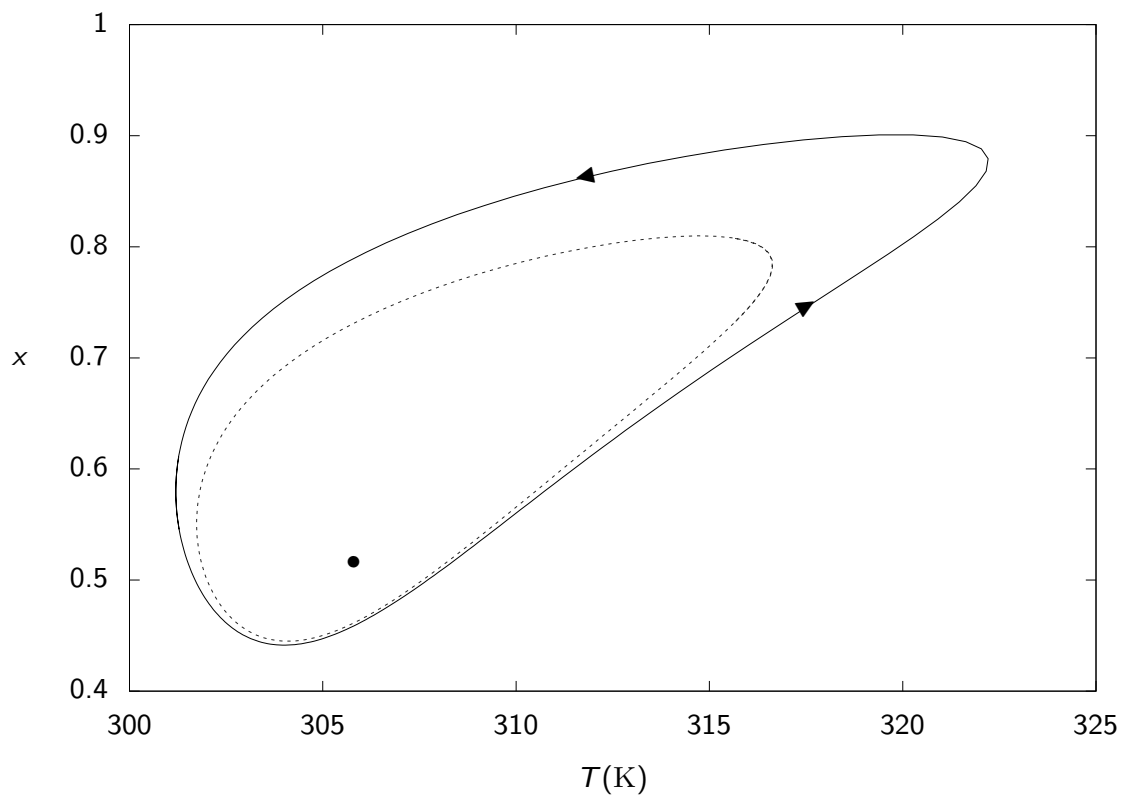


Figure 6.30: Phase portrait of conversion versus temperature at $\tau = 73.1$ min showing stable and unstable limit cycles, and a stable steady state.

The figure depicts the stable steady state, indicated by a solid circle, surrounded by an unstable limit cycle, indicated by the dashed line.

The unstable limit cycle is in turn surrounded by a stable limit cycle. Note that all initial conditions outside of the stable limit cycle would converge to the stable limit cycle from the outside.

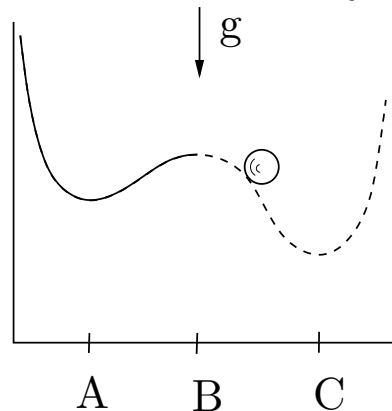
All initial conditions in the region between the unstable and stable limit cycles would converge to the stable limit cycle from the inside.

Finally, all initial conditions inside the unstable limit cycle are attracted to the stable steady state.

We have a quantitative measure of a perturbation capable of knocking the system from the steady state onto a periodic solution.

Mechanical System Analogy

We may modify our simple mechanical system to illustrate somewhat analogous limit-cycle behavior. Consider the marble and track system



We have three steady states; steady-state A is again stable and steady-state B is unstable. At this point we cheat thermodynamics a bit to achieve the desired behavior. Imagine the track consists of a frictionless material to the right of point B.

Without friction in the vicinity of point C, the steady state is not asymptotically stable. Perturbations from point C do not return to the steady state but continually oscillate. The analogy is not perfect because a single limit cycle does not surround the unstable point C as in the chemical reactor. But the analogy may prove helpful in demystifying these kinds of reactor behaviors.

Consider why we were compelled to violate the second law to achieve sustained oscillations in the simple mechanical system but the reactor can continually oscillate without such violation.

