

Total volume	10 ml with
Water	3.64 g
Acetic anhydride	6.84 g
	<hr/>
	10.48 g (10 ml)

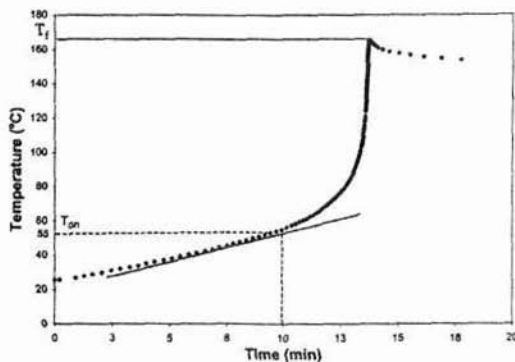


Figure E9-3.1 Temperature-time trajectory for hydrolysis of acetic anhydride.

Solution

Because we are taking our system as the contents inside the bomb as well as the bomb itself, the term $\sum N_i C_{p_i}$ needs to be modified to account for the heat absorbed by the bomb calorimeter that holds the reactants. Thus, we include terms for the mass of the calorimeter, m_b , and the heat capacity of the calorimeter, C_{p_b} , in the sum $\sum N_i C_{p_i}$, that is,

$$\sum N_i C_{p_i} = N_A C_{p_A} + N_B C_{p_B} + N_C C_{p_C} + N_I C_{p_I} + m_b C_{p_b}$$

However, for this example: $N_I = 0$ and we neglect ΔC_p and $m_b C_{p_b}$ to obtain

$$\sum N_i C_{p_i} = N_{A0} \sum \Theta_i C_{p_i} \quad (\text{E9-3.1})$$

We now apply our algorithm to analyzing the ARSST for the reaction



TABLE E9-3.1. BALANCE EQUATIONS

Mole balance: $\frac{dN_A}{dt} = r_A V$ (E9-3.2)

Rate law: $r_A = -k' C_A C_B$ (E9-3.3)

$$k' = A e^{-E/RT} \quad (\text{E9-3.4})$$

Stoichiometry: $V = V_0$

$$C_A = C_{A0}(1 - X) \quad (\text{E9-3.5})$$

$$C_B = C_{A0}(\Theta_B - X) \quad (\text{E9-3.6})$$

$$C_C = 2C_{A0}X \quad (\text{E9-3.7})$$

For $\Theta_B = 3$, as a first approximation we take

$$C_B \approx C_{A0}\Theta_B = C_{B0}$$

(Note: In Problem P9-10_C we do not assume C_{B0} is constant.)

$$r_A = -k' C_{B0} C_A = k C_A \quad (\text{E9-3.8})$$

Combine:

$$k = k' C_{B0}$$

$$\frac{dC_A}{dt} = -k C_A \quad (\text{E9-3.9})$$

Energy balance: $\frac{dT}{dt} = \dot{T}_E + \dot{T}_S$ (E9-3.10)

$$\dot{T}_E = \frac{\dot{Q}_E}{N_{A0} \sum \Theta_i C_{P_i}} \quad (\text{9-19})$$

Recalling $N_i = VC_i$ we can substitute Equations (E9-3.5) and (E9-3.6) into Equation (E9-3.1) and then

$$N_{A0} \sum \Theta_i C_{P_i} = N_{A0} C_{P_A} + N_{B0} C_{P_B} + \Delta C_p N_{A0} X + N_1 C_{P_1} + m_b C_{P_b} \quad (\text{E9-3.11})$$

Neglect

$$= N_{A0} (C_{P_A} + \Theta_B C_{P_B}) \quad (\text{E9-3.12})$$

Usually $N_1 = 0$, $\Delta C_p = 0$, and $m_b C_{P_b}$ are negligible with respect to the other terms.

The self-heating rate is

$$\dot{T}_S = \frac{(-\Delta H_{R_x})(-r_A V)}{N_{A0} \sum \Theta_i C_{P_i}} = \frac{(-\Delta H_{R_x})(C_{B0} A e^{-E/RT} C_A V)}{N_{A0} \sum \Theta_i C_{P_i}} \quad (\text{9-20})$$



Following the Algorithm

Calculating the Heat of Reaction

The heat of reaction for adiabatic operation can be found from the adiabatic temperature rise for complete conversion $X = 1$. The onset temperature is taken as the point at which the self-heating rate is greater than the electrical heating rate. From Figure E9-3.1 we see the onset temperature is 55°C and the maximum temperature is 165°C .

Recalling Equation (8-29) with $\Delta C_p = 0$

$$X = \sum \Theta_i C_{p_i} [(T - T_0) / (-\Delta H_{R_x}^\circ)]$$

For $X = 1$, $T = T_f$

$$-\Delta H_{R_x}^\circ = (C_{p_A} + \Theta_B C_{p_B})(T_f - T_0)$$

$$\sum \Theta_i C_{p_i} = [189.7 + 3(75.4)] = 415 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\Delta H_{R_x}^\circ = \left(415 \frac{\text{J}}{\text{mol} \cdot ^\circ\text{C}}\right)(165 - 55)^\circ\text{C} = 45,650 \text{ J/mol}$$

$$\boxed{\Delta H_{R_x}^\circ = -(45,650) \frac{\text{J}}{\text{mol}}}$$

Determining the Activation Energy

The self-heating rate \dot{T}_S is shown as a function of temperature in Figure (E9-3.2). The ARSST software will differentiate the data shown in Figure E9-3.1 directly to give \dot{T}_S or (dT/dt) can be found from T versus t data using any of the differential techniques discussed in Chapter 5. One notes that the self-heating rate goes to zero at $T = 138^\circ\text{C}$ as a result of the reactants having been consumed at this point.

The electrical heating rate, \dot{T}_E , either is shut off or becomes negligible wrt \dot{T}_S after the onset temperature T_{onset} is reached. Applying Equation (9-20) to our reaction, we obtain

$$\frac{dT}{dt} \equiv \dot{T}_S = \left(\frac{-\Delta H_{R_x}^\circ V C_{B_0}}{N_{A_0} \sum \Theta_i C_{p_i}} \right) A e^{-E/RT} C_A \quad (\text{E9.3-13})$$

We now take the log of the self-heating rate, \dot{T}_S , using Equation (E9.3-13) to obtain

$$\ln \dot{T}_S = \ln \left(\frac{-\Delta H_{R_x}^\circ C_{B_0} V}{N_{A_0} \sum \Theta_i C_{p_i}} \right) + \ln A + \ln C_A - \frac{E}{RT} \quad (\text{E9.3-14})$$

After the onset temperature is reached, we can obtain the activation energy from the slope of a plot of $[\ln(dT/dt)]$ as a function of $(1/T)$, neglecting changes in $\ln C_A$. The slope of the line will be $(-E/R)$, as shown in Figure E9-3.3.

