

Nonisothermal Reactors

9.1 | The Nature of the Problem

In Chapter 3, the isothermal material balances for various ideal reactors were derived (see Table 3.5.1 for a summary). Although isothermal conditions are most useful for the measurement of kinetic data, real reactor operation is normally nonisothermal. Within the limits of heat exchange, the reactor can operate isothermally (maximum heat exchange) or adiabatically (no heat exchange); recall the limits of reactor behavior given in Table 3.1.1. Between these bounds of heat transfer lies the most common form of reactor operation—the nonisothermal regime (some extent of heat exchange). The three types of reactor operations yield different temperature profiles within the reactor and are illustrated in Figure 9.1.1 for an exothermic reaction.

If a reactor is operated at nonisothermal or adiabatic conditions then the material balance equation must be written with the temperature, T , as a variable. For example with the PFR, the material balance becomes:

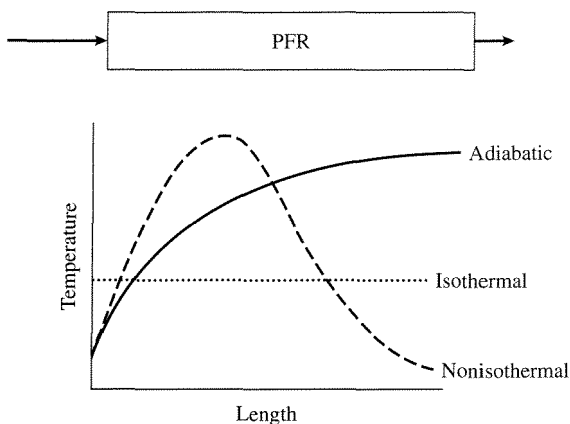
$$\frac{dF_i}{dV_R} = v_i r(F_i, T) \quad (9.1.1)$$

Since the reaction rate expression now contains the independent variable T , the material balance cannot be solved alone. The solution of the material balance equation is only possible by the simultaneous solution of the energy balance. Thus, for nonisothermal reactor descriptions, an energy balance must accompany the material balance.

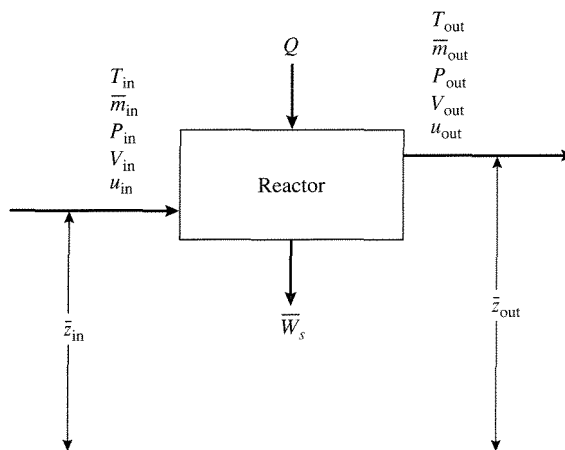
9.2 | Energy Balances

Consider a generalized flow reactor as illustrated in Figure 9.2.1. Applying the first law of thermodynamics to the reactor shown in Figure 9.2.1, the following is obtained:

$$Q - (\bar{W}_s + P_{\text{out}} V_{\text{out}} - P_{\text{in}} V_{\text{in}}) = \bar{U}_{\text{out}} + \bar{m}_{\text{out}}(\bar{z}_{\text{out}}(g/g_c) + \frac{1}{2} u_{\text{out}}^2/g_c) - \bar{U}_{\text{in}} - \bar{m}_{\text{in}}(\bar{z}_{\text{in}}(g/g_c) + \frac{1}{2} u_{\text{in}}^2/g_c) \quad (9.2.1)$$

**Figure 9.1.1 |**

Temperature profiles in a PFR accomplishing an exothermic reaction.

**Figure 9.2.1 |**

Schematic of flow reactor and energy terms.

where \bar{W}_s is “shaft work,” that is, pump or turbine work, \bar{U}_i is the internal energy of stream i , \bar{m}_i is the mass of stream i , P_i is the pressure of stream i , V_i is the volume of mass i , u_i is the velocity of stream i , \bar{z}_i is the height of stream i above a datum plane, and g_c is the gravitational constant, for i denoting either the outlet or inlet stream. For most normal circumstances:

$$\bar{W}_s = 0 \quad (9.2.2)$$

and

$$\bar{m}_{\text{out}} (\bar{z}_{\text{out}}(g/g_c) + \frac{1}{2} u_{\text{out}}^2/g_c) \cong \bar{m}_{\text{in}} (\bar{z}_{\text{in}}(g/g_c) + \frac{1}{2} u_{\text{in}}^2/g_c)$$

Using these assumptions to simplify Equation (9.2.1) yields:

$$Q = (\bar{U}_{\text{out}} + P_{\text{out}} V_{\text{out}}) - (\bar{U}_{\text{in}} + P_{\text{in}} V_{\text{in}}) \quad (9.2.3)$$

Recall that the enthalpy, H , is:

$$H = \bar{U} + PV \quad (9.2.4)$$

Thus, Equation (9.2.3) can be written as:

$$Q = H_{\text{out}} - H_{\text{in}} \quad (9.2.5)$$

However, since it is more typical to deal with rates of energy transfer, \dot{Q} , rather than energy, Q , when dealing with reactors, Equation (9.2.5) can be differentiated with respect to time to give:

$$\dot{Q} = h_{\text{out}} \dot{m}_{\text{out}} - h_{\text{in}} \dot{m}_{\text{in}} \quad (9.2.6)$$

where \dot{Q} is the rate of heat transfer, h_i is the enthalpy per unit mass of stream i , and \dot{m} is the mass flow rate of stream i . Generalizing Equation (9.2.6) to multi-input, multi-output reactors yields a generalized energy balance subject to the assumptions stated above:

$$\dot{Q} = \sum_{\text{outlet streams}} h_{\text{out}} \dot{m}_{\text{out}} - \sum_{\text{inlet streams}} h_{\text{in}} \dot{m}_{\text{in}} \quad (\text{conservation of energy}) \quad (9.2.7)$$

$$0 = \sum_{\text{outlet streams}} \dot{m}_{\text{out}} - \sum_{\text{inlet streams}} \dot{m}_{\text{in}} \quad (\text{conservation of mass}) \quad (9.2.8)$$

Note that the enthalpy includes sensible heat and heat of reaction effects as will be illustrated below.

For a closed reactor (e.g., a batch reactor), the potential and kinetic energy terms in Equation (9.2.1) are not relevant. Additionally, $\bar{W}_s \cong 0$ for most cases (including the work input from the stirring impellers). Since most reactions carried out in closed reactors involve condensed phases, $\Delta(PV)$ is small relative to $\Delta\bar{U}$, and for this case is:

$$Q = \Delta\bar{U} = \bar{U}_{\text{products}} - \bar{U}_{\text{reactants}} \quad (9.2.9)$$

or from Equations (9.2.9) and (9.2.4):

$$Q = \Delta H, PV = \text{constant} \quad (\text{conservation of energy}) \quad (9.2.10)$$

9.3 | Nonisothermal Batch Reactor

Consider the batch reactor schematically illustrated in Figure 9.3.1. Typically, reactants are charged into the reactor from point (I), the temperature of the reactor

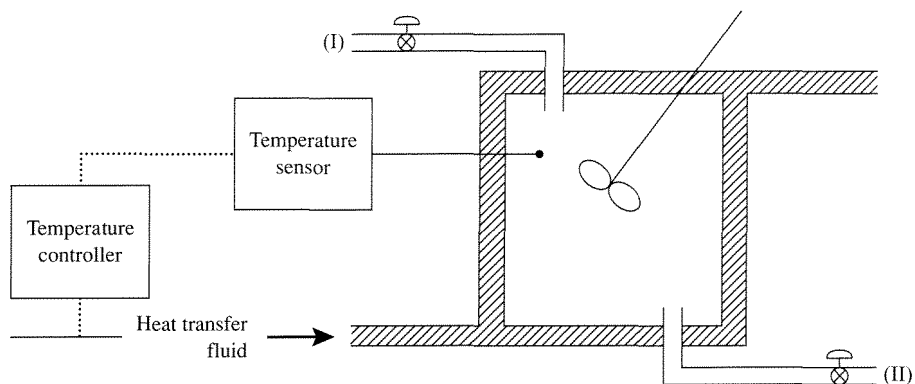


Figure 9.3.1 |
Schematic of a batch reactor.

is increased by elevating the temperature in the heat transfer fluid, a temperature maximum is reached, the reactor is then cooled by decreasing the temperature of the heat transfer fluid and products discharged via point (II).

