

The Polymath code is modified by replacing $T_0 = 1150\text{K}$ in Tables E8-5.3 and E8-5.4 by Equation (E8-5.7), and adding the numerical values for \dot{m}_c and C_{p_c} .

TABLE E8-5.5. SUMMARY HEAT EXCHANGE WITH VARIABLE T_a **POLYMATH Results**

Example 8-5 Production of Acetic Anhydride with Heat Exchange (Variable T_a) 08-16-2004, Rev5.1.232

Differential equations as entered by the user

- [1] $d(X)/d(V) = -ra/Fao$
- [2] $d(T)/d(V) = (Ua*(Ta-T)+ra*\delta H)/(Fao*(Cpa+X*\delta C_p))$
- [3] $d(Ta)/d(V) = Ua*(T-Ta)/mc/Cpc$

Explicit equations as entered by the user

- [1] $Fao = .0376$
- [2] $Cpa = 163$
- [3] $\delta C_p = -9$
- [4] $Ca0 = 18.8$
- [5] $To = 1035$
- [6] $\delta H = 80770 + \delta C_p*(T-298)$
- [7] $ra = -Ca0*3.58*\exp(34222*(1/To - 1/T))*(1-X)*(To/T)/(1+X)$
- [8] $Ua = 16500$
- [9] $mc = .111$
- [10] $Cpc = 34.5$

PFR with
heat exchange
variable ambient
temperature T_a

The temperature and conversion profiles are shown in Figure E8-5.4.

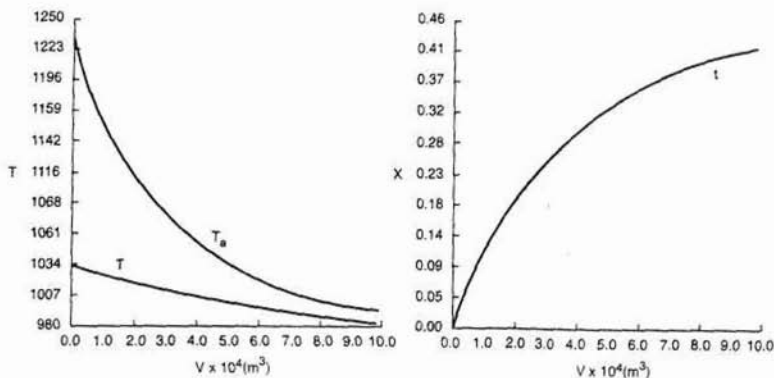


Figure E8-5.4 (a) Temperature and (b) conversion profiles in PFR with a variable heating medium temperature, T_a

8.5 Equilibrium Conversion

The highest conversion that can be achieved in reversible reactions is the equilibrium conversion. For endothermic reactions, the equilibrium conversion increases with increasing temperature up to a maximum of 1.0. For exothermic reactions, the equilibrium conversion decreases with increasing temperature.

For reversible reactions, the equilibrium conversion, X_e , is usually calculated first.

8.5.1 Adiabatic Temperature and Equilibrium Conversion

Exothermic Reactions. Figure 8-4(a) shows the variation of the concentration equilibrium constant as a function of temperature for an exothermic reaction (see Appendix C), and Figure 8-4(b) shows the corresponding equilibrium conversion X_e as a function of temperature. In Example 8-3, we saw that for a first-order reaction the equilibrium conversion could be calculated using Equation (E8-3.13)

First-order reversible
reaction

$$X_e = \frac{K_C}{1 + K_C} \quad (\text{E8-3.13})$$

Consequently, X_e can be calculated directly using Figure 8-4(a).

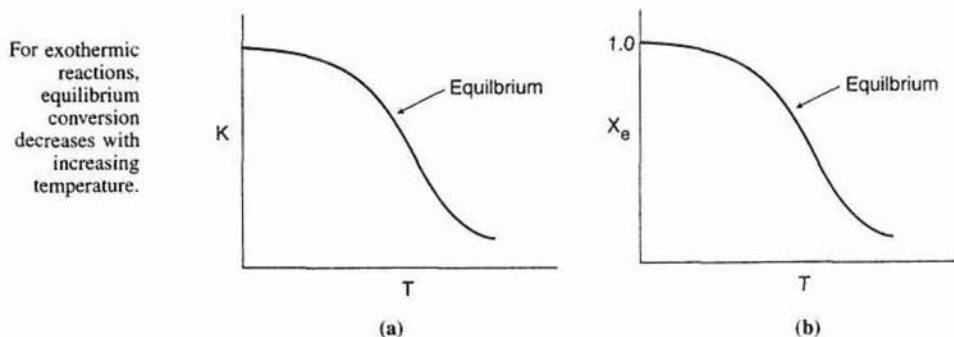


Figure 8-4 Variation of equilibrium constant and conversion with temperature for an exothermic reaction.