From the slope of the plot we find the activation to be

$$E = -R \cdot \text{Slope} = 1.987 \frac{\text{cal}}{\text{mol} \cdot \text{K}} \times (-7,750 \text{ K})$$

$$\boxed{E = 15.4 \frac{\text{kcal}}{\text{mol}}}$$

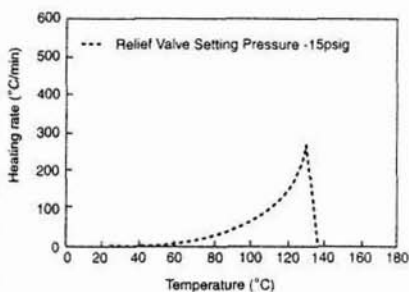


Figure E9-3.2 Self-heating curve for the hydrolysis of acetic anhydride.

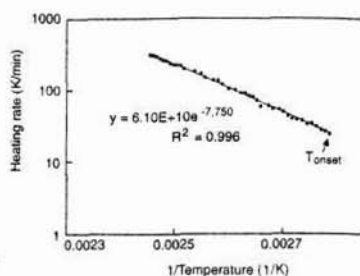


Figure E9-3.3 Arrhenius plot of self-heat rate for acetic anhydride.

Calculating the Frequency Factor, A

We will now make an approximate calculation to determine the frequency factor A . The intricate details of a more accurate calculation are given in *Professional Reference Shelf* R9.1 where the conversion obtained during the electrical heating phase is taken into account. Neglecting the conversion during electrical heating, $C_A = C_{A0}$, and Equation (E9-3.13) can be arranged in the form

$$A = \left[\dot{T}_s \Big|_{\text{onset}} \cdot \left[\frac{N_{A0} \sum \Theta_i C_{p_i}}{-\Delta H_{Rx} C_{A0} C_{B0} V} \right] \right] e^{E/RT_{\text{onset}}} \quad (\text{E9-})$$

At the *onset*, $T_{\text{onset}} = 55^\circ\text{C}$; at 10 minutes the self-heat rate can be estimated from slope of the plot of T versus t shown in Figure E9-3.1 to be $\dot{T}_s \Big|_{\text{onset}} = 5.2 \text{ K/min}$.

Evaluating the parameters,

$$\begin{aligned} N_{A0} \sum \Theta_i C_{p_i} &= \left(6.7 \frac{\text{mol}}{\text{dm}^3} \right) (0.01 \text{ dm}^3) \left[415 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right] \\ &= 28 \text{ J/K} \end{aligned}$$

We now calculate the frequency factor to be

$$A = \frac{5.2 \text{ K}}{\text{min}} \left[\frac{28 \text{ J/K}}{\left(45,650 \frac{\text{J}}{\text{mol}} \right) \left(6.7 \frac{\text{mol}}{\text{dm}^3} \right) \left(20.2 \frac{\text{mol}}{\text{dm}^3} \right) \cdot 0.01 \text{ dm}^3} \right] \exp \left[\frac{15,400 \text{ cal/mol}}{(1,987 \text{ cal/mol})} \right]$$

$$\boxed{A = 3.73 \times 10^7 \text{ dm}^3/\text{mol}/\text{min}}$$

Now that we have the activation energy E and the Arrhenius factor A , we can use Polymath to simulate the equations in Table E9-3.1 and compare with the experimental results. The Polymath program is shown in Table E9-3.2, and the corresponding output is shown in Figure E9-3.4.

TABLE E9-3.2. POLYMATH PROGRAM

ODE Report (RK45)

Differential equations as entered by the user

- [1] $d(CA)/d(t) = rA$
 [2] $d(T)/d(t) = T_{\text{edot}} + T_{\text{sdot}}$

Explicit equations as entered by the user

- [1] $CB0 = 20.2$
 [2] $V = 0.01$
 [3] $\text{SUMNA0THEiCpi} = 28$
 [4] $dH_{\text{rx}} = -45650$
 [5] $A = 3.734e7$
 [6] $E = 15400$
 [7] $R = 1.987$
 [8] $T_{\text{edot}} = \text{if } (T > 55 + 273) \text{ then } 0 \text{ else } 2$
 [9] $rA = -A \cdot \exp(-E/R/T) \cdot CA \cdot CB0$
 [10] $T_{\text{sdot}} = (-dH_{\text{rx}}) \cdot (-rA \cdot V) / \text{SUMNA0THEiCpi}$

Comments

- [1] $d(CA)/d(t) = rA$
Mole balance on Acetic Anhydride
 [2] $d(T)/d(t) = T_{\text{edot}} + T_{\text{sdot}}$
Energy Balance
 [3] $rA = -A \cdot \exp(-E/R/T) \cdot CA \cdot CB0$
Rate of the reaction-mol/l.min
 [4] $V = 0.01$
Volume of the reactive solution-l
 [5] $\text{SUMNA0THEiCpi} = 28$
J/mol.C
 [6] $dH_{\text{rx}} = -45650$
Heat of reaction-J/mol
 [7] $A = 3.734e7$
rate constant- 1/min
 [8] $E = 15400$
cal/mol
 [9] $R = 1.987$
cal/mol.K
 [10] $T_{\text{edot}} = \text{if } (T > 55 + 273) \text{ then } 0 \text{ else } 2$
(oK/min) After the onset point, electrical heating is only to compensate for heat loss
 [11] $T_{\text{sdot}} = (-dH_{\text{rx}}) \cdot (-rA \cdot V) / \text{SUMNA0THEiCpi}$
Self-heating rate (oK/min)



Living Example Problem

$$\text{Where } \text{SUMNA0THEiCpi} = N_{A0} \sum \Theta_i C_{P_i} = 28$$

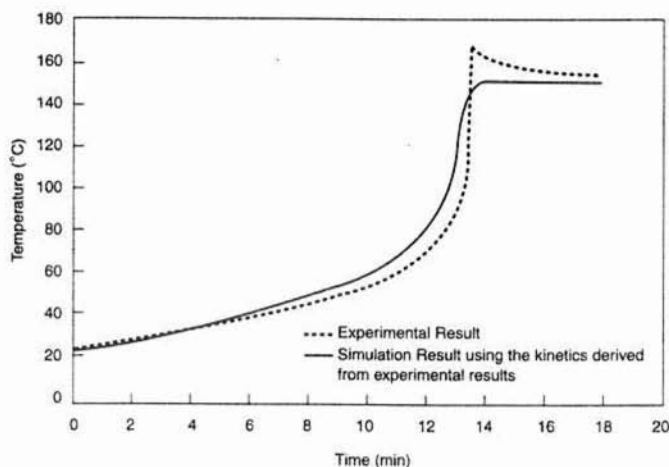
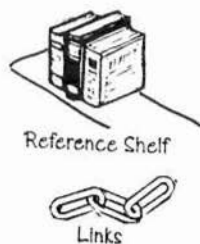


Figure E9-3.4 Temperature-time trajectory for hydrolysis of acetic anhydride.