To describe this process, material and energy balances are required. Recall that the mass balance on a batch reactor can be written as [refer to Equation (3.2.1)]:

$$\frac{1}{V} \frac{dn_i}{dt} = v_i r(n_i, T) \quad (9.3.1)$$

If in the rare case that the reactor is accomplishing a constant pressure gas-phase reaction at nonisothermal conditions:

$$V = V_0 (1 + \varepsilon_i f_i) \left(\frac{T}{T_0} \right) \quad (9.3.2)$$

To solve the mass balance, it must be accompanied by the simultaneous solution of the energy balance (i.e., the solution of Equation (9.2.9)). To do this, Equation (9.2.9) can be written in more convenient forms. Consider that the enthalpy contains both sensible heat and heat of reaction effects. That is to say that Equation (9.2.10) can be written as:

$$\begin{aligned} \text{heat exchange} = & (\text{change in sensible heat effects}) \\ & + (\text{the energy consumed or released} \\ & \text{by reaction}) \end{aligned} \quad (9.3.3)$$

or

$$Q = \int_{T_{\text{initial}}}^{T_{\text{final}}} \Phi_{\text{final}} (\overline{MS} \langle \overline{C}_p \rangle dT + \Delta H_r d\Phi) \quad (9.3.4)$$

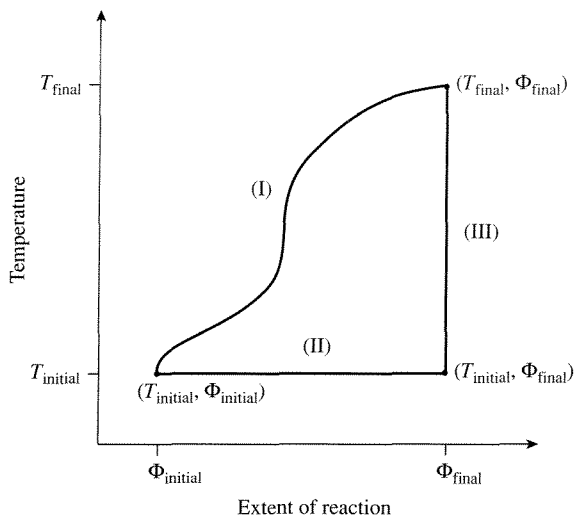


Figure 9.3.2 |
Enthalpy pathways.

where Φ is the extent of reaction (see Chapter 1), ΔH_r is the heat of reaction, \overline{MS} is the total mass of the system, and $\langle \overline{C}_p \rangle$ is an average heat capacity per unit mass for the system. Since enthalpy is a state variable, the solution of the integral in Equation (9.3.4) is path independent. Referring to Figure 9.3.2, a simple way to analyze the integral [pathway (I)] is to allow the reaction to proceed isothermally [pathway (II)] and then evaluate the sensible heat changes using the product composition [pathway (III)]. That is,

$$Q = \Delta H_r|_{T_{\text{initial}}}(\Phi_{\text{final}} - \Phi_{\text{initial}}) + \int_{T_{\text{initial}}}^{T_{\text{final}}} \overline{MS}_{\text{final}} \langle \overline{C}_{p_{\text{final}}} \rangle dT \quad (9.3.5)$$

where a positive value for the heat of reaction denotes an endothermic reaction. Since the reaction-rate expressions normally employ moles of species in their evaluation:

$$\int_{T_{\text{initial}}}^{T_{\text{final}}} \overline{MS}_{\text{final}} \langle \overline{C}_{p_{\text{final}}} \rangle dT = \int_{T_{\text{initial}}}^{T_{\text{final}}} \sum_i (n_i C_{p_i}) dT \quad (9.3.6)$$

where n_i is the moles of species i , and C_{p_i} is the molar heat capacity of species i . Note also that the heat exchange is the integral over time of the heat transfer rate, that is,

$$Q = \int \dot{Q} dt = \int UA_H (T^* - T) dt \quad (9.3.7)$$

where U is an overall heat transfer coefficient, A_H is the heat transfer area, and T^* is the reference temperature. Combining Equations (9.3.7), (9.3.6), and (9.3.5)

and recalling the definition of the extent of reaction in terms of the fractional conversion [Equation (1.2.10)] gives:

$$\int_0^t UA_H (T^* - T) d\bar{t} = \frac{-\Delta H_r|_{T^0}}{v_\ell} n_\ell^0 f_\ell + \sum_i \left(n_i \int_{T_{\text{initial}}}^{T_{\text{final}}} C_{p_i} dT \right) \quad (9.3.8)$$

or in differential form:

$$UA_H (T^* - T) = \frac{-\Delta H_r|_{T^0}}{v_\ell} n_\ell^0 \frac{df_\ell}{dt} + \sum_i (n_i C_{p_i}) \frac{dT}{dt} \quad (9.3.9)$$

Notice that [see Equations (1.2.10) and (1.3.2)]:

$$\frac{n_\ell^0}{-v_\ell} \frac{df_\ell}{dt} = \frac{d\Phi}{dt} = rV \quad (9.3.10)$$

Using Equation (9.3.10) in Equation (9.3.9) yields:

$$UA_H (T^* - T) = \Delta H_r|_{T^0} rV + \sum_i (n_i C_{p_i}) \frac{dT}{dt} \quad (9.3.11)$$

Equations (9.3.11), (9.3.9), and (9.3.8) each define the energy balance for a batch reactor.

EXAMPLE 9.3.1

Show that the general energy balance, Equation (9.3.9), can simplify to an appropriate form for either adiabatic or isothermal reactor operation.

■ Answer

For adiabatic operation there is no heat transfer to the surroundings (i.e., $U = 0$). For this case, Equation (9.3.9) can be written as:

$$0 = \frac{-\Delta H_r|_{T^0}}{v_\ell} n_\ell^0 \frac{df_\ell}{dt} + \sum_i (n_i C_{p_i}) \frac{dT}{dt}$$

or when integrated as:

$$T = T^0 + \frac{\Delta H_r|_{T^0} n_\ell^0 f_\ell}{v_\ell \sum_i (n_i C_{p_i})} \quad (9.3.12)$$

If the reactor is operated at isothermal conditions, then no sensible heat effects occur and Equation (9.3.9) becomes:

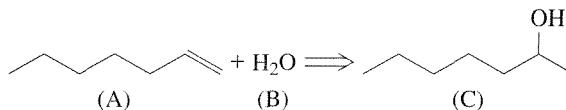
$$UA_H (T^* - T^0) = \frac{-\Delta H_r|_{T^0}}{v_\ell} n_\ell^0 \frac{df_\ell}{dt} \quad (9.3.13)$$

The description of the nonisothermal batch reactor then involves Equation (9.3.1) and either Equation (9.3.9) or (9.3.11) for nonisothermal operation or Equation (9.3.12)

for adiabatic operation. Notice that for adiabatic conditions, Equation (9.3.12) provides a relationship between T and f_t . Insertion of Equation (9.3.12) into Equation (9.3.1) allows for direct solution of the mass balance.

EXAMPLE 9.3.2

The hydration of 1-hexene to 2-hexanol is accomplished in an adiabatic batch reactor:



The reactor is charged with 1000 kg of a 10 wt. % H_2SO_4 solution and 200 kg of 1-hexene at 300 K. Assuming that the heat capacities for the reactants and products do not vary with temperature, the heat of reaction does not vary with temperature, and the presence of H_2SO_4 is ignored in the calculation of the heat capacity, determine the time required to achieve 50 percent conversion and the reactor temperature at that point.

Data:

| | C_p (cal/(mol·K)) | ΔH_f^0 (kcal/mol) |
|----------------------|---------------------|---------------------------|
| 1-hexene | 43.8 | -10.0 |
| H_2O | 16.8 | -68.0 |
| 2-hexanol | 54.0 | -82.0 |

reaction rate constant: $k = 10^4 \exp[-10^4/(R_s T)] \text{ (s}^{-1}\text{)}$

■ Answer

The material balance on the batch reactor is:

$$\frac{dC_A}{dt} = -kC_A$$

or

$$\frac{df_A}{dt} = k(1 - f_A)$$

since the reaction is first-order (units on k and large excess of water; 1-hexene is the limiting reagent). The energy balance is:

$$T = T^0 + \frac{\Delta H_r|_{T^0} n_t^0 f_t}{v_t \sum_i (n_i C_{p_i})}$$

where $v_t = -1$. In order to calculate the heat of reaction, the standard heats of formation can be used as follows:

$$\Delta H_r^0 = -82 + 68 + 10 = -4 \text{ kcal/mol}$$

Thus, the energy balance equation can be written:

$$T = T^0 + \frac{(4000) n_A^0 f_A}{n_A^0 (1 - f_A) C_{p_A} + n_A^0 (\bar{M} - f_A) C_{p_B} + n_A^0 f_A C_{p_C}}$$

where

$$\bar{M} = n_B^0 / n_A^0$$

The values of n_A^0 and n_B^0 are:

$$n_A^0 = (2 \times 10^5 \text{ g})(1 \text{ mol}/84 \text{ g}) = 2381 \text{ mol}$$

$$n_B^0 = (9 \times 10^5 \text{ g})(1 \text{ mol}/18 \text{ g}) = 50000 \text{ mol}$$

so that:

$$n_B^0 / n_A^0 = 21$$

By placing the values for n_A^0 , \bar{M} , T^0 , and the C_p into the energy balance, the result is:

$$T = 300 + \frac{4000 f_A}{421.8 - 7.8 f_A}$$

The material balance equation is then solved with $k(T)$ being first converted to $k(f_A)$ by substitution of the energy balance for T :

$$k = 10^4 \exp \left[\frac{-10^4}{R_g \left(300 + \frac{4000 f_A}{421.8 - 7.8 f_A} \right)} \right]$$

The material balance equation must be solved numerically to give $t = 1111 \text{ s}$ or 18.52 min . The reactor temperature at this point is obtained directly from the energy balance with $f_A = 0.5$ to give $T = 304.8 \text{ K}$.