To determine the maximum conversion that can be achieved in an exothermic reaction carried out adiabatically, we find the intersection of the equilibrium conversion as a function of temperature [Figure 8-4(b)] with temperature–conversion relationships from the energy balance (Figure 8-2) as shown in Figure 8-5

$$X_{EB} = \frac{\sum \Theta_i C_{P_i} (T - T_0)}{-\Delta H_{R_x}(T)} \quad (8)$$

If the entering temperature is increased from T_0 to T_{01} , the energy balance line will be shifted to the right and will be parallel to the original line shown by the dashed line. Note that as the inlet temperature increases, the adiabatic equilibrium conversion decreases.

Adiabatic
equilibrium
conversion for
exothermic
reactions

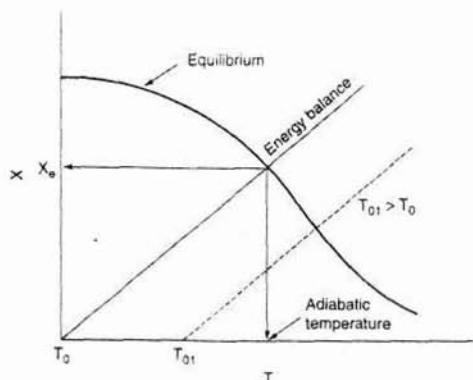
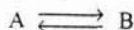


Figure 8-5 Graphical solution of equilibrium and energy balance equations to obtain the adiabatic temperature and the adiabatic equilibrium conversion X_e .

Example 8-6 Calculating the Adiabatic Equilibrium Temperature

For the elementary solid-catalyzed liquid-phase reaction



make a plot of equilibrium conversion as a function of temperature. Determine the adiabatic equilibrium temperature and conversion when pure A is fed to the reactor at a temperature of 300 K.

Additional information:

$$H_A^\circ(298 \text{ K}) = -40,000 \text{ cal/mol} \quad H_B^\circ(298 \text{ K}) = -60,000 \text{ cal/mol}$$

$$C_{P_A} = 50 \text{ cal/mol} \cdot \text{K} \quad C_{P_B} = 50 \text{ cal/mol} \cdot \text{K}$$

$$K_e = 100,000 \text{ at } 298 \text{ K}$$

Solution

1. Rate Law:

$$-r_A = k \left(C_A - \frac{C_B}{K_e} \right) \quad (\text{E8-6.1})$$

2. Equilibrium: $-r_A = 0$; so

$$C_{Ae} = \frac{C_{Be}}{K_e}$$

3. Stoichiometry: ($v = v_0$) yields

$$C_{A0}(1 - X_e) = \frac{C_{A0}X_e}{K_e}$$



Following the Algorithm

Solving for X_e gives

$$X_e = \frac{K_e(T)}{1 + K_e(T)} \quad (\text{E8-6.2})$$

4. Equilibrium Constant: Calculate ΔC_p , then $K_e(T)$

$$\Delta C_p = C_{p_B} - C_{p_A} = 50 - 50 = 0 \text{ cal/mol} \cdot \text{K}$$

For $\Delta C_p = 0$, the equilibrium constant varies with temperature according to the relation

$$K_e(T) = K_e(T_1) \exp \left[\frac{\Delta H_{R_x}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{E8-6.3})$$

$$\Delta H_{R_x}^\circ = H_B^\circ - H_A^\circ = -20,000 \text{ cal/mol}$$

$$K_e(T) = 100,000 \exp \left[\frac{-20,000}{1.987} \left(\frac{1}{298} - \frac{1}{T} \right) \right]$$

$$K_e = 100,000 \exp \left[-33.78 \left(\frac{T-298}{T} \right) \right] \quad (\text{E8-6.4})$$

Substituting Equation (E8-6.4) into (E8-6.2), we can calculate equilibrium conversion as a function of temperature:

5. Equilibrium Conversion from Thermodynamics

Conversion
calculated from
equilibrium
relationship

$$X_e = \frac{100,000 \exp[-33.78(T-298)/T]}{1 + 100,000 \exp[-33.78(T-298)/T]} \quad (\text{E8-6.5})$$

The calculations are shown in Table E8-6.1.