As one can see there is excellent agreement between the simulation and the experiment. The decrease in temperature at 13.5 minutes in the experimental data is a result of a small heat loss to the surroundings which was not accounted for in the simulation. The CD-ROM (R9.1) describes how to size the vent size from this data.

When using the ARSST in the laboratory to actually size the relief vent, follow the procedure in the *Professional Reference Shelf*, which accounts for the conversion during the electrical heating and also taking the onset temperature at a point where $T_S \gg T_E$. Also see the Fauske web site: www.fauske.com.



Oops! The practical stability limit was exceeded.

9.3 Semibatch Reactors with a Heat Exchanger

In our past discussions of reactors with heat exchangers, we assumed that the ambient temperature T_a was spatially uniform throughout the exchanger. This assumption is true if the system is a tubular reactor with the external pipe surface exposed to the atmosphere or if the system is a CSTR or batch where the coolant flow rate through exchanger is so rapid that the coolant temperatures entering and leaving the exchanger are virtually the same.

We now consider the case where the coolant temperature varies along the length of the exchanger while the temperature in the reactor is spatially uniform. The coolant enters the exchanger at a mass flow rate \dot{m}_c at a temperature T_{a1} and leaves at a temperature T_{a2} (see Figure 9-3). As a first approximation, we assume a quasi-steady state for the coolant flow and neglect the accumulation term (i.e., $dT_a/dt = 0$). As a result, Equation (8-49) will give the rate of heat transfer from the exchanger to the reactor:

$$\dot{Q} = \dot{m}_c C_p (T_{a1} - T) [1 - \exp - UA / (\dot{m}_c C_p)] \quad (8-49)$$

Using Equation (8-49) to substitute for \dot{Q} in Equation (9-9), we obtain

$$\frac{dT}{dt} = \frac{\dot{m}_c C_{p_c} (T_{a1} - T) [1 - \exp(-UA/\dot{m}_c C_{p_c})] + (r_A V)(\Delta H_{R_x}) - \sum F_{i0} C_{p_i} (T - T_0)}{\sum N_i C_{p_i}}$$

(9-21)

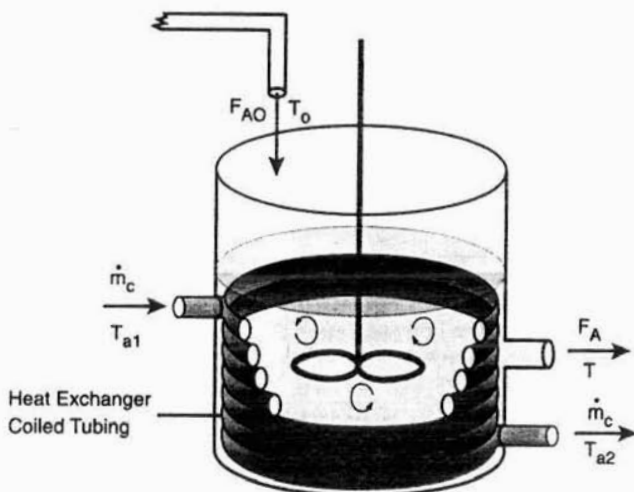


Figure 9-3 Tank reactor with heat exchanger.

At steady state ($dT/dt = 0$) Equation (9-21) can be solved for the conversion X as a function of reaction temperature by recalling that

$$F_{A0}X = -r_A V$$

and

$$\sum F_{i0} C_{p_i} (T - T_0) = F_{A0} \sum \Theta_i C_{p_i} (T - T_0)$$

and neglecting ΔC_p and then rearranging Equation (9-21) to obtain

$$X = \frac{\dot{m}_c C_{p_c} (T_{a1} - T) [1 - \exp(-UA/\dot{m}_c C_{p_c})] - F_{A0} \sum \Theta_i C_{p_i} (T - T_0)}{F_{A0} (\Delta H_{R_x})}$$

(9-22)

We are assuming that there is virtually no accumulation of energy in the coolant fluid, that is,

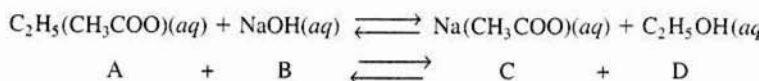
$$\frac{dT_a}{dt} \approx 0$$

Steady-state energy balance



Example 9-4 Heat Effects in a Semibatch Reactor

The second-order saponification of ethyl acetate is to be carried out in a semibatch reactor shown schematically in Figure E9-4.1.



Aqueous sodium hydroxide is to be fed at a concentration of 1 kmol/m^3 , a temperature of 300 K , and a rate of $0.004 \text{ m}^3/\text{s}$ to an initial volume of 0.2 m^3 of water and ethyl acetate. The initial concentrations of ethyl acetate and water are 5 kmol/m^3 and 3 kmol/m^3 , respectively. The reaction is exothermic, and it is necessary to add a heat exchanger to keep its temperature below 315 K . A heat exchanger with $UA = 36 \text{ J/s} \cdot \text{K}$ is available for use. The coolant enters at a rate of 100 kg/s and a temperature of 285 K .

Is the heat exchanger and coolant flow rate adequate to keep the reactor temperature below 315 K ? Plot temperature, C_A , C_B , and C_C as a function of time.

Additional information:³

$$k = 0.39175 \exp \left[5472.7 \left(\frac{1}{273} - \frac{1}{T} \right) \right] \text{ m}^3/\text{kmol} \cdot \text{s}$$

$$K_C = 10^{3885.44/T}$$

$$\Delta H_{\text{Rx}}^\circ = -79,076 \text{ kJ/kmol}$$

$$C_{P_A} = 170.7 \text{ J/mol} \cdot \text{K}$$

$$C_{P_B} = C_{P_C} = C_{P_D} \cong C_{P_W} = C_P = 75.24 \text{ J/mol} \cdot \text{K}$$

$$\text{Feed:} \quad C_{W_0} = 55 \text{ kmol/m}^3 \quad C_{B_0} = 1.0 \text{ kmol/m}^3$$

$$\text{Initially:} \quad C_{W_i} = 30.7 \text{ kmol/m}^3 \quad C_{A_i} = 5 \text{ kmol/m}^3 \quad C_{B_i} = 0$$

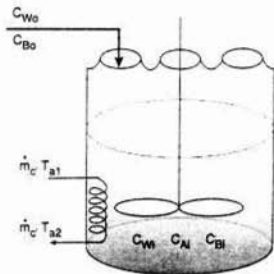


Figure E9-4.1 Semibatch reactor with heat exchange.

³ k from J. M. Smith, *Chemical Engineering Kinetics*, 3rd ed. (New York: McGraw-Hill, 1981), p. 205. ΔH_{Rx} and K_C calculated from values given in *Perry's Chemical Engineers' Handbook*, 6th ed. (New York: McGraw-Hill, 1984), pp. 3-147.