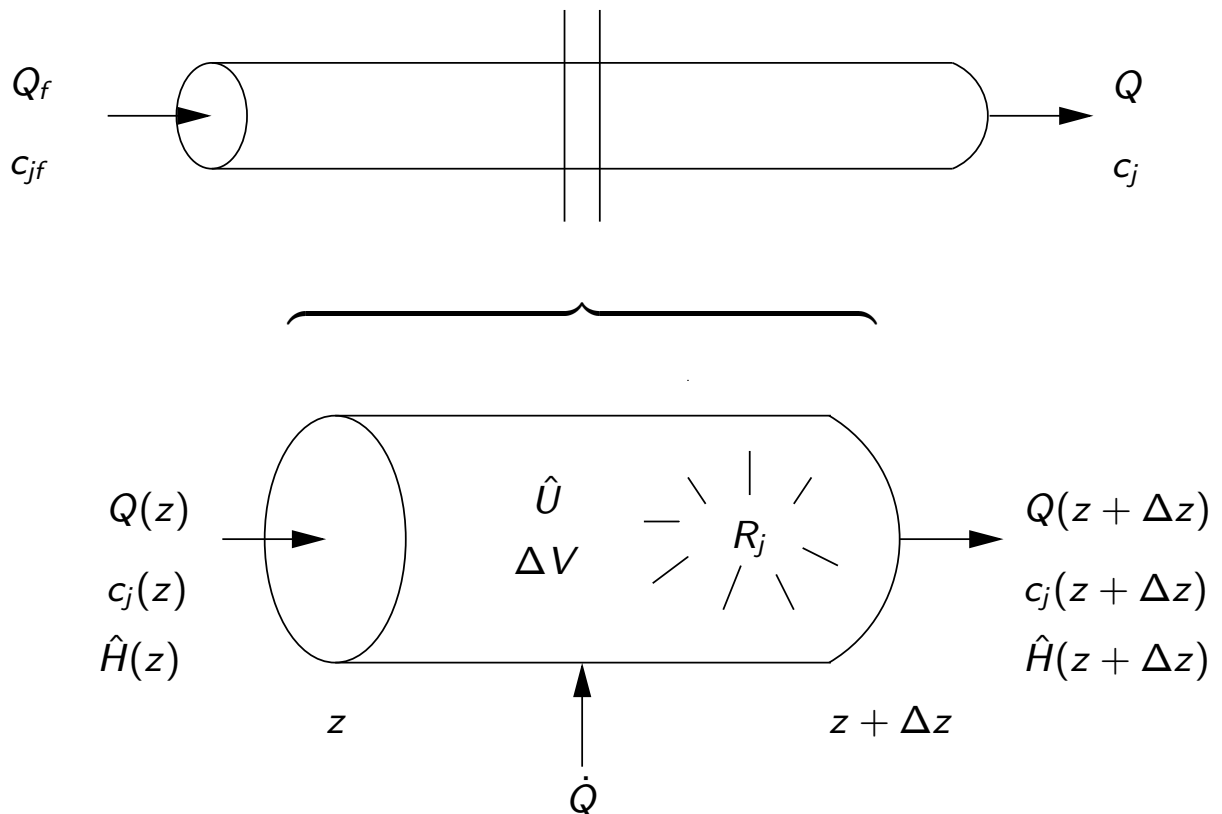
Further Reading on CSTR Dynamics and Stability

Large topic, studied intensely by chemical engineering researchers in the 1970s–1980s. Professor Ray and his graduate students in this department were some of the leading people.

The development of the semi-batch reactor energy balance follows directly from the CSTR energy balance derivation by setting $Q = 0$. The main results are summarized in Table 6.9 at the end of this chapter.

The Plug-Flow Reactor

To derive an energy balance for the plug-flow reactor (PFR), consider the volume element



If we write Equation 6.5 for this element and neglect kinetic and potential energies and shaft work, we obtain

$$\frac{\partial}{\partial t}(\rho \hat{U} A_c \Delta z) = m \hat{H}|_z - m \hat{H}|_{z+\Delta z} + \dot{Q}$$

in which A_c is the cross-sectional area of the tube, R is the tube outer radius, and \dot{Q} is the heat transferred through the wall, normally expressed using an overall heat-transfer coefficient

$$\dot{Q} = U^\circ 2\pi R \Delta z (T_a - T)$$

Dividing by $A_c \Delta z$ and taking the limit $\Delta z \rightarrow 0$, gives

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

in which $\dot{q} = (2/R)U^\circ(T_a - T)$ and we express the mass flowrate as $m = Q\rho$.

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Some therodynamics occurs, and ...

In unpacked tubes, the pressure drop is usually negligible, and for an ideal gas, $\alpha T = 1$. For both of these cases, we have

Ideal gas, or neglect pressure drop.

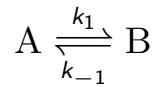
$$\boxed{Q\rho\hat{C}_P \frac{dT}{dV} = -\sum_i \Delta H_{Ri} r_i + \dot{q}} \quad (6.51)$$

Equation 6.51 is the usual energy balance for PFRs in this chapter. The next chapter considers packed-bed reactors in which the pressure drop may be significant.

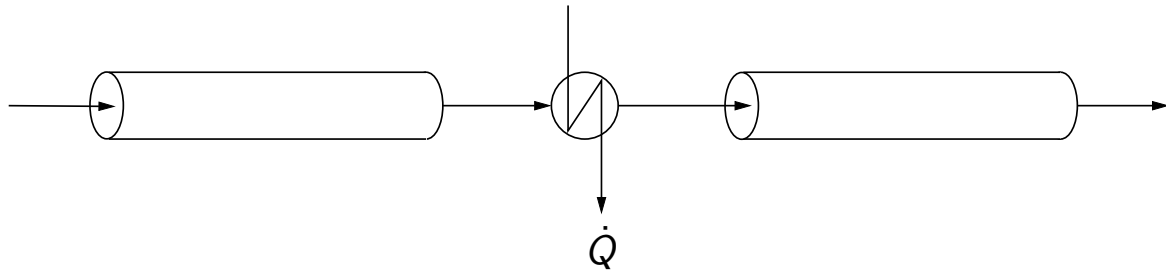
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Example 6.4: PFR and interstage cooling

Consider the reversible, gas-phase reaction



The reaction is carried out in two long, adiabatic, plug-flow reactors with an interstage cooler between them as shown below \dot{Q}



□

- The feed consists of component A diluted in an inert N_2 stream, $N_{Af}/N_{If} = 0.1$, $N_{Bf} = 0$, and $Q_f = 10,000 \text{ ft}^3/\text{hr}$ at $P_f = 180 \text{ psia}$ and $T_f = 830^\circ\text{R}$.