EXAMPLE 9.3.3

Consider accomplishing the reaction $A + B \Rightarrow C$ in a nonisothermal batch reactor. The reaction occurs in the liquid phase. Find the time necessary to reach 80 percent conversion if the coolant supply is sufficient to maintain the reactor wall at 300 K.

Data:

$$C_A^0 = 0.5 \text{ mol/L}$$

$$\Delta H_r = -15 \text{ kJ/mol}$$

$$C_B^0 = 0.6 \text{ mol/L}$$

$$UA_H = 50 \text{ J/(s-K)}$$

$$C_{p_A} = C_{p_B} = 65 \text{ J/(mol-K)}$$

$$C_{p_C} = 150 \text{ J/(mol-K)}$$

$$n_A^0 = 100 \text{ mol}$$

$$k = 5 \times 10^{-3} \exp \left[\frac{20000 \text{ J/mol}}{R_g} \left(\frac{1}{300} - \frac{1}{T} \right) \right] \text{ (L/mol/s)}$$

■ Answer

The material balance for the batch reactor is:

$$\frac{df_A}{dt} = kC_A^0(1 - f_A)(1.2 - f_A)$$

The energy balance can be written as:

$$UA_H(T^* - T) = \Delta H_r n_A^0 \frac{df_A}{dt} + [n_A^0(1 - f_A)C_{p_A} + n_A^0(1.2 - f_A)C_{p_B} + n_A^0 f_A C_{p_C}] \frac{dT}{dt}$$

The material and energy balance equations must be solved simultaneously. A convenient form for solution by numerical techniques is:

$$\begin{aligned} \frac{df_A}{dt} &= g(T, f_A) = k(T)C_A^0(1 - f_A)(1.2 - f_A) \\ \frac{dT}{dt} &= \frac{UA_H(300 - T) - \Delta H_r n_A^0 g(T, f_A)}{n_A^0(1 - f_A)C_{p_A} + n_A^0(1.2 - f_A)C_{p_B} + n_A^0 f_A C_{p_C}} \end{aligned}$$

with $f_A = 0$ and $T = 300$ K at $t = 0$. The results are shown in Figure 9.3.3. From the data given in Figure 9.3.3, it takes 462 s to reach a fractional conversion of 0.8. Additionally, the final temperature is 332 K. Notice that the final temperature is not the maximum temperature achieved during the reaction, in contrast to adiabatic operation.

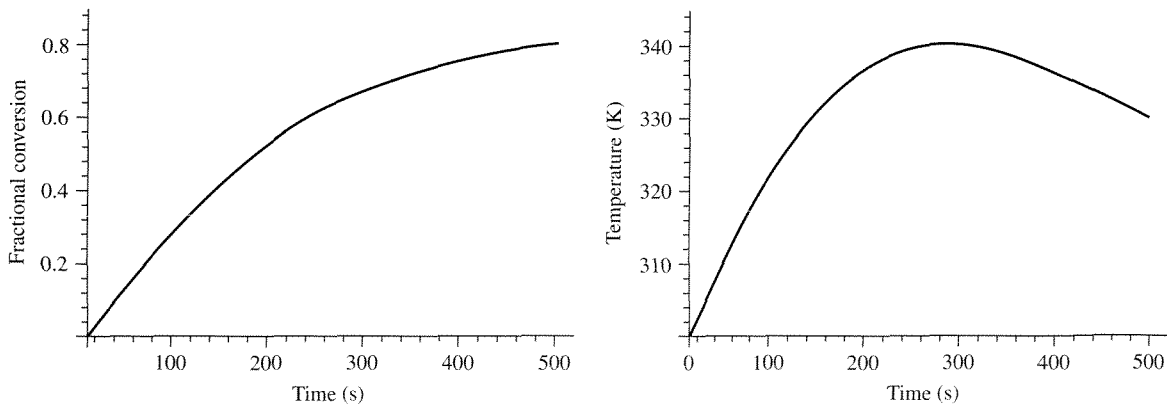


Figure 9.3.3 | Fractional conversion and temperature profiles for the reactor described in Example 9.3.3.

VIGNETTE 9.3.1

M. Kladko [*CHEMTECH*, **1** (1971) 141] presented an interesting case study of performing a liquid-phase, exothermic isomerization reaction. In a 50 gal steam-heated reactor, the reaction of $A \rightarrow B$ was adequately conducted with a 1:1 ratio of A to solvent. However, when scaling-up to a 750 gal glass-lined reactor with a reactant-to-solvent ratio of 2:1, the batch exothermed violently and the reaction ran out of control. The batch erupted through a safety valve and vented. Thus, the effects of the ratio of heat transfer area to reactor volume are nicely demonstrated in this case study. For small vessels the ratio of heat transfer area to reaction volume is higher than for larger vessels and thus the exothermic heat of reaction more efficiently removed.

The analysis of this problem led to the solution illustrated below. A reactor was constructed as a semibatch reactor (solvent initially charged into the reactor and reactant fed over time) and a heating and cooling cycle employed (see Figure 9.3.4). The reactor was operated and the results are shown in Figures 9.3.5–9.3.7.

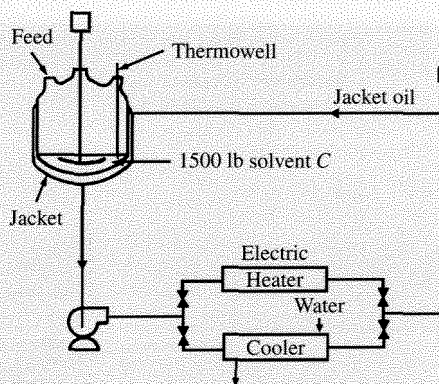


Figure 9.3.4 | Plant installation for “semibatch” isomerization showing heating/cooling circuits. [Adapted from “The Case of a Real Engineering Design Problem” by M. Kladko, *CHEMTECH* (now *Chemical Innovation*), **1** (1971) 141, with permission of the author and the American Chemical Society, copyright 1971.]

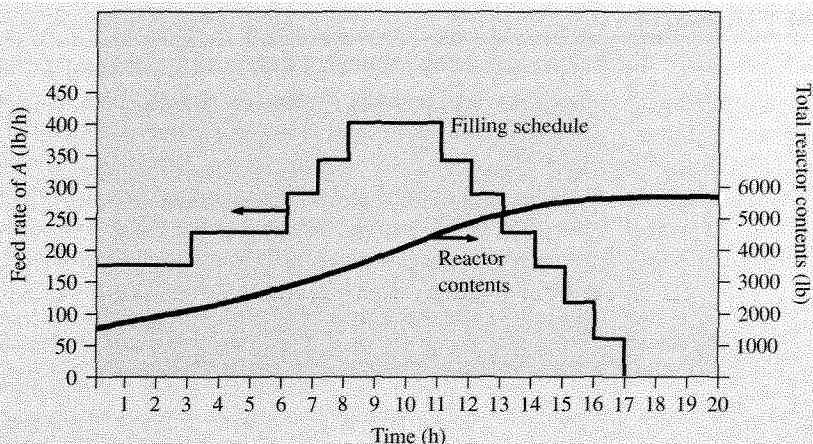


Figure 9.3.5 | Reactor filling schedule and total contents versus time for “semibatch” operation. [Adapted from “The Case of a Real Engineering Design Problem” by M. Kladko, *CHEMTECH* (now *Chemical Innovation*), **1** (1971) 141, with permission of the author and the American Chemical Society, copyright 1971.]

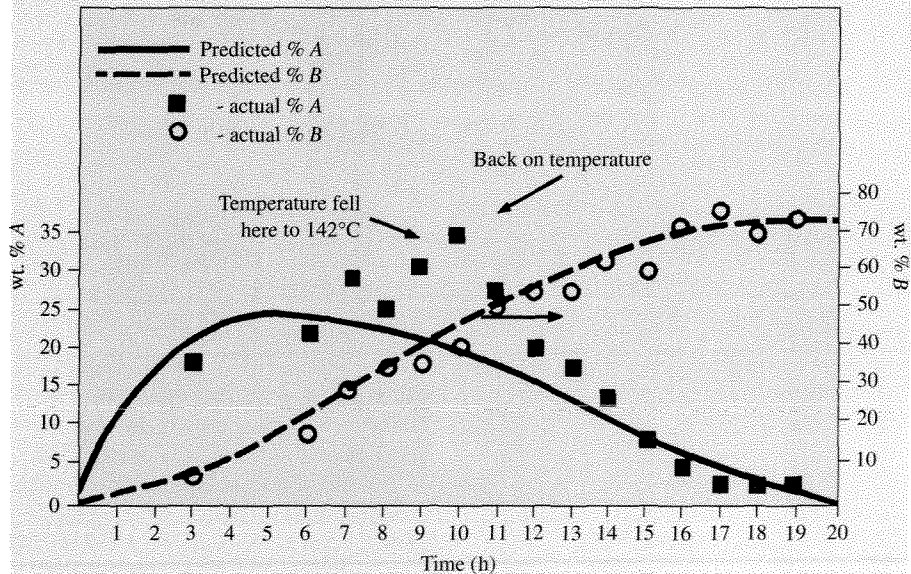


Figure 9.3.6 | Predicted and actual percent A and B versus time. [Adapted from “The Case of a Real Engineering Design Problem” by M. Kladko, *CHEMTECH* (now *Chemical Innovation*), **1** (1971) 141, with permission of the author and the American Chemical Society, copyright 1971.]