TABLE E8-6.1. EQUILIBRIUM CONVERSION
AS A FUNCTION OF TEMPERATURE

T	K_e	X_e
298	100,000.00	1.00
350	661.60	1.00
400	18.17	0.95
425	4.14	0.80
450	1.11	0.53
475	0.34	0.25
500	0.12	0.11

6. Energy Balance

For a reaction carried out adiabatically, the energy balance reduces to

$$X_{EB} = \frac{\sum \Theta_i C_{p_i} (T - T_0)}{-\Delta H_{R_x}} = \frac{C_{p_A} (T - T_0)}{-\Delta H_{R_x}} \quad (\text{E8-6.6})$$

Conversion
calculated from
energy balance

$$X_{EB} = \frac{50(T - 300)}{20,000} = 2.5 \times 10^{-3}(T - 300) \quad (\text{E8-6.7})$$

Data from Table E8-6.1 and the following data are plotted in Figure E8-6.1.

T (K)	300	400	500	600
X_{EB}	0	0.25	0.50	0.75

$$X_e = 0.42 \quad T_e = 465 \text{ K}$$

For a feed temperature of 300 K, the adiabatic equilibrium temperature is 465 K and the corresponding adiabatic equilibrium conversion is only 0.42.

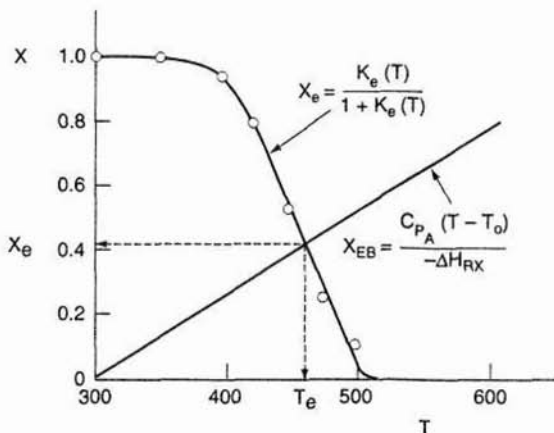


Figure E8-6.1 Finding the adiabatic equilibrium temperature (T_e) and conversion (X_e).

Reactor Staging with Interstate Cooling of Heating

Higher conversions than those shown in Figure E8-6.1 can be achieved for adiabatic operations by connecting reactors in series with interstage cooling:



The conversion–temperature plot for this scheme is shown in Figure 8-6. We see that with three interstage coolers 90% conversion can be achieved compared to an equilibrium conversion of 40% for no interstage cooling.

Adiabatic
equilibrium
conversion and
temperature

Interstage cooling used for exothermic reversible reactions

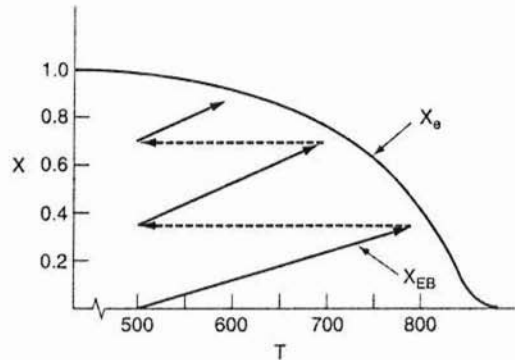
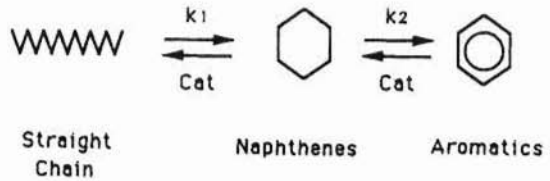


Figure 8-6 Increasing conversion by interstage cooling.

Typical values for gasoline composition

Gasoline	
C ₅	10%
C ₆	10%
C ₇	20%
C ₈	25%
C ₉	20%
C ₁₀	10%
C ₁₁ -C ₁₂	5%

Endothermic Reactions. Another example of the need for interstage transfer in a series of reactors can be found when upgrading the octane number of gasoline. The more compact the hydrocarbon molecule for a given number of carbon atoms is, the higher the octane rating is. Consequently, it is desirable to convert straight-chain hydrocarbons to branched isomers, naphthenes, aromatics. The reaction sequence is



The first reaction step (k_1) is slow compared to the second step, and this step is highly endothermic. The allowable temperature range for which this reaction can be carried out is quite narrow: Above 530°C undesirable side reactions occur, and below 430°C the reaction virtually does not take place. A typical stock might consist of 75% straight chains, 15% naphthas, and 10% aromatics.