Solution

Mole Balances: (See Section 4.10.2.)

$$\frac{dC_A}{dt} = r_A - \frac{v_0 C_A}{V} \quad (\text{E9-4.1})$$

$$\frac{dC_B}{dt} = r_B + \frac{v_0(C_{B0} - C_B)}{V} \quad (\text{E9-4.2})$$

$$\frac{dC_C}{dt} = r_C - \frac{C_C v_0}{V} \quad (\text{E9-4.3})$$

$$C_D = C_C$$

$$\frac{dN_W}{dt} = C_{W0} v_0 \quad (\text{E9-4.4})$$

Initially,

$$N_{wi} = V_i C_{wi} = (0.2)(30.7) = 6.14 \text{ kmol}$$

Rate Law:

$$-r_A = k \left(C_A C_B - \frac{C_C C_D}{K_C} \right) \quad (\text{E9-4.5})$$

Stoichiometry:

$$-r_A = -r_B = r_C = r_D \quad (\text{E9-4.6})$$

$$N_A = C_A V \quad (\text{E9-4.7})$$

$$V = V_0 + v_0 t \quad (\text{E9-4.8})$$

Energy Balance: Next we replace $\sum_{i=1}^n F_{i0} C_{P_i}$ in Equation (9-9). Because only B and water continually flow into the reactor

$$\sum_{i=1}^n F_{i0} C_{P_i} = F_{B0} C_{P_B} + F_{W0} C_W = F_{B0} \left(C_{P_B} + \frac{F_{W0}}{F_{B0}} C_{P_W} \right)$$

However, $C_{P_B} = C_{P_W}$:

$$\sum_{i=1}^n F_{i0} C_{P_i} = F_{B0} C_{P_B} (1 + \Theta_W)$$

where

$$\Theta_W = \frac{F_{W0}}{F_{B0}} = \frac{C_{W0}}{C_{B0}} = \frac{55}{1} = 55$$

$$\frac{dT}{dt} = \frac{\dot{Q} - F_{B0} C_{P_B} (1 + \Theta_W) (T - T_0) + (r_A V) \Delta H_{R_x}}{N_A C_{P_A} + N_B C_{P_B} + N_C C_{P_C} + N_D C_{P_D} + N_W C_{P_W}} \quad (\text{E9-4.9})$$

$$\dot{Q} = \dot{m}_c C_{P_c} (T_{a1} - T) [1 - \exp(-UA/\dot{m}_c C_{P_c})] \quad (8-49)$$

$$\frac{dT}{dt} = \frac{\dot{m}_c C_{P_c} (T_{a1} - T) [1 - \exp(-UA/\dot{m}_c C_{P_c})] - F_{B0} C_P (1 + \Theta_w)(T - T_0) + (r_A V) \Delta H_{Rx}}{C_P (N_B + N_C + N_D + N_W) + C_{P_A} N_A} \quad (E9-4.10)$$

Recalling Equation (8-47) for the outlet temperature of the fluid in the heat exchanger

$$T_{a2} = T - (T - T_{a1}) \exp\left[-\frac{UA}{\dot{m}_c C_{P_c}}\right] \quad (8-47)$$

The Polymath program is given in Table E9-4.1. The solution results are shown in Figures E9-4.2 and E9-4.3.

TABLE E9-4.1. POLYMATH PROGRAM FOR SEMIBATCH REACTOR

ODE Report (RK45)

Differential equations as entered by the user

- [1] d(Ca)/d(t) = ra-(v0*Ca)/V
- [2] d(Cb)/d(t) = rb+(v0*(Cb0-Cb))/V
- [3] d(Cc)/d(t) = rc-(Cc*v0)/V
- [4] d(T)/d(t) = (Qr-Fb0*cp*(1+55)*(T-T0)+ra*V*dh)/NCp
- [5] d(Nw)/d(t) = v0*Cw0

Explicit equations as entered by the user

- [1] v0 = 0.004
- [2] Cb0 = 1
- [3] UA = 3000
- [4] Ta = 290
- [5] cp = 75240
- [6] T0 = 300
- [7] dh = -7.9076e7
- [8] Cw0 = 55
- [9] k = 0.39175*exp(5472.7*((1/273)-(1/T)))
- [10] Cd = Cc
- [11] Vi = 0.2
- [12] Kc = 10^(3885.44/T)
- [13] cps = 170700
- [14] V = Vi+v0*t
- [15] Fb0 = Cb0*v0
- [16] ra = -k*((Ca*Cb)-((Cc*Cd)/Kc))
- [17] Na = V*Ca
- [18] Nb = V*Cb
- [19] Nc = V*Cc
- [20] rb = ra
- [21] rc = -ra
- [22] Nd = V*Cd
- [23] rate = -ra
- [24] NCp = cp*(Nb+Nc+Nd+Nw)+cps*Na
- [25] Cpc = 18
- [26] Ta1 = 285
- [27] mc = 100
- [28] Qr = mc*Cpc*(Ta1-T)*(1-exp(-UA/mc/Cpc))
- [29] Ta2 = T-(T-Ta1)*exp(-UA/mc/Cpc)



Living Example Problem

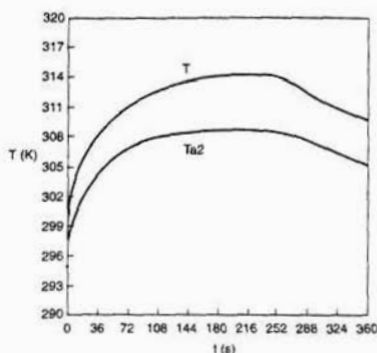


Figure E9-4.2 Temperature-time trajectory in a semibatch reactor

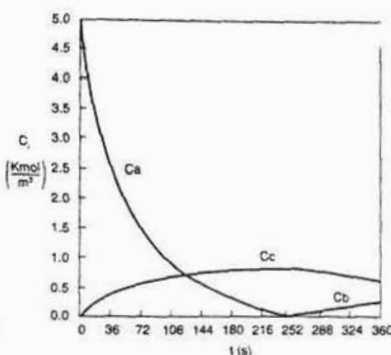


Figure E9-4.3 Concentration-time trajectories in a semibatch reactor.

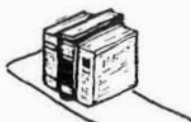
9.4 Unsteady Operation of a CSTR

9.4.1 Startup

Startup of a CSTR

In reactor startup it is often very important *how* temperature and concentrations approach their steady-state values. For example, a significant overshoot in temperature may cause a reactant or product to degrade, or the overshoot may be unacceptable for safe operation. If either case were to occur, we would say that the system exceeded its *practical stability limit*. Although we can solve the unsteady temperature-time and concentration-time equations numerically to see if such a limit is exceeded, it is often more insightful to study the approach to steady state by using the *temperature-concentration phase plane*. To illustrate these concepts we shall confine our analysis to a liquid-phase reaction carried out in a CSTR.