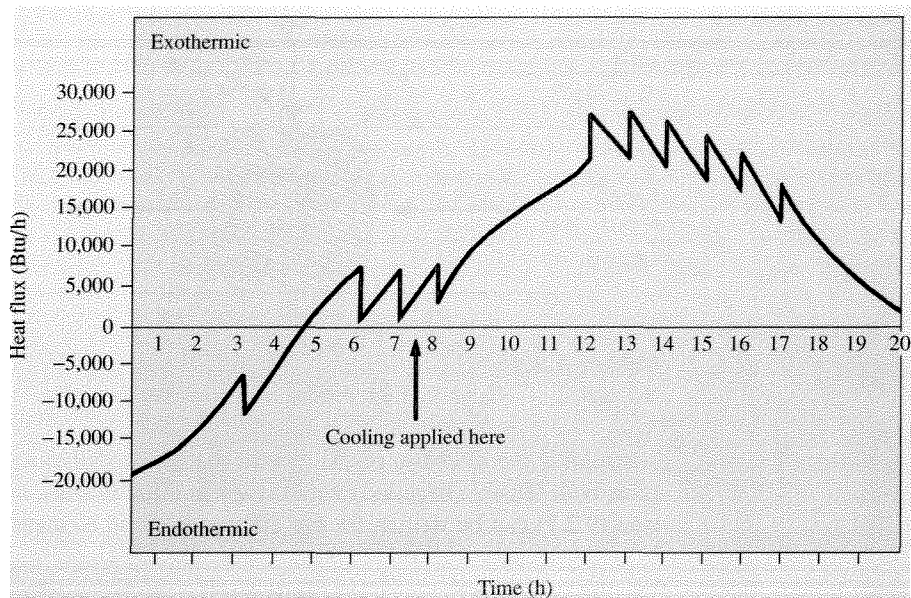


Figure 9.3.7 | Heat flux versus time. [Adapted from “The Case of a Real Engineering Design Problem” by M. Kladko, *CHEMTECH* (now *Chemical Innovation*), **1** (1971) 141, with permission of the author and the American Chemical Society, copyright 1971.]

9.4 | Nonisothermal Plug Flow Reactor

Consider a PFR operating at nonisothermal conditions (refer to Figure 9.4.1). To describe the reactor performance, the material balance, Equation (9.1.1), must be solved simultaneously with the energy balance, Equation (9.2.7). Assuming that the PFR is a tubular reactor of constant cross-sectional area and that T and C_i do not vary over the radial direction of the tube, the heat transfer rate \dot{Q} can be written for a differential section of reactor volume as (see Figure 9.4.1):

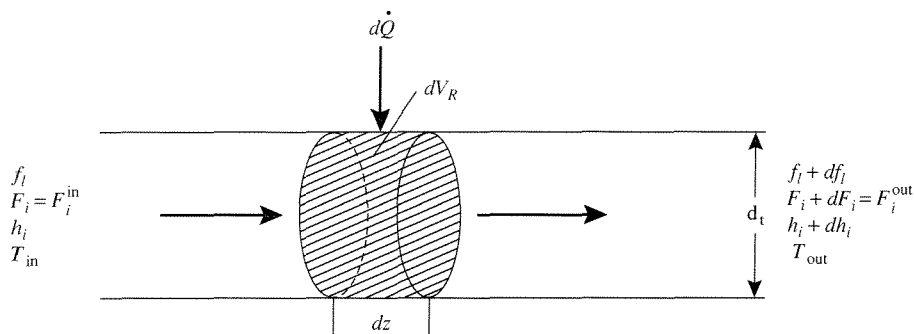
$$d\dot{Q} = U(T^* - T)dA_H = U(T^* - T) \frac{4}{d_i} dV_R \quad (9.4.1)$$

since

$$dA_H = \pi d_i dz \quad (\text{differential area for heat transfer})$$

and

$$dV_R = \frac{\pi d_i^2}{4} dz \quad (\text{differential reactor volume})$$

**Figure 9.4.1 |**

Schematic of differential fluid volume in a nonisothermal PFR.

where d_t is the diameter of the tubular reactor. Recall again that the enthalpy contains both sensible heat and heat of reaction effects. Thus, the energy balance Equation (9.2.7) can be written for the differential fluid element of the PFR as:

$$d\dot{Q} = \sum_i \left(F_i^{\text{out}} \int_{T^0}^{T_{\text{out}}} C_{p_i} dT \right) - \sum_i \left(F_i^{\text{in}} \int_{T^0}^{T_{\text{in}}} C_{p_i} dT \right) - \frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0 df_\ell \quad (9.4.2)$$

where the heat of reaction is evaluated at a reference temperature T^0 and C_{p_i} is the molar heat capacity of species i . Normally, T^0 is taken as the reactor entrance temperature.

EXAMPLE 9.4.1

Show that the general energy balance, Equation (9.4.2), can simplify to an appropriate form for either adiabatic or isothermal reactor operation.

■ Answer

For adiabatic operation $d\dot{Q} = 0$. Thus, Equation (9.4.2) simplifies to:

$$\sum_i \left(F_i^{\text{out}} \int_{T^0}^{T_{\text{out}}} C_{p_i} dT \right) - \sum_i \left(F_i^{\text{in}} \int_{T^0}^{T_{\text{in}}} C_{p_i} dT \right) = \frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0 df_\ell \quad (9.4.3)$$

If T^0 is the temperature at the reactor entrance and the conversion is zero at this point, then Equation (9.4.3) can be written for any point in the PFR as:

$$\sum_i F_i \int_{T^0}^T C_{p_i} dT = \frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0 f_\ell \quad (9.4.4)$$

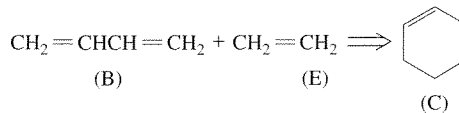
Equation (9.4.4) relates the conversion to the temperature for an adiabatic PFR. If the reactor is operated isothermally, then:

$$d\dot{Q} = - \frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0 df_\ell \quad (9.4.5)$$

EXAMPLE 9.4.2

(From C. G. Hill, *An Introduction to Chemical Engineering Kinetics and Reactor Design*, Wiley, 1977, pp. 362–364.)

Butadiene and ethylene can be reacted together to form cyclohexene as follows:



If equimolar butadiene and ethylene at 450°C and 1 atm are fed to a PFR operating adiabatically, what is the space time necessary to reach a fractional conversion of 0.10?

Data:

$$k = 10^{7.5} \exp[-27,500/(R_g T)] \text{ L/mol/s}$$

$$\Delta H_r = -30000 \text{ cal/mol}$$

$$C_{p_B} = 36.8 \text{ cal/mol/K}$$

$$C_{p_E} = 20.2 \text{ cal/mol/K}$$

$$C_{p_C} = 59.5 \text{ cal/mol/K}$$

■ Answer

Assume that each C_{p_i} is not a strong function of temperature over the temperature range obtained within the PFR (i.e., each is not a function of T). The material and energy balance equations are:

$$\frac{dF_B}{dV_R} = -kC_B^2 = -k(C_B^0)^2 \left[\frac{1-f_B}{1+\varepsilon_B f_B} \right]^2 \left(\frac{T^0}{T} \right)^2$$

and

$$\sum_i F_i \int_{T^0}^T C_{p_i} dT = \frac{\Delta H_r|_{T^0}}{v_B} F_B^0 f_B$$

$$\text{Since } F_B = F_B^0 (1 - f_B) = C_B v:$$

$$\frac{dF_B}{dV_R} = -F_B^0 \frac{df_B}{dV_R} = -\frac{F_B^0}{v_0} \frac{df_B}{d(V_R/v_0)} = -C_B^0 \frac{df_B}{d\tau}$$

Thus, the material balance can be written as:

$$\frac{df_B}{d\tau} = kC_B^0 \left[\frac{1-f_B}{1-0.5f_B} \right]^2 \left(\frac{T^0}{T} \right)^2$$

since $\varepsilon_B = 0.5 \left[\frac{1-2}{1-1} \right] = -0.5$. Now for the energy balance,

$$\sum_i F_i \int_{T^0}^T C_{p_i} dT = \sum_i F_i C_{p_i} \int_{T^0}^T dT \quad \text{since } C_{p_i} \neq C_{p_i}(T)$$

Thus,

$$\sum_i F_i C_{p_i} \int_{T^0}^T dT = F_B^0 (1 - f_B) (36.8) (T - T^0) + F_B^0 (1 - f_B) (20.2) (T - T^0) \\ + F_B^0 f_B (59.5) (T - T^0)$$

or

$$\sum_i F_i C_{p_i} \int_{T^0}^T dT = (57 + 2.5 f_B) F_B^0 (T - T^0)$$

The energy balance then becomes:

$$(57 + 2.5 f_B) F_B^0 (T - T^0) = \frac{(-30,000)}{(-1)} F_B^0 f_B$$

or

$$T = 723 + \frac{(30,000) f_B}{57 + 2.5 f_B}$$

The solution of the material balance equation:

$$\tau = \int_0^{0.10} \frac{df_B}{k C_B^0 \left[\frac{1 - f_B}{1 - 0.5 f_B} \right]^2 \left(\frac{723}{T} \right)^2}$$

with T from the energy balance gives a value of $\tau = 47.1$ s. Additionally, the exit temperature is 775 K.