One arrangement currently used to carry out these reactions is shown in Figure 8-7. Note that the reactors are not all the same size. Typical sizes are on the order of 10 to 20 m high and 2 to 5 m in diameter. A typical feed rate for gasoline is approximately 200 m³/h at 2 atm. Hydrogen is usually separated from the product stream and recycled.

Spring 2005
\$2.20/gal for octane
number (ON)
ON = 89

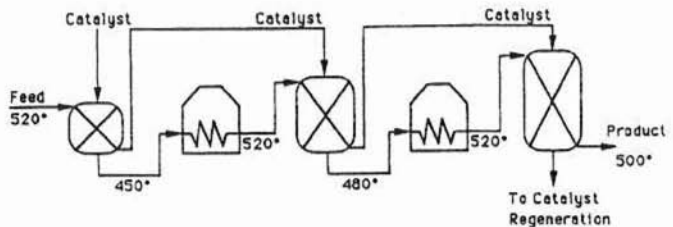


Figure 8-7 Interstage heating for gasoline production in moving-bed reactors.

Because the reaction is endothermic, equilibrium conversion increases with increasing temperature. A typical equilibrium curve and temperature-conversion trajectory for the reactor sequence are shown in Figure 8-8.

Interstage heating

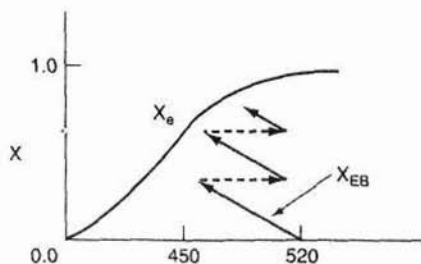


Figure 8-8 Temperature-conversion trajectory for interstage heating of an endothermic reaction analogous to Figure 8-6.

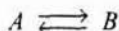
Example 8-7 Interstage Cooling for Highly Exothermic Reactions

What conversion could be achieved in Example 8-6 if two interstage coolers that had the capacity to cool the exit stream to 350 K were available? Also determine the heat duty of each exchanger for a molar feed rate of A of 40 mol/s. Assume that 95% of equilibrium conversion is achieved in each reactor. The feed temperature to the first reactor is 300 K.

Solution

1. Calculate Exit Temperature

We saw in Example 8-6



that for an entering temperature of 300 K the adiabatic equilibrium conversion was 0.42. For 95% of equilibrium conversion ($X_c = 0.42$), the conversion exiting the first reactor is 0.4. The exit temperature is found from a rearrangement of Equation (E8-6.7):

$$T = 300 + 400X = 300 + (400)(0.4) \quad (\text{A})$$

$$T_1 = 460 \text{ K}$$

We now cool the gas stream exiting the reactor at 460 K down to 350 K in a heat exchanger (Figure E8-7.2).

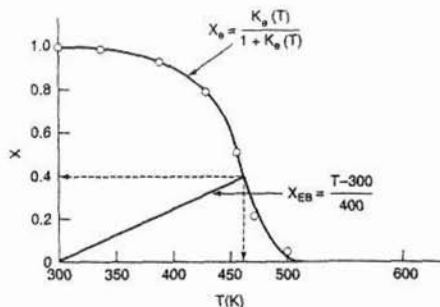


Figure E8-7.1 Determining exit conversion and temperature in the first stage.

2. Calculate the Heat Load

There is no work done on the reaction gas mixture in the exchanger, and the reaction does not take place in the exchanger. Under these conditions ($F_{i|in} = F_{i|out}$), the energy balance given by Equation (8-10)

$$\dot{Q} - \dot{W}_s + \sum F_{i0}H_{i0} - \sum F_iH_i = 0 \quad (8-10)$$

for $\dot{W}_s = 0$ becomes

$$\dot{Q} = \sum F_iH_i - \sum F_{i0}H_{i0} = \sum F_{i0}(H_i - H_{i0}) \quad (E8-7.1)$$

$$= \sum F_iC_{p_i}(T_2 - T_1) = (F_A C_{p_A} + F_B C_{p_B})(T_2 - T_1) \quad (E8-7.2)$$