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PFR and interstage cooling II

- Because the inert stream is present in such excess, we assume that the heat capacity of the mixture is equal to the heat capacity of nitrogen and is independent of temperature for the temperature range we expect.
- The heat of reaction is $\Delta H_R = -5850 \text{ BTU/lbmol}$ and can be assumed constant. The value of the equilibrium constant is $K = k_1/k_{-1} = 1.5$ at the feed temperature.

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Questions I

- 1 Write down the mole and energy balances that would apply in the reactors. Make sure all variables in your equations are expressed in terms of T and N_A . What other assumptions did you make?
- 2 If the reactors are long, we may assume that the mixture is close to equilibrium at the exit. Using the mole balance, express N_A at the exit of the first reactor in terms of the feed conditions and the equilibrium constant, K .
- 3 Using the energy balance, express T at the exit of the first reactor in terms of the feed conditions and N_A .
- 4 Notice we have two equations and two unknowns because K is a strong function of T . Solve these two equations numerically and determine the temperature and conversion at the exit of the first reactor. Alternatively, you can substitute the material balance into the energy balance to obtain one equation for T . Solve this equation to determine the temperature at the exit of the first reactor. What is the conversion at the exit of the first reactor?
- 5 Assume that economics dictate that we must run this reaction to 70% conversion to make a profit. How much heat must be removed in the interstage cooler to be able to achieve this conversion at the exit of the second reactor? What are the temperatures at the inlet and outlet of the second reactor?
- 6 How would you calculate the *actual* conversion achieved for two PFRs of *specified* sizes (rather than “long” ones) with this value of \dot{Q} ?

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Answers I

- 1 The steady-state molar flow of A is given by the PFR material balance

$$\frac{dN_A}{dV} = R_A = -r \quad (6.53)$$

and the rate expression for the reversible reaction is given by

$$r = k_1 c_A - k_{-1} c_B = (k_1 N_A - k_{-1} N_B) / Q$$

The molar flow of B is given by $dN_B/dV = r$, so we conclude

$$N_B = N_{A_f} + N_{B_f} - N_A = N_{A_f} - N_A$$

If we assume the mixture behaves as an ideal gas at these conditions, $c = P/RT$ or

$$Q = \frac{RT}{P} \sum_{j=1}^{ns} N_j$$

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Answers II

- 2 The material balance for inert gives $dN_I/dV = 0$, so we have the total molar flow is $\sum_{j=1}^{n_s} N_j = N_{Af} + N_{If}$ and the volumetric flowrate is

$$Q = \frac{RT}{P}(N_{Af} + N_{If})$$

and the reaction rate is

$$r = \frac{P}{RT} \left(\frac{k_1 N_A - k_{-1}(N_{Af} - N_A)}{N_{Af} + N_{If}} \right)$$

which is in terms of T and N_A . The adiabatic PFR energy balance for an ideal gas is given by

$$\frac{dT}{dV} = -\frac{\Delta H_R}{Q\rho\hat{C}_P} r \quad (6.54)$$

- 3 For long reactors, $r = 0$ or

$$k_1 N_A - k_{-1}(N_{Af} - N_A) = 0$$

Dividing by k_{-1} and solving for N_A gives

$$N_A = \frac{N_{Af}}{1 + K_1}$$

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Answers III

- 4 Substituting $r = -dN_A/dV$ into the energy balance and multiplying through by dV gives

$$dT = \frac{\Delta H_R}{Q\rho\hat{C}_P} dN_A$$

The term $Q\rho = m$ in the denominator is the mass flowrate, which is constant and equal to the feed mass flowrate. If we assume the heat of reaction and the heat capacity are weak functions of temperature and composition, we can perform the integral yielding

$$T_1 - T_{1f} = \frac{\Delta H_R}{m\hat{C}_P} (N_A - N_{Af})$$

- 5 $T - 830 + 80.1 \left(\frac{1}{1 + 0.0432e^{2944/T}} - 1 \right) = 0,$

$$T_1 = 874^\circ\text{R}, \quad x = 0.56$$

- 6 $\dot{Q} = 200,000 \text{ BTU/hr}, \quad T_{2f} = 726^\circ\text{R}, \quad T_2 = 738^\circ\text{R}$

- 7 Integrate Equations 6.53 and 6.54.

The results are summarized in Figure 6.34.

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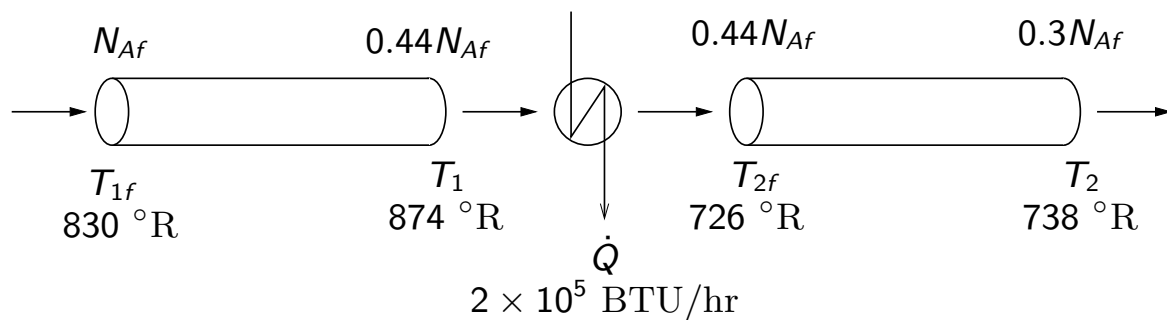