VIGNETTE 9.4.1

Over the first year of a child's life in the United States, the child receives vaccines for immunization against hepatitis B, diphtheria, tetanus, pertussis (whooping cough), haemophilus influenzae, polio, measles, mumps, rubella, and chicken pox. Numerous vaccines are based on viruses in some form. The growth of viral-based vaccines typically occurs in bioreactors that are just tanks. However, when the aqueous medium that is used to grow the viral products is to be expelled, it must be "decontaminated." To do so, the fluid is mixed with H_2O_2 and flows through a tubular reactor. The H_2O_2 is used to kill any living material in the tubular reactor. Thus, τ must be fixed to a sufficiently long time to assure complete death of all living matter prior to exiting the reactor. The temperature of this reactor must be maintained below a critical value so that the hydrogen peroxide does not decompose to form dioxygen. Thus, the material balance for the reactor must be solved simultaneously with the energy balance as illustrated in Section 9.4 to properly define the correct τ for complete decontamination.

The energy balance for the PFR can also be written as follows by combining Equations (9.4.1) and (9.4.2):

$$U(T^* - T) \frac{4}{d_t} dV_R = \sum_i F_i C_{p_i} dT - \frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0 df_\ell \quad (9.4.6)$$

or

$$U(T^* - T) \frac{4}{d_t} = \sum_i F_i C_{p_i} \frac{dT}{dV_R} - \frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0 \frac{df_\ell}{dV_R} \quad (9.4.7)$$

Using the fact that:

$$F_\ell^0 \frac{df_\ell}{dV_R} = (-v_\ell)r$$

Equation (9.4.7) can be written as:

$$\sum_i F_i C_{p_i} \frac{dT}{dV_R} = (-\Delta H_r|_{T^0})r - U(T - T^*) \frac{4}{d_t} \quad (9.4.8)$$

Thus, the material and energy balances for the PFR can be written as ($F_\ell = C_\ell v = C_\ell \pi d_t^2 u/4$; $dV_R = \pi d_t^2 dz/4$):

$$\left. \begin{aligned} -u \frac{dC_\ell}{dz} &= (-v_\ell)r \\ u\rho\bar{C}_p \frac{dT}{dz} &= (-\Delta H_r|_{T^0})r - \frac{4U}{d_t} (T - T^*) \end{aligned} \right\} \quad (9.4.9)$$

with $C_\ell = C_\ell^0$ and $T = T^0$ at $z = 0$, where u is the superficial linear velocity, ρ is the average density of the fluid, and \bar{C}_p is the average heat capacity per unit mass. Equation (9.4.9) is only applicable when the density of the fluid is not changing in the reactor and when \bar{C}_p is not a function of temperature, since the following relationship is used to obtain Equation (9.4.9):

$$\sum F_i C_{p_i} = v\rho\bar{C}_p \quad (9.4.10)$$

EXAMPLE 9.4.3

A PFR of dimensions $L = 2$ m and $d_t = 0.2$ m is accomplishing a homogeneous reaction. The inlet concentration of the limiting reactant is $C_\ell^0 = 0.3$ kmol/m³ and the inlet temperature is 700 K. Other data are: $-\Delta H_r|_{T^0} = 10^4$ kJ/kmol, $\bar{C}_p = 1$ kJ/(kg·K), $E = 100$ kJ/mol, $\rho = 1.2$ kg/m³, $u = 3$ m/s, and $\bar{A} = 5$ s⁻¹. Calculate the dimensionless concentration ($y = C_\ell/C_\ell^0$) and temperature ($\bar{\theta} = T/T^0$) profiles for adiabatic ($U = 0$) and nonisothermal ($U = 70$ J/(m²·s·K)) operations. (Example adapted from J. Villadsen and M. L. Michelsen, *Solution of Differential Equation Models by Polynomial Approximation*, Prentice-Hall, Englewood Cliffs, 1978, p. 59.)

■ Answer

From the units on \bar{A} , it is clear that the reaction rate is first order. Using Equation (9.4.9) with a first-order reaction rate expression gives:

$$-u \frac{dC_\ell}{dz} = \bar{A} \exp[-E/(R_g T)] C_\ell$$

$$u \rho \bar{C}_p \frac{dT}{dz} = (-\Delta H_r) \bar{A} \exp[-E/(R_g T)] C_\ell - \frac{4U}{d_i} (T - T^0)$$

Let $x = z/L$, $y = C_\ell/C_\ell^0$ and $\bar{\theta} = T/T^0$. Using these dimensionless variables in the material and energy balance relationships yields:

$$\frac{dy}{dx} = -(\bar{D}a)y \exp\left[\gamma\left(1 - \frac{1}{\bar{\theta}}\right)\right]$$

$$\frac{d\bar{\theta}}{dx} = \beta_T(\bar{D}a)y \exp\left[\gamma\left(1 - \frac{1}{\bar{\theta}}\right)\right] - H_w(\bar{\theta} - 1)$$

with $y = 1$ at $x = 0$ and where:

$$\bar{D}a = \frac{L\bar{k}}{u}, \quad \bar{k} = \bar{A} \exp[-E/(R_g T^0)]$$

$$\beta_T = \frac{C_\ell^0 (-\Delta H_r)}{\rho \tau T^0}$$

$$\gamma = \frac{E}{R_g T^0}$$

$$H_w = \frac{4U}{d_i} \left(\frac{L}{\rho \bar{C}_p u} \right)$$

Notice that all the groupings $\bar{D}a$, β_T , γ , and H_w are dimensionless. For adiabatic operation, $H_w = 0$. For this case, the mass balance equation can be multiplied by β_T and added to the energy balance to give:

$$\frac{d}{dx} (\bar{\theta} + \beta_T y) = 0$$

Integration of this equation with $y = \bar{\theta} = 1$ at $x = 0$ leads to:

$$\bar{\theta} = 1 + \beta_T(1 - y) \quad (9.4.11)$$

Equation (9.4.11) is the adiabatic relationship between temperature and conversion in dimensionless form. The mass balance can then be written as:

$$\frac{dy}{dx} = -(\bar{D}a)y \exp\left[\frac{\gamma\beta_T(1 - y)}{1 + \beta_T(1 - y)}\right]$$

with

$$y = 1 \text{ at } x = 0$$

The solution of this differential equation is straightforward and is shown in Figure 9.4.2. For the nonisothermal case, the material and energy balances must be solved simultaneously by

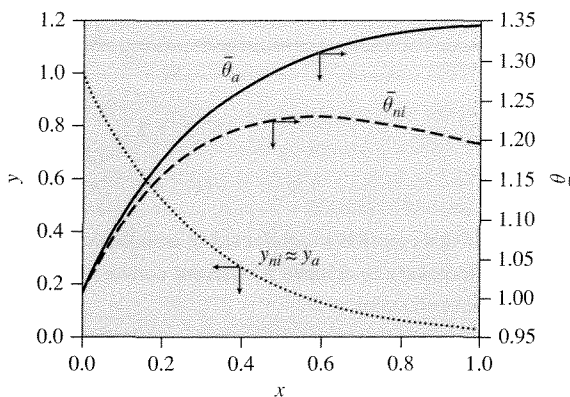


Figure 9.4.2 | Dimensionless concentration and temperature profiles for adiabatic and nonisothermal operation. y_a and $\bar{\theta}_a$ are for adiabatic conditions while y_{ni} and $\bar{\theta}_{ni}$ are for nonisothermal operation.

numerical methods. The nonisothermal results are plotted also in Figure 9.4.2. Notice that there is a maximum in the value of $\bar{\theta}_{ni}$ that occurs at $x = 0.57$ and gives $T = 860$ K. The maximum in the temperature profile from nonisothermal operation is normally denoted as the *hot spot* in the reactor.

9.5 | Temperature Effects in a CSTR

Although the assumption of perfect mixing in the CSTR implies that the reactor contents will be at uniform temperature (and thus the exit stream will be at this temperature), the reactor inlet may not be at the same temperature as the reactor. If this is the case and/or it is necessary to determine the heat transferred to or from the reactor, then an energy balance is required.

The energy balance for a CSTR can be derived from Equation (9.2.7) by again carrying out the reaction isothermally at the inlet temperature and then evaluating sensible heat effects at reactor outlet conditions, that is,

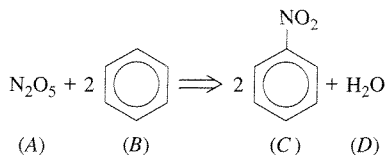
$$\dot{Q} = \frac{F_\ell^0 (\Delta H_r|_{T^0})(f_\ell^f - f_\ell^0)}{(-v_\ell)} + \sum \left(F_i^f \int_{T^0}^{T^f} C_{p_i} dT \right) \quad (9.5.1)$$

where the superscript f denotes the final or outlet conditions. For adiabatic operation, $\dot{Q} = 0$.