But $C_{p_A} = C_{p_B}$,

$$\dot{Q} = (F_A + F_B)(C_{p_A})(T_2 - T_1) \quad (E8-7.3)$$

Also, $F_{A0} = F_A + F_B$,

$$\begin{aligned} \dot{Q} &= F_{A0}C_{p_A}(T_2 - T_1) \\ &= \frac{40 \text{ mol}}{\text{s}} \cdot \frac{50 \text{ cal}}{\text{mol} \cdot \text{K}} (350 - 460) \text{ K} \\ &= -220 \frac{\text{kcal}}{\text{s}} \end{aligned} \quad (E8-7.4)$$

That is, 220 kcal/s must be removed to cool the reacting mixture from 460 K to 350 K for a feed rate of 40 mol/s.

3. Calculate the Coolant Flow Rate

We see that 220 kcal/s is removed from the reaction system mixture. The rate at which energy must be absorbed by the coolant stream in the exchanger is

$$\dot{Q} = \dot{m}_c C_{p_c} (T_{out} - T_{in}) \quad (E8-7.5)$$

We consider the case where the coolant is available at 270 K but cannot be heated above 400 K and calculate the coolant flow rate necessary to remove 220 kcal/s from the reaction mixture. Rearranging Equation (E8-7.5) and noting that this coolant has a heat capacity of 18 cal/mol·K gives

$$\begin{aligned} \dot{m}_c &= \frac{\dot{Q}}{C_{p_c} (T_{out} - T_{in})} = \frac{220,000 \text{ cal/s}}{18 \frac{\text{cal}}{\text{mol} \cdot \text{K}} (400 - 270) \text{ K}} \\ &= 94 \text{ mol/s} = 1692 \text{ g/s} = 1.69 \text{ kg/s} \end{aligned} \quad (E8-7.6)$$

The necessary coolant flow rate is 1.69 kg/s.

4. Calculate the Heat Exchanger Area

Let's next determine the counter current heat exchanger area. The exchanger inlet and outlet temperatures are shown in Figure E8-7.2. The rate of heat transfer in a counter current heat exchanger is given by the equation⁵

Energy balance on the reaction gas mixture in the heat exchanger

Sizing the interstage heat exchanger and coolant flow rate

⁵ See page 268 of C. J. Geankoplis, *Transport Processes and Unit Operations* (Upper Saddle River, N.J.: Prentice Hall, 1993).

Bonding with unit operations

$$\dot{Q} = UA \frac{[(T_{h2} - T_{c2}) - (T_{h1} - T_{c1})]}{\ln \left(\frac{T_{h2} - T_{c2}}{T_{h1} - T_{c1}} \right)} \quad (\text{E8-7.7})$$

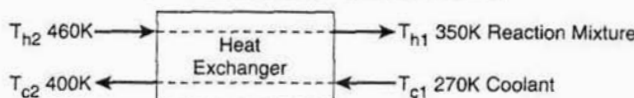


Figure E8-7.2 Counter current heat exchanger.

Rearranging Equation (E8-7.7), assuming a value of U of $100 \text{ cal/s} \cdot \text{m}^2 \cdot \text{K}$, and then substituting the appropriate values gives

Sizing the heat exchanger

$$A = \frac{\dot{Q} \ln \left(\frac{T_{h2} - T_{c2}}{T_{h1} - T_{c1}} \right)}{U [(T_{h2} - T_{c2}) - (T_{h1} - T_{c1})]} = \frac{220,000 \frac{\text{cal}}{\text{s}} \ln \left(\frac{460 - 400}{350 - 270} \right)}{100 \frac{\text{cal}}{\text{s} \cdot \text{m}^2 \cdot \text{K}} [(460 - 400) - (350 - 270)] \text{K}}$$

$$= \frac{2,200 \ln(0.75)}{-20} \text{m}^2$$

$$= 31.6 \text{m}^2$$

The heat-exchanger surface area required to accomplish this rate of heat transfer is 31.6 m^2 .

5. Second Reactor

Now let's return to determine the conversion in the second reactor. The conditions entering the second reactor are $T = 350 \text{ K}$ and $X = 0.4$. The energy balance starting from this point is shown in Figure E8-7.3. The corresponding adiabatic equilibrium conversion is 0.63 . Ninety-five percent of the equilibrium conversion is 60% and the corresponding exit temperature is $T = 350 + (0.6 - 0.4)400 = 430 \text{ K}$.