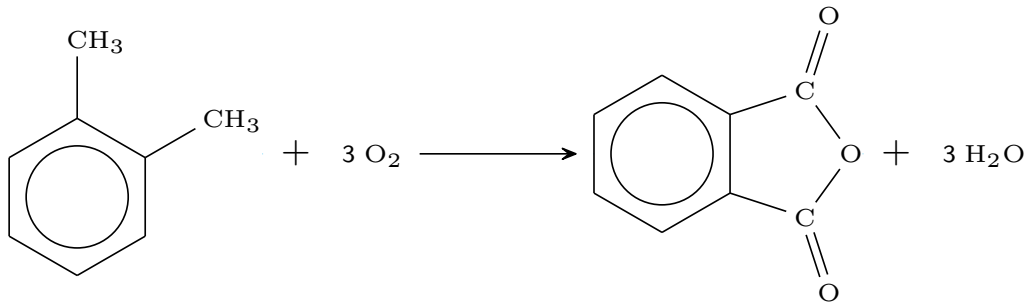
Figure 6.34: Temperatures and molar flows for tubular reactors with interstage cooling.

Plug-Flow Reactor Hot Spot and Runaway

- For exothermic, gas-phase reactions in a PFR, the heat release generally leads to the formation of a reactor hot spot, a point along the reactor length at which the temperature profile achieves a maximum.
- If the reaction is highly exothermic, the temperature profile can be very sensitive to parameters, and a small increase in the inlet temperature or reactant feed concentration, for example, can lead to large changes in the temperature profile.
- A sudden, large increase in the reactor temperature due to a small change in feed conditions is known as reactor runaway.
- Reactor runaway is highly dangerous, and operating conditions are normally chosen to keep reactors far from the runaway condition.

Example 6.5: Oxidation of o-xylene to phthalic anhydride

The gas-phase oxidation of o-xylene to phthalic anhydride



is highly exothermic.

The reaction is carried out in PFR tube bundles with molten salt circulating as the heat transfer fluid [2]. The o-xylene is mixed with air before entering the PFR.

The reaction rate is limited by maintaining a low concentration of hydrocarbon in the feed. The mole fraction of o-xylene is less than 2%.

Under these conditions, the large excess of oxygen leads to a pseudo-first-order rate expression

$$r = k_m \exp \left[-E \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] c_x$$

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Oxidation of o-xylene to phthalic anhydride II

in which c_x is the o-xylene concentration.

The operating pressure is atmospheric.

Calculate the temperature and o-xylene composition profiles.

The kinetic parameters are adapted from Van Welsenaere and Froment and given in Table 6.5 [7].

Parameter	Value	Units
k_m	1922.6	s^{-1}
T_a	625	K
T_m	625	K
P_f	1.0	atm
l	1.5	m
R	0.0125	m
\hat{C}_p	0.992	kJ/kg K
U°	0.373	kJ/m ² s K
y_{xf}	0.019	
E/R	1.3636×10^4	K
ΔH_R	-1.361×10^3	kJ/kmol
$Q\rho$	2.6371×10^{-3}	kg/s

Table 6.5: PFR operating conditions and parameters for o-xylene example.

□

Solution I

If we assume constant thermochemical properties, an ideal gas mixture, and express the mole and energy balances in terms of reactor length, we obtain

$$\begin{aligned}\frac{dN_x}{dz} &= -A_c r \\ \frac{dT}{dz} &= -\beta r + \gamma(T_a - T) \\ r &= k \frac{P}{RT} \frac{N_x}{N}\end{aligned}$$

in which

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

and the total molar flow is constant and equal to the feed molar flow because of the stoichiometry.

Figure 6.35 shows the molar flow of o-xylene versus reactor length for several values of the feed temperature. The corresponding temperature profile is shown in Figure 6.36.

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Solution II

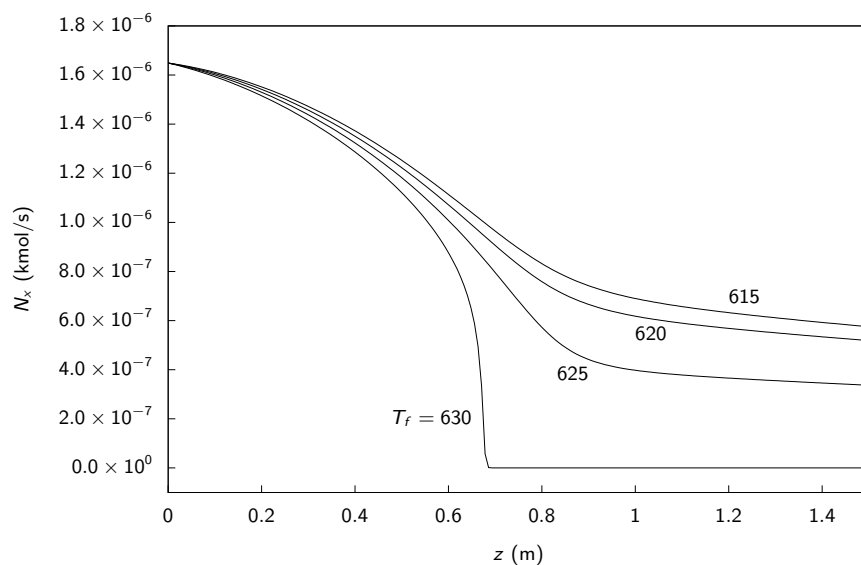


Figure 6.35: Molar flow of o-xylene versus reactor length for different feed temperatures.