EXAMPLE 9.5.1

The nitration of aromatic compounds is a highly exothermic reaction that generally uses catalysts that tend to be corrosive (e.g., $\text{HNO}_3/\text{H}_2\text{SO}_4$). A less corrosive reaction employs N_2O_5

as the nitrating agent as illustrated below:



If this reaction is conducted in an adiabatic CSTR, what is the reactor volume and space time necessary to achieve 35 percent conversion of N_2O_5 ? The reaction rate is first order in A and second order in B.

Data:

$$\begin{array}{ll} \Delta H_r = -370.1 \text{ kJ/mol} & T^0 = 303 \text{ K} \\ C_{p_A} = 84.5 \text{ J/(mol}\cdot\text{K)} & F_A^0 = 10 \text{ mol/min} \\ C_{p_B} = 137 \text{ J/(mol}\cdot\text{K)} & F_B^0 = 30 \text{ mol/min} \\ C_{p_C} = 170 \text{ J/(mol}\cdot\text{K)} & v = 1000 \text{ L/min} \\ C_{p_D} = 75 \text{ J/(mol}\cdot\text{K)} & C_A^0 = 0.01 \text{ mol/L} \end{array}$$

$$k = 0.090 \exp \left[\frac{(40 \text{ kJ/mol})}{R_g} \left(\frac{1}{303} - \frac{1}{T} \right) \right] \quad (\text{L/mol})^2 (\text{min})^{-1}$$

■ Answer

The reaction occurs in the liquid-phase and the concentrations are dilute so that mole change with reaction does not change the overall density of the reacting fluid. Thus,

$$\begin{aligned} C_A &= C_A^0 (1 - f_A), & F_A &= F_A^0 (1 - f_A) \\ C_B &= C_A^0 (3 - 2f_A), & F_B &= F_A^0 (3 - 2f_A) \\ F_C &= 2F_A^0 f_A, & F_D &= F_A^0 f_A \end{aligned}$$

The material balance on the CSTR can be written as:

$$V = \frac{F_A^0 f_A}{k(C_A^0)^3 (1 - f_A)(3 - 2f_A)^2}$$

The energy balance for the adiabatic CSTR is:

$$\begin{aligned} 0 &= \Delta H_r F_A^0 f_A + F_A^0 (1 - f_A) C_{p_A} (T - T^0) + F_A^0 (3 - 2f_A) C_{p_B} (T - T^0) \\ &\quad + 2F_A^0 f_A C_{p_C} (T - T^0) + F_A^0 f_A C_{p_D} (T - T^0) \end{aligned}$$

For $f_A = 0.35$, the energy balance yields $T = 554 \text{ K}$. At 554 K , the value of the rate constant is $k = 119.8 \text{ L}^2/(\text{mol}^2\cdot\text{min})$. Using this value of k in the material balance gives $V = 8,500 \text{ L}$ and thus $\tau = 8.5 \text{ min}$.

EXAMPLE 9.5.2

Consider the aromatic nitration reaction illustrated in Example 9.5.1. Calculate the reactor volume required to reach 35 percent conversion if the reactor is now cooled.

Data:

$$\begin{aligned} UA_H &= 9000 \text{ J}/(\text{min}\cdot\text{K}) \\ T_C^0 &= 323 \text{ K (and is constant)} \\ v &= 100 \text{ L/min} \\ C_A^0 &= 0.10 \text{ mol/L} \end{aligned}$$

All other data are from Example 9.5.1.

■ Answer

The material balance equation remains the same as in Example 9.5.1. The energy balance is now:

$$\begin{aligned} UA_H (T_C^0 - T) &= \Delta H_r F_A^0 f_A + F_A^0 (1 - f_A) C_{pA} (T - T^0) + F_A^0 (3 - 2f_A) C_{pB} (T - T^0) \\ &\quad + 2F_A^0 f_A C_{pC} (T - T^0) + F_A^0 f_A C_{pD} (T - T^0) \end{aligned}$$

when $f_A = 0.35$, the energy balance yields $T = 407 \text{ K}$. At 407 K , the reaction rate constant is $k = 5.20 \text{ L}^2/(\text{mol}^2\cdot\text{min})$. Using this value of k and $C_A^0 = 0.10 \text{ mol/L}$ in the material balance equation gives $V = 196 \text{ L}$.

9.6 | Stability and Sensitivity of Reactors Accomplishing Exothermic Reactions

Consider the CSTR illustrated in Figure 9.6.1. The reactor is accomplishing an exothermic reaction and therefore must transfer heat to a cooling fluid in order to remain at temperature T . Assume that the heat transfer is sufficiently high to maintain the reactor wall temperature at T_c . Therefore,

$$\dot{Q} = \underbrace{UA_H(T - T_c)}_{\text{heat removed from reactor}} = \underbrace{v_c C_{p_c}(T_c - T_c^0)}_{\text{sensible heat change of coolant}} \quad (9.6.1)$$

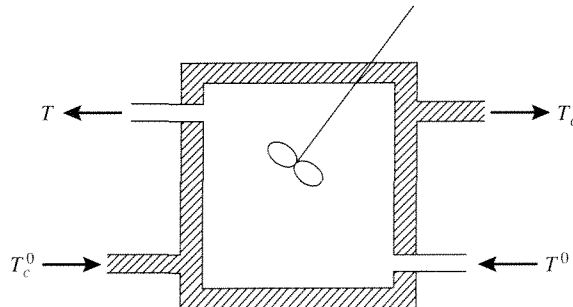


Figure 9.6.1 |

Schematic illustration of a CSTR that is maintained at temperature T by transferring heat to a coolant fluid ($T_c > T_c^0$).

where v_c is the volumetric flow rate of the coolant and C_{p_c} is the heat capacity of the coolant and is not a function of temperature. Solving for T_c and then substituting the expression back into the heat transfer equation yields:

$$\dot{Q} = \frac{UA_H v_c C_{p_c}}{UA_H + v_c C_{p_c}} (T - T_c^0) = \lambda_\lambda (T - T_c^0) \quad (9.6.2)$$

The energy balance on the CSTR can be written as [from Equation (9.5.1) with a first-order reaction rate expression]:

$$\dot{Q} = \frac{\Delta H_r|_{T^0} F_\ell^0 (f_\ell - f_\ell^0)}{(-v_\ell)} + \sum \left(F_i \int_{T^0}^T C_{p_i} dT \right)$$

or since:

$$-v_\ell rV = F_\ell^0 (f_\ell - f_\ell^0) \quad (\text{material balance})$$

as:

$$\dot{Q} = (\Delta H_r|_{T^0}) k C_\ell V + v^p \rho C_p (T - T^0) \quad (\text{first-order reaction rate}) \quad (9.6.3)$$

where v^p is the volumetric flow rate of the product stream and ρ and C_p are the average density and heat capacity of the outlet stream. Rearranging Equation (9.6.3) and substituting Equation (9.6.2) for \dot{Q} gives (note that \dot{Q} is heat removed):

$$\frac{\lambda_\lambda}{v^p \rho C_p} (T_c^0 - T) = \frac{k C_\ell \tau (\Delta H_r|_{T^0})}{\rho C_p} + (T - T^0) \quad (9.6.4)$$

Let:

$$\alpha\alpha_1 = \frac{\lambda_\lambda}{v^p \rho C_p}$$

$$\alpha\alpha_2 = \frac{-k\tau (\Delta H_r|_{T^0})}{\rho C_p}$$

so that Equation (9.6.4) can be written as:

$$(1 + \alpha\alpha_1)T - (T^0 + \alpha\alpha_1 T_c^0) = \alpha\alpha_2 C_\ell \quad (9.6.5)$$

Since:

$$C_\ell = C_\ell^0 / (1 + k\tau)$$

from the solution of the material balance equation, Equation (9.6.5) can be formulated as:

$$(1 + \alpha\alpha_1)T - (T^0 + \alpha\alpha_1 T_c^0) = \frac{\alpha\alpha_2 C_\ell^0}{1 + k\tau} \quad (9.6.6)$$

$$Q_r \text{ (heat removed)} = Q_g \text{ (heat generated)}$$

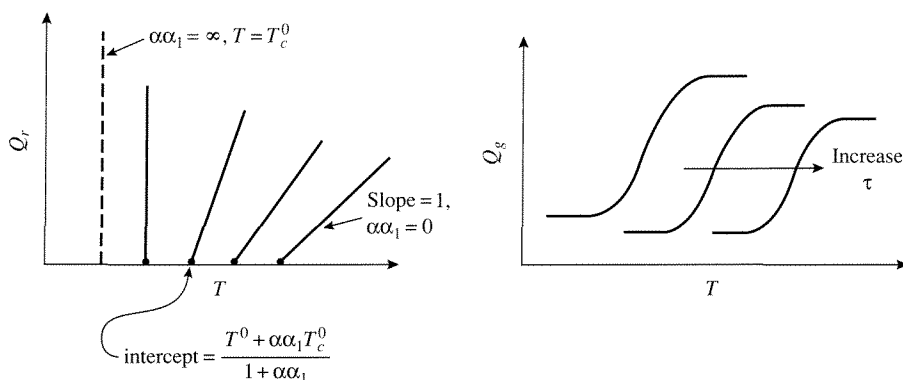


Figure 9.6.2 |
Schematic illustration of Q_r and Q_g as functions of T .