A qualitative discussion of how a CSTR approaches steady state is given in PRS R9.4. This analysis, summarized in Figure S-1 in the Summary for this chapter, is developed to show the four different regions into which the phase plane is divided and how they allow one to sketch the approach to the steady state.



Reference Shelf

Example 9-5 Startup of a CSTR

Again we consider the production of propylene glycol (C) in a CSTR with a heat exchanger in Example 8-8. Initially there is only water at 75°F and 0.1 wt % H₂SO₄ in the 500-gallon reactor. The feed stream consists of 80 lb mol/h of propylene oxide (A), 1000 lb mol/h of water (B) containing 0.1 wt % H₂SO₄, and 100 lb mol/h of methanol (M). Plot the temperature and concentration of propylene oxide as a function of time, and a concentration vs. temperature graph for different entering temperatures and initial concentrations of A in the reactor.

The water coolant flows through the heat exchanger at a rate of 5 lb/s (10 lb mol/h). The molar densities of pure propylene oxide (A), water (B), and methanol (M) are $\rho_{A0} = 0.932$ lb mol/ft³, $\rho_{B0} = 3.45$ lb mol/ft³, and $\rho_{M0} = 1.54$ mol/ft³, respectively.

$$UA = 16,000 \frac{\text{Btu}}{\text{h} \cdot ^\circ\text{F}} \text{ with } T_{a1} = 60^\circ\text{F}, \dot{m}_w = 1000 \text{ lb mol/h with } C_{P_w} = 18 \text{ Btu/lb mol}$$

$$C_{P_A} = 35 \text{ Btu/lb mol} \cdot ^\circ\text{F}, C_{P_B} = 18 \text{ Btu/lb mol} \cdot ^\circ\text{F},$$

$$C_{P_C} = 46 \text{ Btu/lb mol} \cdot ^\circ\text{F}, C_{P_M} = 19.5 \text{ Btu/lb mol} \cdot ^\circ\text{F}$$

Solution



Mole Balances:

	Initial Conditions	
A: $\frac{dC_A}{dt} = r_A + \frac{(C_{A0} - C_A)v_0}{V}$	0	(E9-5)

B: $\frac{dC_B}{dt} = r_B + \frac{(C_{B0} - C_B)v_0}{V}$	$C_{B0} = 3.45 \frac{\text{lb mol}}{\text{ft}^3}$	(E9-5)
--	---	--------

C: $\frac{dC_C}{dt} = r_C + \frac{-C_C v_0}{V}$	0	(E9-5)
---	---	--------

M: $\frac{dC_M}{dt} = \frac{v_0(C_{M0} - C_M)}{V}$	0	(E9-5)
--	---	--------

Rate Law: $-r_A = kC_A$ (E9-5)

Stoichiometry: $-r_A = -r_B = r_C$ (E9-5)

Energy Balance:

$$\frac{dT}{dt} = \frac{\dot{Q} - F_{A0} \sum \Theta_i C_{P_i} (T - T_0) + (\Delta H_{R_x})(r_A V)}{\sum N_i C_{P_i}} \quad (\text{E9-5})$$

with

$$\dot{Q} = \dot{m}_w C_{P_w} (T_{a1} - T_{a2}) = \dot{m}_w C_{P_w} (T_{a1} - T) \left[1 - \exp\left(-\frac{UA}{\dot{m}_w C_{P_w}}\right) \right] \quad (\text{E9-5})$$

and

$$T_{a2} = T - (T - T_{a1}) \exp\left(-\frac{UA}{\dot{m}_w C_{P_w}}\right)$$

Evaluation of parameters:

$$\begin{aligned}\sum N_i C_{P_i} &= C_{P_A} N_A + C_{P_B} N_B + C_{P_C} N_C + C_{P_M} N_M \\ &= 35(C_A V) + 18(C_B V) + 46(C_C V) + 19.5(C_M V)\end{aligned}$$

$$\begin{aligned}\sum \Theta_i C_{P_i} &= C_{P_A} + \frac{F_{B0}}{F_{A0}} C_{P_B} + \frac{F_{M0}}{F_{A0}} C_{P_M} \\ &= 35 + 18 \frac{F_{B0}}{F_{A0}} + 19.5 \frac{F_{M0}}{F_{A0}}\end{aligned}$$

$$v_0 = \frac{F_{A0}}{\rho_{A0}} + \frac{F_{B0}}{\rho_{B0}} + \frac{F_{M0}}{\rho_{M0}} = \left(\frac{F_{A0}}{0.923} + \frac{F_{B0}}{3.45} + \frac{F_{M0}}{1.54} \right) \text{ft}^3/\text{h}$$

Neglecting ΔC_p because it changes the heat of reaction insignificantly over the temperature range of the reaction, the heat of reaction is assumed constant at

$$\Delta H_{Rx} = -36,000 \frac{\text{Btu}}{\text{lb mol A}}$$

The Polymath program is shown in Table E9-5.1.

TABLE E9-5.1. POLYMATH PROGRAM FOR CSTR STARTUP

ODE Report (RK45)

Differential equations as entered by the user

- [1] d(Ca)/d(t) = 1/tau*(Ca0-Ca)+ra
- [2] d(Cb)/d(t) = 1/tau*(Cb0-Cb)-rb
- [3] d(Cc)/d(t) = 1/tau*(0-Cc)+rc
- [4] d(Cm)/d(t) = 1/tau*(Cm0-Cm)
- [5] d(T)/d(t) = (Q-Fa0*ThetaCp*(T-T0)+(-36000)*ra*V)/NCp

Explicit equations as entered by the user

- [1] Fa0 = 80
- [2] T0 = 75
- [3] V = (1/7.484)*500
- [4] UA = 16000
- [5] Ta1 = 60
- [6] k = 16.96e12*exp(-32400/(1.987*(T+460)))
- [7] Fb0 = 1000
- [8] Fm0 = 100
- [9] mc = 1000
- [10] ra = -k*Ca
- [11] rb = -k*Ca
- [12] rc = k*Ca
- [13] Nm = Cm*V
- [14] Na = Ca*V
- [15] Nb = Cb*V
- [16] Nc = Cc*V
- [17] ThetaCp = 35+Fb0/Fa0*18+Fm0/Fa0*19.5
- [18] v0 = Fa0/0.923+Fb0/3.45+Fm0/1.54
- [19] Ta2 = T-(T-Ta1)*exp(-UA/(18*mc))
- [20] Ca0 = Fa0/v0
- [21] Cb0 = Fb0/v0
- [22] Cm0 = Fm0/v0
- [23] Q = mc*18*(Ta1-Ta2)
- [24] tau = V/v0
- [25] NCp = Na*35+Nb*18+Nc*46+Nm*19.5



Figures (E9-5.1) and (E9-5.2) show the reactor concentration and temperature of propylene oxide as a function of time, respectively, for an initial temperature of 75°F and only water in the tank (i.e., $C_{Ai} = 0$). One observes, both the temperature and concentration oscillate around their steady-state values ($T = 138^\circ\text{F}$, $C_A = 0.039$ lb mol/ft³). Figure (E9-5.3) shows the phase plane of temperature and propylene oxide concentration for three different sets of initial conditions ($T_i = 75^\circ\text{F}$, $C_{Ai} = 0$; $T_i = 150^\circ\text{F}$, $C_{Ai} = 0$; and $T_i = 160^\circ\text{F}$, $C_{Ai} = 0.14$ lb mol/ft³), keeping T_0 constant.