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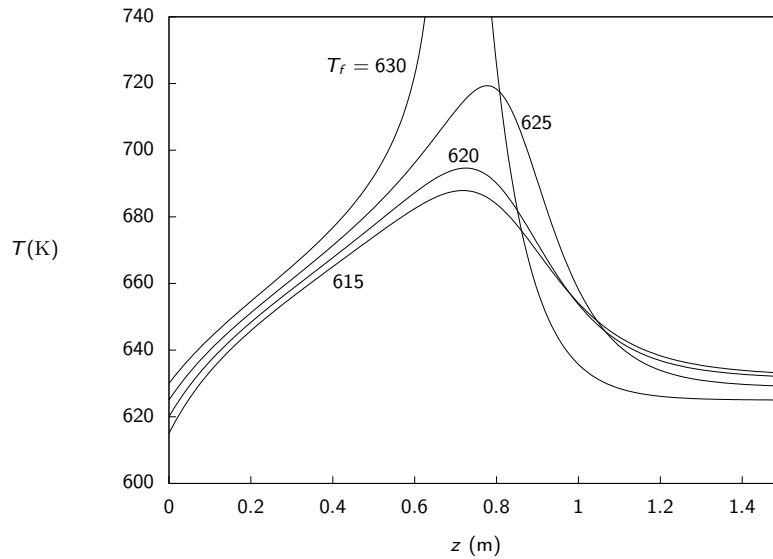


Figure 6.36: Reactor temperature versus length for different feed temperatures.

Solution IV

- We see a hotspot in the reactor for each feed temperature.
- Notice the hotspot temperature increases and moves down the tube as we increase the feed temperature.
- Finally, notice if we increase the feed temperature above about 631 K, the temperature spikes quickly to a large value and all of the o-xylene is converted by $z = 0.6$ m, which is a classic example of reactor runaway.
- To avoid this reactor runaway, we must maintain the feed temperature below a safe value.
- This safe value obviously also depends on how well we can control the composition and temperature in the feed stream. Tighter control allows us to operate safely at higher feed temperatures and feed o-xylene mole fractions, which increases the production rate.

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 following heat integration scheme

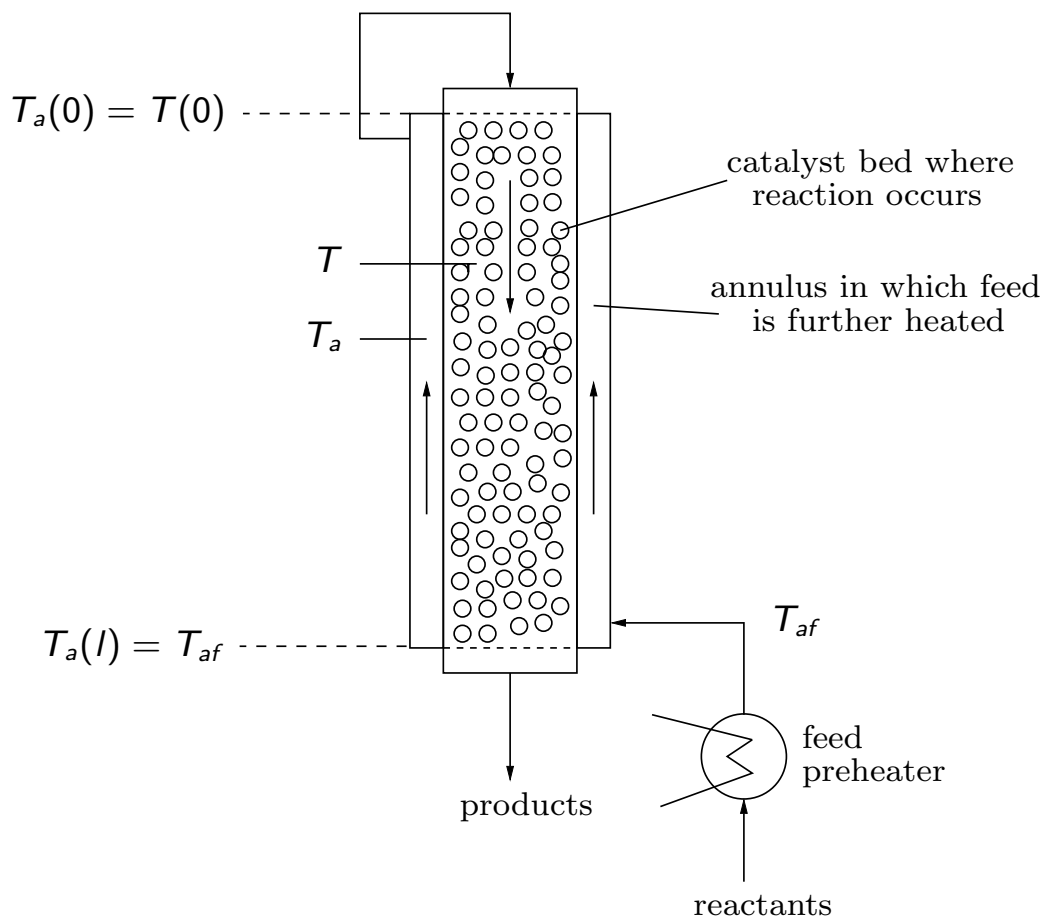


Figure 6.37: Autothermal plug-flow reactor; the heat released by the exothermic reaction is used to preheat the feed.

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.

The added complexity of heat integration

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 had a large impact on the early development of the chemical engineering discipline. Quoting Aftalion [1, p. 101]

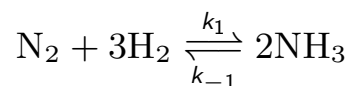
While physicists and chemists were linking up to understand the structure of matter and giving birth to physical chemistry, another discipline was emerging, particularly in the United States, at the beginning of the twentieth century, that of chemical engineering . . . it was undoubtedly the synthesis 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.