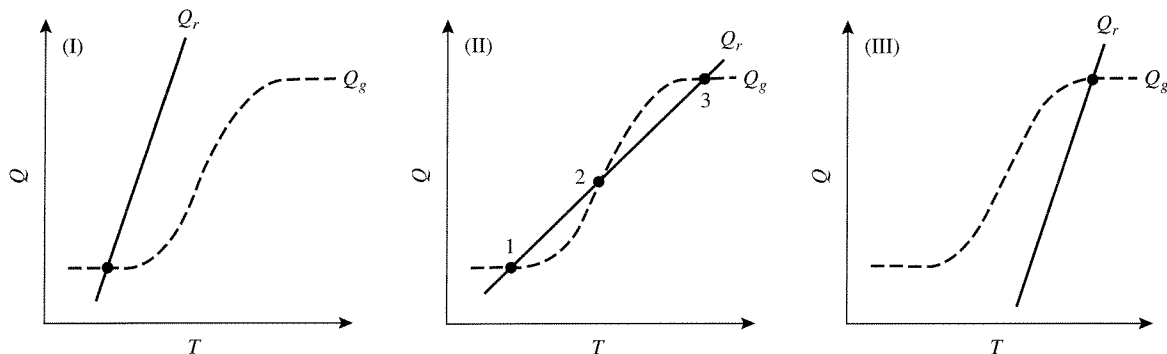


Figure 9.6.3 |
Steady-state solutions to Equation (9.6.3).

If Q_r and Q_g are plotted versus the reaction temperature, T , the results are illustrated in Figure 9.6.2. A solution of Equation (9.6.6) occurs when Q_r equals Q_g , and this can happen as shown in Figure 9.6.3. Notice that for cases (I) and (III) a single solution exists. However, for case (II) three steady-states are possible. An important question of concern with case (II) is whether all three steady-states are stable. This is easy to rationalize as follows. At steady-state 1, if T is increased then $Q_r > Q_g$ so the reactor will return to point 1. Additionally, if T is decreased, $Q_g > Q_r$ so the reactor will also return to point 1 in this case. Thus, steady-state 1 is stable since small perturbations from this position cause the reactor to return to the steady-state. Likewise steady-state 3 is a stable steady-state. However, for steady-state 2, if T is increased, $Q_g > Q_r$ and the reactor will move to position 3. If T is decreased below that of point 2, $Q_r > Q_g$ and the reactor will move to point 1. Therefore, steady-state 2 is unstable. It is important to determine the stability of reactor operation since perturbations from steady-state always occur in a real system. Finally, what determines whether the reactor achieves steady-state 1 or 3 is the start-up of the reactor.

EXAMPLE 9.6.1

Calculate the steady-states for the following reactor configuration. Is there an unstable steady-state?

Data:

$A + B \Rightarrow 2C$ in the liquid phase, $V = 1 \text{ L}$, $k = 33 \times 10^9 \exp [-20,000/(R_g T)] \text{ L}/(\text{mol} \cdot \text{min})$, $-\Delta H_r = 20 \text{ kcal/mol}$, $C_A^0 = 20 \text{ mol/L}$, $C_B^0 = 3 \text{ mol/L}$, $v = 100 \text{ cm}^3/\text{min}$, $T^0 = 17^\circ\text{C}$, $T_c^0 = 87^\circ\text{C}$, $\rho C_p = 650 \text{ cal}/(\text{L} \cdot ^\circ\text{C})$, $U = 0.1 \text{ cal}/(\text{cm}^2 \cdot \text{min} \cdot \text{K})$, and $A_H = 250 \text{ cm}^2$.

■ Answer

The reaction rate expression is:

$$(-v_B)r = kC_A C_B = k(C_B^0)^2 (1 - f_B)(\bar{M} - f_B), \bar{M} = C_A^0/C_B^0$$

giving the following material balance:

$$0 = C_B^0 f_B - \tau k(C_B^0)^2 (1 - f_B)(\bar{M} - f_B)$$

Therefore,

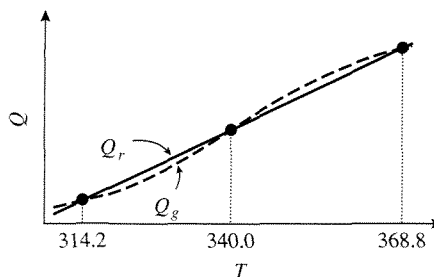
$$Q_r = (1 + \alpha\alpha_1)T - (T^0 + \alpha\alpha_1 T_c^0)$$

$$Q_g = \frac{-k(C_B^0)^2 \tau (\Delta H_r)(1 - f_B)(\bar{M} - f_B)}{\rho C_p}$$

First, solve the material balance equation for f_B (gives two values for f_B —one will have physical meaning) at a particular T and next calculate Q_r and Q_g . A sampling of results is provided below (assume $v_c C_{p_c} \gg UA_H$ for the calculation of Q_r):

| T (K) | f_B | Q_r | Q_g |
|-------|-------|-------|-------|
| 310 | 0.049 | 0.77 | 4.55 |
| 320 | 0.124 | 14.62 | 11.45 |
| 330 | 0.264 | 28.46 | 24.40 |
| 340 | 0.461 | 42.31 | 42.50 |
| 350 | 0.658 | 56.20 | 60.77 |
| 360 | 0.807 | 70.00 | 74.78 |
| 370 | 0.898 | 83.80 | 82.85 |

If these data are plotted, they yield:



Thus, there are three steady-states and they are:

| Steady-state | T (K) | T (°C) | f_B |
|--------------|---------|----------|-------|
| 1 | 314.2 | 41.2 | 0.079 |
| 2 | 340.0 | 67.0 | 0.460 |
| 3 | 368.8 | 95.8 | 0.888 |

Steady-state 2 is unstable. Notice the vast differences in f_B for the three steady-states. Thus, it is clear that attempts by a naïve designer to operate at steady-state 2 would not succeed since the reactor would not settle into this steady-state at all.

In addition to knowing the existence of multiple steady-states and that some may be unstable, it is important to assess how stable the reactor operation is to variations in the processing parameters (i.e., the sensitivity). In the above example for the CSTR, it is expected that the stable steady-states have low sensitivity to variations in the processing parameters, while clearly the unstable steady-state would not.

To provide an example of how the sensitivity may be elucidated, consider a tubular reactor accomplishing an exothermic reaction and operating at nonisothermal conditions. As described in Example 9.4.3, hot spots in the reactor temperature pro-

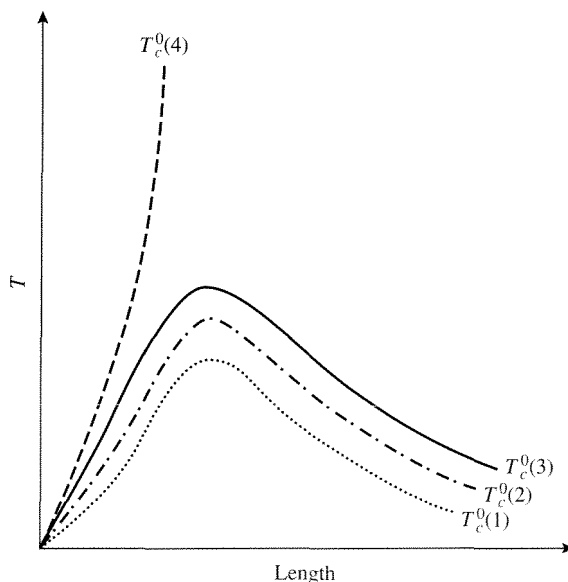


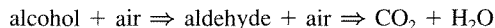
Figure 9.6.4 |

Temperature profiles in a tubular reactor operating nonisothermally and conducting an exothermic reaction. T_c^0 is the temperature of the coolant fluid.

file can occur for this situation. Figure 9.6.4 illustrates what a typical reactor temperature profile would look like. Consider what could happen as the temperature of the coolant fluid, T_c^0 , increases. As T_c^0 becomes warmer $T_c^0(i+1) > T_c^0(i)$, $i = 1, 2, 3$, then less heat is removed from the reactor and the temperature at the reactor hot spot increases in value. Eventually, heat is generated at a sufficiently high rate that it cannot be removed [illustrated for $T_c^0(4)$] such that the hot spot temperature exceeds some physical limit (e.g., phase change of fluid, explosions or fire, the catalyst melts, etc.) and this condition is called *runaway*. Thus, reactor operation close to a runaway point would not be prudent, and determining the sensitivity towards the tendency of runaway a critical factor in the reactor analysis. Several criteria have been developed to assess the sensitivity of reactors; each involves the use of critical assumptions [see, for example, G. F. Froment and K. B. Bischoff, *Chemical Reaction Analysis and Design*, Wiley, New York, 1977, Chapter 1]. Here, an example of how reactor stability can be assessed is illustrated and was provided by J. B. Cropley.