An upper limit of 180°F should not be exceeded in the tank. This temperature is the *practical stability limit*. The practical stability limit represent a temperature above which it is undesirable to operate because of unwanted side reactions, safety considerations, or damage to equipment. Consequently, we see if we started at an initial temperature of 160°F and an initial concentration of 0.14 mol/dm³, the practical stability limit of 180°F would be exceeded as the reactor approached its steady-state temperature of 138°F. See the concentration–temperature trajectory in Figure E9-5.4.

Unacceptable
startup

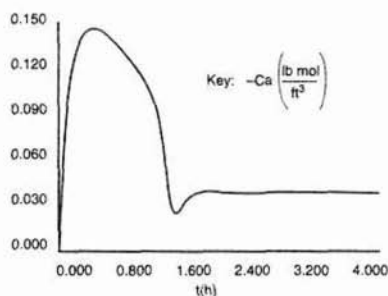


Figure E9-5.1 Propylene oxide concentration as a function of time.

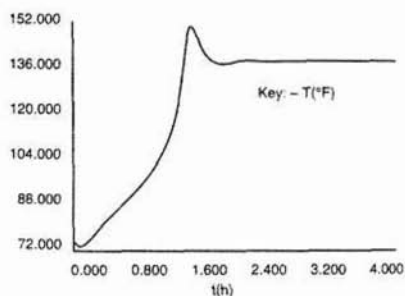


Figure E9-5.2 Temperature–time trajectory for CSTR startup.

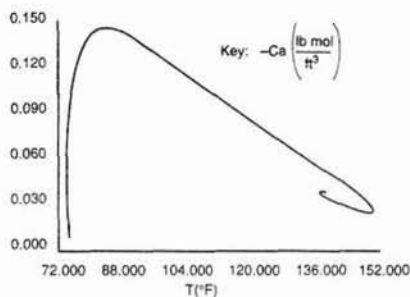


Figure E9-5.3 Concentration–temperature phase-plane trajectory.

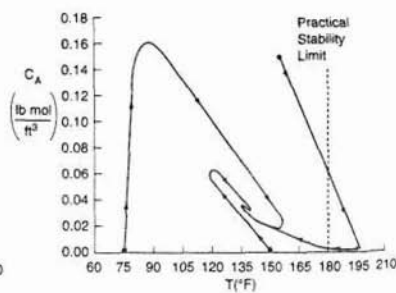


Figure E9-5.4 Concentration–temperature phase plane.

Oops! The practical
stability limit was
exceeded.

After about 1.6 h the reactor is operating at steady state with the following values:

$$\begin{aligned} C_A &= 0.0379 \text{ lb mol/ft}^3 & C_C &= 0.143 \text{ lb mol/ft}^3 \\ C_B &= 2.12 \text{ lb mol/ft}^3 & C_M &= 0.2265 \text{ lb mol/ft}^3 \\ T &= 138.5^\circ\text{F} \end{aligned}$$

9.4.2 Falling Off the Steady State

We now consider what can happen to a CSTR operating at an upper steady state when an upset occurs in either the ambient temperature, the entering temperature, the flow rate, the reactor temperature, or some other variable. To illustrate, let's reconsider the production of propylene glycol in a CSTR, which we just discussed.

Example 9-6 Falling Off the Upper Steady State

In Example 9-5 we saw how a 500-gal CSTR used for the production of propylene glycol approached steady state. For the flow rates and conditions (e.g., $T_0 = 75^\circ\text{F}$, $T_{a1} = 60^\circ\text{F}$), the steady-state temperature was 138°F , and the corresponding conversion was 75.5%. Determine the steady-state temperature and conversion that would result if the entering temperature were to drop from 75°F to 70°F , assuming that all other conditions remain the same. First, sketch the steady-state conversions calculated from the mole and energy balances as a function of temperature before and after the drop in entering temperature occurred. Next, plot the "conversion," concentration of A, and the temperature in the reactor as a function of time after the entering temperature drops from 75°F to 70°F .

Solution

The steady-state conversions can be calculated from the mole balance,

$$X_{\text{MB}} = \frac{\tau A e^{-E/RT}}{1 + \tau A e^{-E/RT}} \quad (\text{E8-5.5})$$

and from the energy balance,

$$X_{\text{EB}} = \frac{\sum \Theta_i C_{p_i} (T - T_0) + [\dot{Q}/F_{A0}]}{-[\Delta H_{\text{Rx}}(T_R)]} \quad (\text{E8-5.6})$$

before ($T_0 = 75^\circ\text{F}$) and after ($T_0 = 70^\circ\text{F}$) the upset occurred. We shall use the parameter values given in Example 9-5 (e.g., $F_{A0} = 80 \text{ lb mol/h}$, $UA = 16,000 \text{ Btu/h} \cdot ^\circ\text{F}$) to obtain a sketch of these conversions as a function of temperature, as shown in Figure E9-6.1.

We see that for $T_0 = 70^\circ\text{F}$ the reactor has dropped below the extinction temperature and can no longer operate at the upper steady state. In Problem P9-16, we will see it is not always necessary for the temperature to drop below the extinction temperature in order to fall to the lower steady state. The equations describing the dynamic drop from the upper steady state to the lower steady state are identical to those given in Example 9-5; only the initial conditions and entering temperature are different. Consequently, the same Polymath and MATLAB programs can be used with these modifications. (See *Living Example 9-6* on the CD-ROM.)



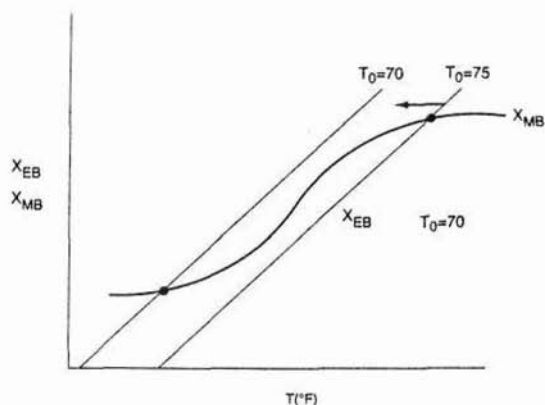


Figure E9-6.1 Conversion from mole and energy balances as a function of temperature.

Initial conditions are taken from the final steady-state values given in Example 9-5.