Ammonia synthesis I

Example 6.6: Ammonia synthesis

Calculate the steady-state conversion for the synthesis of ammonia using the autothermal process shown previously

A rate expression for the reaction



over an iron catalyst at 300 atm pressure is suggested by Temkin [4]

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

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.

Ammonia synthesis II

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

$$Q\rho\hat{C}_P \frac{dT}{dV} = -\Delta H_R r + \dot{q} \quad (6.55)$$

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

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

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Ammonia synthesis III

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
$\gamma = \frac{2\pi R U^\circ}{Q\rho\hat{C}_P}$	0.5	1/m
$\beta = \frac{\Delta H_R A_c}{Q\rho\hat{C}_P}$	-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 ammonia example

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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

$$Q_a \rho_a \hat{C}_{P_a} \frac{dT_a}{dV_a} = -\dot{q} \quad (6.56)$$

$$T_a(0) = T_{af}$$

in which the subscript a represents the fluid in the feed-heating section. Notice the heat terms are of opposite signs in Equations 6.56 and 6.55. If we assume the fluid properties do not change significantly over the temperature range of interest, and switch the direction of integration in Equation 6.56 using $dV_a = -dV$, we obtain

$$Q \rho \hat{C}_P \frac{dT_a}{dV} = \dot{q} \quad (6.58)$$

$$T_a(V_R) = T_{af}$$

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 $z = 0$, $T(0) = T_a(0)$.

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Ammonia synthesis V

Combining these balances and boundary conditions and converting to reactor length in place of volume gives the model

$\frac{dN_A}{dz} = 2A_c r$	$N_A(0) = N_{Af}$	(6.59)
$\frac{dT}{dz} = -\beta r + \gamma(T_a - T)$	$T(0) = T_a(0)$	
$\frac{dT_a}{dz} = \gamma(T_a - T)$	$T_a(l) = T_{af}$	

in which

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

Equation 6.59 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. \square

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Solution I

Figure 6.38 shows the results for the parameter values listed in Table 6.6, which are based on those used by van Heerden [6].

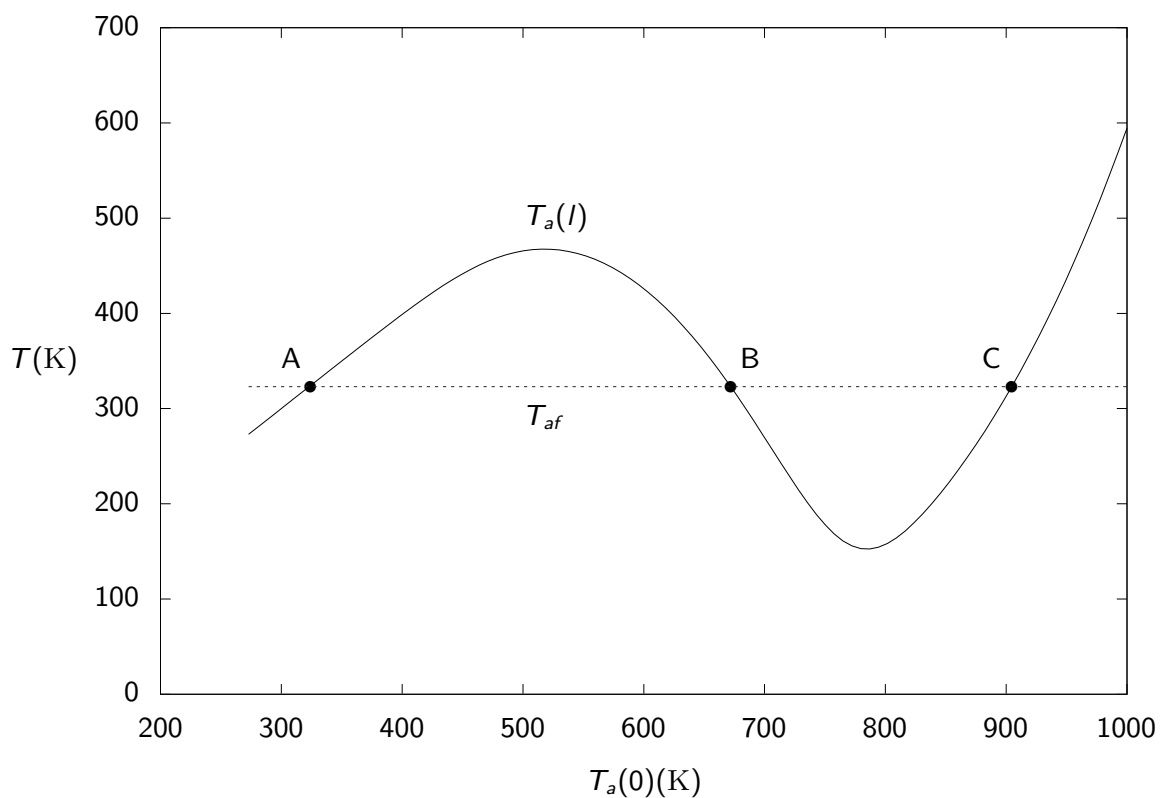
For given values of $T_a(0)$, we solve the initial-value problem, Equation 6.59, and plot the resulting $T_a(V_R)$ as the solid line in Figure 6.38.

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.

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Solution II



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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).

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.