EXAMPLE 9.6.2

A tubular reactor packed with a heterogeneous catalyst is accomplishing an oxidation reaction of an alcohol to an aldehyde. The reactions are:

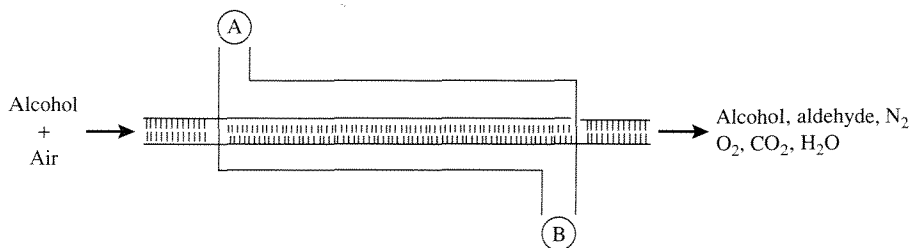


In this series reaction pathway, the desired species is the aldehyde. Since both reactions are exothermic (second reaction is highly exothermic), the reactor is operated nonisothermally. The reactor is a shell-and-tube heat exchanger consisting of 2500 tubes of 1 inch diameter. Should the heat exchanger be operated in a cocurrent or countercurrent fashion in order to provide a greater stabilization against thermal runaway?

■ Answer

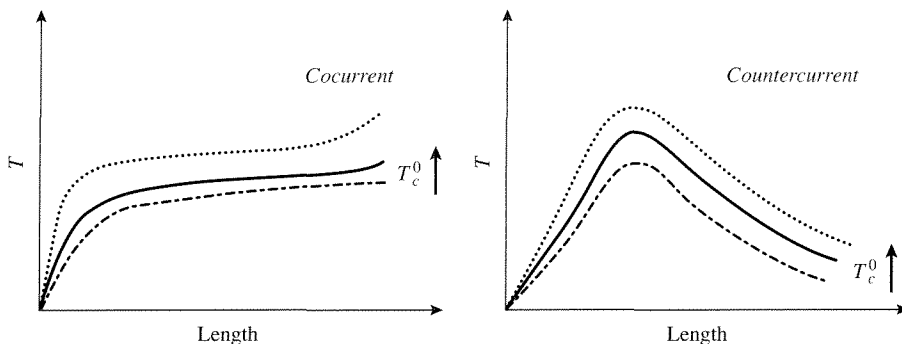
Since this example comes from the simulation of a real reactor, the amount of data necessary to completely describe it is very high. Thus, only the trends observed will be illustrated in order to conserve the length of presentation.

Schematically, the reactor can be viewed as:

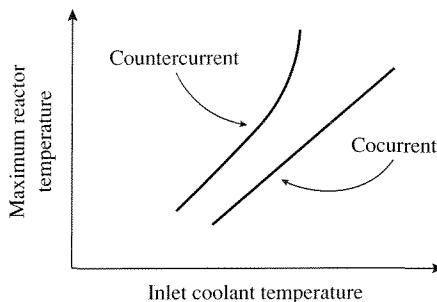


The cooling fluid is fed at point A or at point B for cocurrent and countercurrent operation, respectively. Next, the reactor temperature profiles from the two modes of operation

are illustrated. The three profiles in each graph are for different coolant feed temperatures, T_c^0 . Notice that a hot spot occurs with countercurrent operation. In order to access the sensitivity,



Cropley suggests plotting the maximum temperature in the reactor as a function of the inlet coolant temperature. The results look like:



The slope of the line would be an indication of the reactor stability to variations in the inlet coolant temperature. Clearly, cocurrent operation provides better sensitivity and this conclusion is a general one. The reason for this is that by operating in a cocurrent manner the greatest ability to remove heat [largest $\Delta T (T_{\text{reactor}} - T_{\text{coolant}})$] can occur in the region of highest heat generation within the reactor.

Exercises for Chapter 9

1. Calculate the final temperature and time required to reach 50 percent conversion in the batch reactor described in Example 9.3.2 if the heat of reaction is now -40 kcal/mol. Do you think that this time is achievable in a large reactor system?
2. Find the final temperature and time required to reach 90 percent conversion in the reactor system of Exercise 1.

- Plot the fractional conversion and temperature as a function of time for the batch reactor system described in Example 9.3.3 if the reactor is now adiabatic ($U = 0$). Compare your results to those for the nonisothermal situation given in Figure 9.3.3. How much energy is removed from the reactor when it is operated nonisothermally?
- Consider what happens in the batch reactor given in Example 9.3.3 if the wall temperature does not remain constant. For comparison to the constant wall temperature, calculate the fractional conversion and reactor temperature as a function of time when:

$$T^* = 300 + 0.1t$$

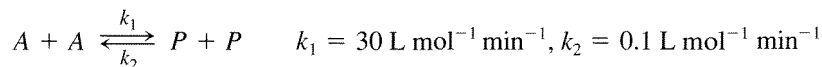
where t is in seconds.

- Calculate the exit temperature and τ for the PFR described in Example 9.4.2 when mole change with reaction is ignored (i.e., $\varepsilon_B = 0$). How much error is introduced by making this change?
- Calculate the exit temperature and τ for the PFR described in Example 9.4.2 when the temperature effects on the concentration are ignored. Is this a reasonable simplification or not?
- An adiabatic PFR can be described by the following set of equations:

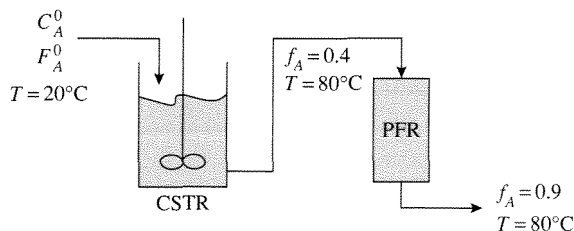
$$\begin{aligned}\frac{dy}{dx} &= -4y \exp \left[18 \left(1 - \frac{1}{\theta} \right) \right] \\ \frac{d\bar{\theta}}{dx} &= 0.2y \exp \left[18 \left(1 - \frac{1}{\theta} \right) \right] \\ y = \bar{\theta} &= 1 \text{ at } x = 0\end{aligned}$$

Solve these equations and plot y and $\bar{\theta}$ as a function of x for 0 (entrance) $\leq x \leq 1$ (exit). What happens if the heat of reaction is doubled?

- Ascertain whether the following exothermic reaction:



(k_1 and k_2 at 80°C) could be carried out in the reactor shown below:



Calculate the volume and heat removed from the CSTR and the PFR. Do the magnitudes of the heat being removed appear feasible? Why or why not?

Data:

$$\begin{aligned}C_{p_A} &= 45 \text{ cal mol}^{-1} \text{ K}^{-1} \\C_{p_P} &= 40 \text{ cal mol}^{-1} \text{ K}^{-1} \\-\Delta H_r &= 10,000 \text{ cal mol}^{-1} \\C_A^0 &= 1.5 \text{ mol L}^{-1} \\F_A^0 &= 100 \text{ mol min}^{-1}\end{aligned}$$

9. The ester of an organic base is hydrolyzed in a CSTR. The rate of this irreversible reaction is first-order in each reactant. The liquid volume in the vessel is 6500 L. A jacket with coolant at 18°C maintains the reactant mixture at 30°C. Additional data:

Ester feed stream—1 M, 30°C, 20 L/s

Base feed stream—4 M, 30°C, 10 L/s

Rate constant = $10^{14} \exp(-11,000/T) \text{ M}^{-1} \text{ s}^{-1}$, T in K

$\Delta H_r = -45 \text{ kcal/mol ester}$

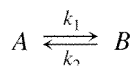
The average heat capacity is approximately constant at $1.0 \text{ kcal L}^{-1} \text{ }^\circ\text{C}^{-1}$.

- What is the conversion of ester in the reactor?
 - Calculate the rate at which energy must be removed to the jacket to maintain 30°C in the reactor. If the heat transfer coefficient is $15 \text{ kcal s}^{-1} \text{ m}^{-2} \text{ K}^{-1}$, what is the necessary heat transfer area?
 - If the coolant supply fails, what would be the maximum temperature the reactor could reach?
10. A reaction is carried out in an adiabatic CSTR with a volume of 10,000 L. The feed solution with reactant A, at a concentration of 5 M, is supplied at 10 L s^{-1} . The reaction is first-order with rate constant:

$$k = 10^{13} \exp(-12500/T) \text{ s}^{-1}, \text{ where } T \text{ is in K}$$

The density is 1000 kg m^{-3} and $C_p = 1.0 \text{ kcal kg}^{-1} \text{ K}^{-1}$. The heat of reaction is $\Delta H_r = -70 \text{ kJ mol}^{-1}$.

- Calculate the reactor temperature and exit concentration for feed temperatures of 280, 300, and 320 K.
 - To maintain the reactor temperature below 373 K, a well-mixed cooling jacket at 290 K is used. Show that it is possible to get 90 percent conversion in this reactor with a feed temperature of 320 K. Do you anticipate any start-up problems?
11. The reversible, first-order reaction shown below takes place in a CSTR.



The following data are known:

$$k_1 = 10^3 \exp(-2500/T) \text{ s}^{-1}, T \text{ in K}$$

$$\Delta H_r = -10 \text{ kcal mol}^{-1}$$

$$K = 8 \text{ at } 300 \text{ K}$$

$$C_p = 1 \text{ kcal kg}^{-1} \text{ K}^{-1}$$

$$\rho = 1 \text{ kg L}^{-1}$$

- (a) For a reactor space time of 10 min, what is the conversion for a 300 K operating temperature? What is the conversion at 500 K? (Remember: the equilibrium constant depends on temperature.)
- (b) If the feed temperature is 330 K and the feed concentration is 5 M, what is the necessary heat-removal rate per liter of reactor volume to maintain a 300 K operating temperature?