$C_{A_i} = 0.039 \text{ lb mol/ft}^3$	$C_{C_i} = 0.143 \text{ lb mol/ft}^3$
$C_{B_i} = 2.12 \text{ lb mol/ft}^3$	$C_{M_i} = 0.226 \text{ lb mol/ft}^3$
$T_i = 138.5^\circ\text{F}$	
Change T_0 to 70°F	

Because the system is not at steady state, we cannot rigorously define a conversion in terms of the number of moles reacted because of the accumulation within the reactor. However, we can approximate the conversion by the equation $X = (1 - C_A/C_{A_i})$. This equation is valid after the steady state is reached. Plots of the temperature and the conversion as a function of time are shown in Figures E9-6.2 and E9-6.3, respectively. The new steady-state temperature and conversion are $T = 83.6^\circ\text{F}$ and $X = 0$.

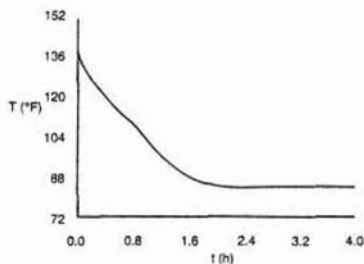


Figure E9-6.2 Temperature versus time.

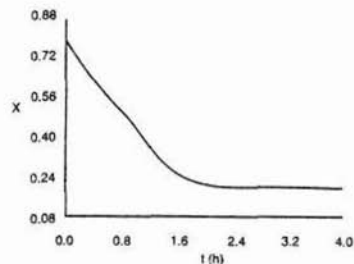


Figure E9-6.3 Conversion versus time.



Reference Shelf

We could now see how we can make adjustments for upsets in the reactor operating conditions (such as we just saw in the drop in the entering temperature) so that we do not fall to the lower steady-state values. We can prevent this drop in conversion by adding a controller to the reactor. The addition of a controller is discussed in the *Professional Reference Shelf* R9.2 on the CD-ROM.

9.5 Nonisothermal Multiple Reactions

For multiple reactions occurring in either a semibatch or batch reactor, Equation (9-21) can be generalized in the same manner as the steady-state energy balance, to give

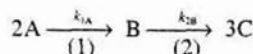
$$\frac{dT}{dt} = \frac{\dot{m}_C C_{P_C} (T_{a1} - T) [1 - \exp(-UA/\dot{m}_C C_{P_C})] + \sum_{i=1}^q r_{ij} V \Delta H_{R_{xij}}(T) - \sum F_{i0} C_{P_i} (T - T_0)}{\sum N_i C_{P_i}} \quad (9-23)$$

For large coolant rates Equation (9-23) becomes

$$\frac{dT}{dt} = \frac{UA(T_a - T) - \sum F_{i0} C_{P_i} (T - T_0) + V \sum_{i=1}^q r_{ij} \Delta H_{R_{xij}}}{\sum_{i=1}^n N_i C_{P_i}} \quad (9-24)$$

Example 9-7 Multiple Reactions in a Semibatch Reactor

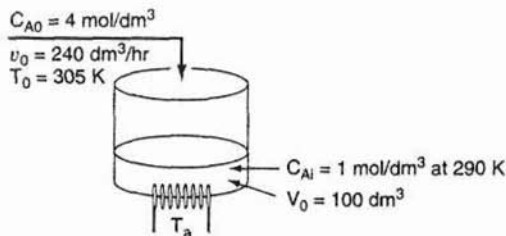
The series reactions



are catalyzed by H_2SO_4 . All reactions are first order in the reactant concentration. The reaction is to be carried out in a semibatch reactor that has a heat exchanger inside with $UA = 35,000 \text{ cal/h} \cdot \text{K}$ and an exchanger temperature, T_a , of 298 K. Pure A enters at a concentration of 4 mol/dm^3 , a volumetric flow rate of $240 \text{ dm}^3/\text{h}$, and a temperature of 305 K. Initially there is a total of 100 dm^3 in the reactor, which contains 1.0 mol/dm^3 of A and 1.0 mol/dm^3 of the catalyst H_2SO_4 . The reaction rate is independent of the catalyst concentration. The initial temperature of the reactor is 290 K. Plot the species concentrations and temperature as a function of time.



Living Example Problem



Additional information:

$$k_{1A} = 1.25 \text{ h}^{-1} \text{ at } 320 \text{ K with } E_{1A} = 9500 \text{ cal/mol} \quad C_{P_A} = 30 \text{ cal/mol} \cdot \text{K}$$

$$k_{2B} = 0.08 \text{ h}^{-1} \text{ at } 300 \text{ K with } E_{2B} = 7000 \text{ cal/mol} \quad C_{P_B} = 60 \text{ cal/mol} \cdot \text{K}$$

$$\Delta H_{R_{x1A}} = -6500 \text{ cal/mol A} \quad C_{P_C} = 20 \text{ cal/mol} \cdot \text{K}$$

$$\Delta H_{R_{x2B}} = +8000 \text{ cal/mol B} \quad C_{P_{H_2SO_4}} = 35 \text{ cal/mol} \cdot \text{K}$$

Solution

Mole Balances:

$$\frac{dC_A}{dt} = r_A + \frac{(C_{A0} - C_A)}{V} v_0 \quad (\text{E9-7.1})$$

$$\frac{dC_B}{dt} = r_B - \frac{C_B}{V} v_0 \quad (\text{E9-7.2})$$

$$\frac{dC_C}{dt} = r_C - \frac{C_C}{V} v_0 \quad (\text{E9-7.3})$$

Rate Laws:

$$-r_{1A} = k_{1A} C_A \quad (\text{E9-7.4})$$

$$-r_{2B} = k_{2B} C_B \quad (\text{E9-7.5})$$

Stoichiometry (liquid phase): Use C_A , C_B , C_C

Relative rates:

$$r_{1B} = -\frac{1}{2} r_{1A} \quad (\text{E9-7.6})$$

$$r_{2C} = -3 r_{2B} \quad (\text{E9-7.7})$$

Net rates:

$$r_A = r_{1A} = -k_{1A} C_A \quad (\text{E9-7.8})$$

$$r_B = r_{1B} + r_{2B} = \frac{-r_{1A}}{2} + r_{2B} = \frac{k_{1A} C_A}{2} - k_{2B} C_B \quad (\text{E9-7.9})$$

$$r_C = 3 k_{2B} C_B \quad (\text{E9-7.10})$$

$$N_i = C_i V \quad (\text{E9-7.11})$$

$$V = V_0 + v_0 t \quad (\text{E9-7.12})$$

$$N_{H_2SO_2} = (C_{H_2SO_4,0}) V_0 = \frac{1 \text{ mol}}{\text{dm}^3} \times 100 \text{ dm}^3 = 100 \text{ mol}$$

$$F_{A0} = \frac{4 \text{ mol}}{\text{dm}^3} \times 240 \frac{\text{dm}^3}{\text{h}} = 960 \frac{\text{mol}}{\text{h}}$$