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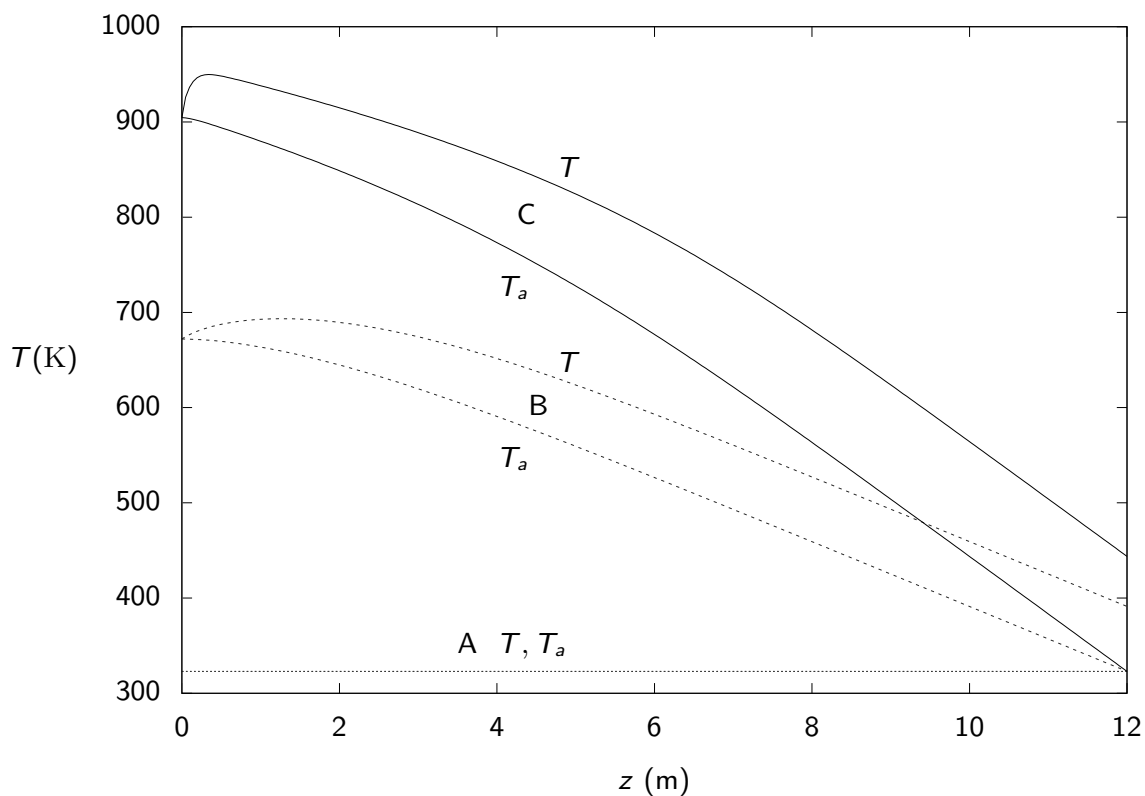


Figure 6.39: Reactor and coolant temperature profiles versus reactor length; lower (A), unstable middle (B), and upper (C) steady states.

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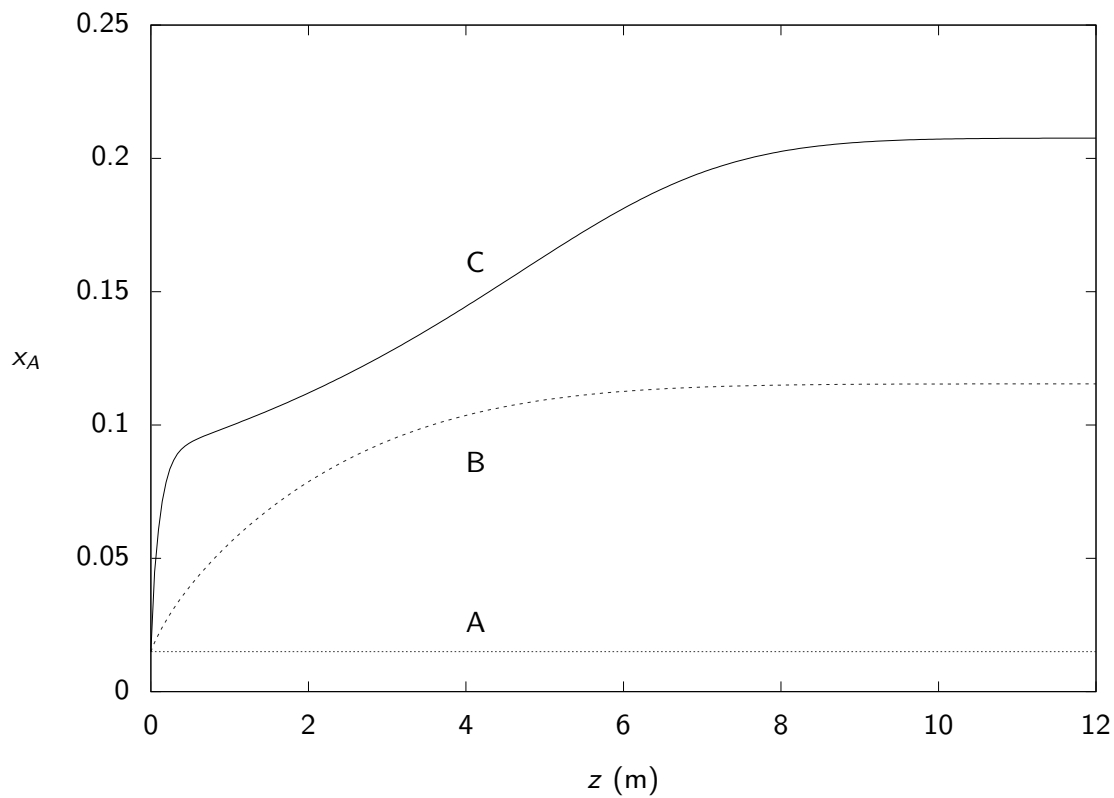


Figure 6.40: Ammonia mole fraction versus reactor length; lower (A), unstable middle (B), and upper (C) steady states.

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 energy balance.
- Hopefully these tables will help you to choose an appropriate energy balance.