2 **Energy Balance:**

$$\frac{dT}{dt} = \frac{UA(T_a - T) - \sum F_{i0} C_{P_i} (T - T_0) + V \sum_{i=1}^q \Delta H_{R_{xij}} r_{ij}}{\sum N_i C_{P_i}} \quad (9-24)$$

$$\frac{dT}{dt} = \frac{UA(T_a - T) - F_{A0} C_{P_A} (T - T_0) + [(\Delta H_{R_{x1A}})(r_{1A}) + (\Delta H_{R_{x2B}})(r_{2B})] V}{[C_A C_{P_A} + C_B C_{P_B} + C_C C_{P_C}] V + N_{H_2SO_4} C_{P_{H_2SO_4}}} \quad (E9-7.13)$$

$$\frac{dT}{dt} = \frac{35,000(298 - T) - (4)(240)(30)(T - 305) + [(-6500)(-k_{1A} C_A) + (+8000)(-k_{2B} C_B)] V}{(30C_A + 60C_B + 20C_C)(100 + 240t) + (100)(35)} \quad (E9-7.14)$$

Equations (E9-7.1) through (E9-7.3) and (E9-7.8) through (E9-7.12) can be solved simultaneously with Equation (E9-7.14) using an ODE solver. The Polymath program is shown in Table E9-7.1 and the Matlab program is on the CD-ROM. The time graphs are shown in Figures E9-7.1 and E9-7.2.

TABLE E9-7.1. POLYMATH PROGRAM

ODE Report (RKF45)

Differential equations as entered by the user

- ```
[1] d(Ca)/dt = ra + (Cao - Ca)*vo/V
[2] d(Cb)/dt = rb - Cb*vo/V
[3] d(Cc)/dt = rc - Cc*vo/V
[4] d(T)/dt = (35000*(298 - T) - Cao*vo*30*(T - 305) + (-6500)*(-k1a*Ca) + (8000)*(-k2b*Cb))/V / ((Ca*30 + Cb*60 + Cc*20)*V + 100*35)
```

Explicit equations as entered by the user

- ```
[1] Cao = 4
[2] vo = 240
[3] k1a = 1.25*exp((9500/1.987)*(1/320 - 1/T))
[4] k2b = 0.08*exp((7000/1.987)*(1/290 - 1/T))
[5] ra = -k1a*Ca
[6] V = 100*vo*t
[7] rc = 3*k2b*Cb
[8] rb = k1a*Ca/2 - k2b*Cb
```



Living Example Problem

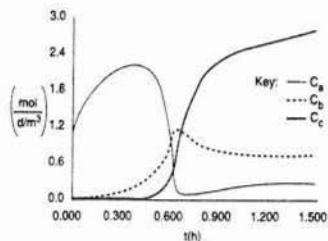


Figure E9-7.1 Concentration-time.

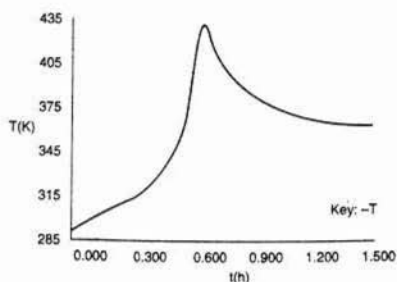


Figure E9-7.2 Temperature (K)-time (h).



Reference Shelf

Transient energy balance on a PFR

9.6 Unsteady Operation of Plug-Flow Reactors

In the CD-ROM, the unsteady energy balance is derived for a PFR. Neglecting changes in total pressure and shaft work, the following equation is derived:

$$Ua(T_a - T) - \left(\sum_{i=1}^n F_i C_{P_i} \right) \frac{\partial T}{\partial V} + (-r_A) [-\Delta H_{R_x}(T)] = \sum_{i=1}^n C_i C_{P_i} \frac{\partial T}{\partial t} \quad (9)$$

This equation must be coupled with the mole balances:

Numerical solution required for these three coupled equations

$$-\frac{\partial F_i}{\partial V} + v_i(-r_A) = \frac{\partial C_i}{\partial t} \quad (9)$$



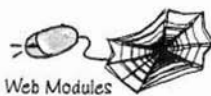
Reference Shelf

and the rate law,

$$-r_A = k(T) \cdot \text{fn}(C_i) \quad (9)$$

and solved numerically. A variety of numerical techniques for solving equations of this type can be found in the book *Applied Numerical Methods*.⁴

One can use FEMLAB to solve PFR and laminar flow reactors for time-dependent temperature and concentration profiles. See the FEMLAB problems and web module in Chapter 8 and on the FEMLAB CD-ROM enclosed with this book. A simpler approach would be to model the PFR as a number of CSTRs in series and then apply Equation (9-9) to each CSTR.



Web Modules

Closure. After completing this chapter, the reader should be able to apply the unsteady-state energy balance to CSTRs, semibatch and batch reactors. The reader should be able to discuss reactor safety using two examples: on a case study of an explosion and the other the use of the ARSST to help prevent explosions. Included in the reader's discussion should be how to start up a reactor so as not to exceed the practical stability limit. After reading these examples, the reader should be able to describe how to operate reactors in a safe manner for both single and multiple reactions.

⁴ B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods* (New York: Wiley, 1969).

SUMMARY

1. Unsteady operation of CSTRs and semibatch reactors

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum_{i=1}^n F_{i0} C_{P_i} (T - T_{i0}) + [-\Delta H_{R_x}(T)](-r_A V)}{\sum_{i=1}^n N_i C_{P_i}} \quad (\text{S9-1})$$

For large heat-exchanger coolant rates ($T_{a1} = T_{a2}$)

$$\dot{Q} = UA(T_a - T) \quad (\text{S9-2})$$

For moderate to low coolant rates

$$\dot{Q} = \dot{m}_c C_{P_c} (T - T_{a1}) \left[1 - \exp\left(-\frac{UA}{\dot{m}_c C_{P_c}}\right) \right] \quad (\text{S9-3})$$

2. Batch reactors

a. Nonadiabatic

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s + (-\Delta H_{R_x})(-r_A V)}{N_{A0}(\sum \Theta_i C_{P_i} + \Delta C_P X)} \quad (\text{S9-4})$$

Where \dot{Q} is given by either Equation (S9-2) or (S9-3).

b. Adiabatic

$$X = \frac{C_{P_s}(T - T_0)}{-\Delta H_{R_x}(T)} = \frac{\sum \Theta_i C_{P_i}(T - T_0)}{-\Delta H_{R_x}(T)} \quad (\text{S9-5})$$

$$T = T_0 + \frac{[-\Delta H_{R_x}(T_0)]X}{C_{P_s} + X \Delta C_P} = T_0 + \frac{[-\Delta H_{R_x}(T_0)]X}{\sum_{i=1}^n \Theta_i C_{P_i} + X \Delta C_P} \quad (\text{S9-6})$$

3. Startup of a CSTR (Figure S-1) and the approach to the steady state (CD-ROM). By mapping out regions of the concentration-temperature phase plane, one can view the approach to steady state and learn if the practical stability limit is exceeded.