Neglect kinetic and potential energies

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

Neglect shaft work

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

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

Single phase

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha T V_R \frac{dP}{dt} + \sum_j \bar{H}_j \frac{dn_j}{dt} = \dot{Q}$$

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

a. Incompressible-fluid or constant-pressure reactor

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

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b. Constant-volume reactor

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

b.1 Constant-volume reactor, ideal gas

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

Table 6.7: Energy balances for the batch reactor.

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Neglect kinetic and potential energies

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

Neglect shaft work

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

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

Single phase

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha TV_R \frac{dP}{dt} + \sum_j \bar{H}_j \frac{dn_j}{dt} = Q_f \rho_f \hat{H}_f - Q_p \hat{H} + \dot{Q}$$

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha TV_R \frac{dP}{dt} = - \sum_i \Delta H_{Ri} r_i V_R + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j) + \dot{Q}$$

a. Incompressible-fluid or constant-pressure reactor

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

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b. Constant-volume reactor

$$V_R \rho \hat{C}_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - \alpha TV_R \sum_j \nu_{ij} P_{nj}) r_i V_R + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j) + \alpha TV_R \sum_j P_{nj} (c_{jf} Q_f - c_j Q) + \dot{Q}$$

b.1 Constant-volume reactor, ideal gas

$$V_R \rho \hat{C}_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - RT \bar{\nu}_i) r_i V_R + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j) + RT \sum_j (c_{jf} Q_f - c_j Q) + \dot{Q}$$

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

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

Table 6.8: Energy balances for the CSTR.

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Neglect kinetic and potential energies

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

Neglect shaft work

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

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

Single phase

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha TV_R \frac{dP}{dt} + \sum_j \bar{H}_j \frac{dn_j}{dt} = Q_f \rho_f \hat{H}_f + \dot{Q}$$

$$V_R \rho \hat{C}_P \frac{dT}{dt} - \alpha TV_R \frac{dP}{dt} = - \sum_i \Delta H_{Ri} r_i V_R + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j) + \dot{Q}$$

a. Incompressible-fluid or constant-pressure reactor

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

a.1 Constant \hat{C}_P

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

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

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Neglect kinetic and potential energies and shaft work

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

Heat transfer with an overall heat-transfer coefficient

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

Steady state

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

Single phase

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

a. Neglect pressure drop, or ideal gas

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

b. Incompressible fluid

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

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

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- 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 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.

Notation I

A	heat transfer area
A_c	reactor tube cross-sectional area
A_i	preexponential factor for rate constant i
c_j	concentration of species j
c_{jf}	feed concentration of species j
c_{js}	steady-state concentration of species j
c_{j0}	initial concentration of species j
C_P	constant-pressure heat capacity
\bar{C}_P	partial molar heat capacity
C_{P_s}	heat capacity per volume
\hat{C}_P	constant-pressure heat capacity per mass
\hat{C}_V	constant-volume heat capacity per mass
ΔC_P	heat capacity change on reaction, $\Delta C_P = \sum_j \nu_j \bar{C}_P$
E_i	activation energy for rate constant i
E_k	total energy of stream k
\hat{E}_k	total energy per mass of stream k
ΔG°	Gibbs energy change on reaction at standard conditions
\bar{H}_j	partial molar enthalpy
\hat{H}	enthalpy per unit mass
ΔH_{Ri}	enthalpy change on reaction, $\Delta H_{Ri} = \sum_j \nu_{ij} \bar{H}_j$
ΔH°	enthalpy change on reaction at standard conditions
k_i	reaction rate constant for reaction i
k_m	reaction rate constant evaluated at mean temperature T_m
K_i	equilibrium constant for reaction i
\hat{K}	kinetic energy per unit mass
l	tubular reactor length
m_k	total mass flow of stream k

Notation II

n	reaction order
n_j	moles of species j , $V_R c_j$
n_r	number of reactions in the reaction network
n_s	number of species in the reaction network
N_j	molar flow of species j , $Q c_j$
N_{jf}	feed molar flow of species j , $Q c_j$
P	pressure
P_j	partial pressure of component j
P_{n_j}	$P_{n_j} = (\partial P / \partial n_j)_{T, V, n_k}$
\dot{q}	heat transfer rate per volume for tubular reactor, $\dot{q} = \frac{2}{R} U^\circ (T_a - T)$
Q	volumetric flowrate
Q_f	feed volumetric flowrate
\dot{Q}	heat transfer rate to reactor, usually modeled as $\dot{Q} = U^\circ A (T_a - T)$
r_i	reaction rate for i th reaction
r_{tot}	total reaction rate, $\sum_i r_i$
R	gas constant
R_j	production rate for j th species
t	time
T	temperature
T_a	temperature of heat transfer medium
T_m	mean temperature at which k is evaluated
U°	overall heat transfer coefficient
\hat{U}	internal energy per mass
v_k	velocity of stream k
V	reactor volume variable
\bar{V}_j	partial molar volume of species j
V_j°	specific molar volume of species j

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Notation III

V_R	reactor volume
ΔV_i	change in volume upon reaction i , $\sum_j \nu_{ij} \bar{V}_j$
\dot{W}	rate work is done on the system
x_j	number of molecules of species j in a stochastic simulation
x_j	molar conversion of species j
y_j	mole fraction of gas-phase species j
z	reactor length variable
α	coefficient of expansion of the mixture, $\alpha = (1/V)(\partial V / \partial T)_{P, n_j}$
ε_i	extent of reaction i
τ	reactor residence time, $\tau = V_R / Q_f$
ν_{ij}	stoichiometric coefficient for species j in reaction i
$\bar{\nu}_i$	$\sum_j \nu_{ij}$
ρ	mass density
ρ_k	mass density of stream k
$\hat{\phi}$	potential energy per mass

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