The heat-exchange duty to cool the reacting mixture from 430 K back to 350 K can again be calculated from Equation (E8-7.4):

Rearranging Equation (E8-6.7) for the second reactor

$$T_2 = T_{20} + \Delta X \left(\frac{-\Delta H_{R_X}}{C_{P_A}} \right)$$

$$= 350 + 400\Delta X$$

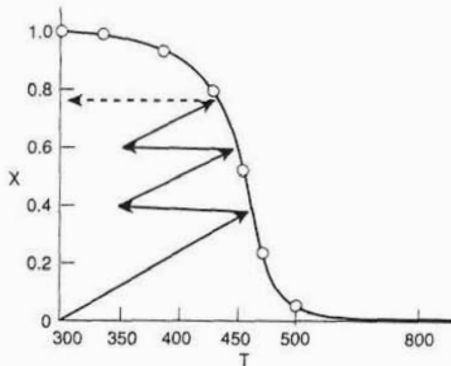


Figure E8-7.3 Three reactors in series with interstage cooling.

$$\begin{aligned}\dot{Q} &= F_{A0}C_{pA}(350 - 430) = \left(\frac{40 \text{ mol}}{\text{s}}\right)\left(\frac{50 \text{ cal}}{\text{mol} \cdot \text{K}}\right)(-80) \\ &= -160 \frac{\text{kcal}}{\text{s}}\end{aligned}$$

6. Subsequent Reactors

For the final reactor we begin at $T_0 = 350$ K and $X = 0.6$ and follow the line representing the equation for the energy balance along to the point of intersection with the equilibrium conversion, which is $X = 0.8$. Consequently, the final conversion achieved with three reactors and two interstage coolers is $(0.95)(0.8) = 0.76$.

8.5.2 Optimum Feed Temperature

We now consider an adiabatic reactor of fixed size or catalyst weight and investigate what happens as the feed temperature is varied. The reaction is reversible and exothermic. At one extreme, using a very high feed temperature, the specific reaction rate will be large and the reaction will proceed rapidly, but equilibrium conversion will be close to zero. Consequently, very little product will be formed. At the other extreme of low feed temperatures, little product will be formed because the reaction rate is so low. A plot of the equilibrium conversion and the conversion calculated from the adiabatic energy balance shown in Figure 8-9. We see that for an entering temperature of 600 K the adiabatic equilibrium conversion is 0.15. The corresponding conversion produced down the the length of the reactor are shown in Figure 8-10. The equilibrium conversion, which can be calculated from an equation similar to Equation (E8-1) also varies along the length of the reactor as shown by the dashed line in Figure 8-10. We also see that because of the high entering temperature, the rate is very rapid and equilibrium is achieved very near the reactor entrance.

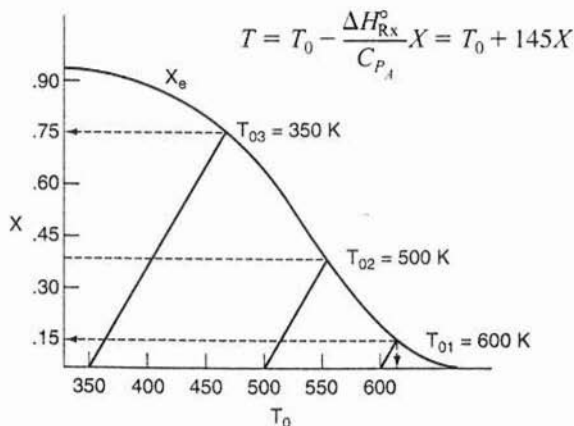


Figure 8-9 Equilibrium conversion for different feed temperatures.

Observe how the temperature profile changes as the entering temperature is decreased from 600 K.

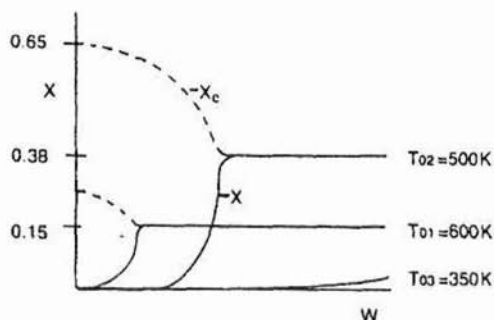


Figure 8-10 Adiabatic conversion profiles for different feed temperatures.

We notice that the conversion and temperature increase very rapidly over a short distance (i.e., a small amount of catalyst). This sharp increase is sometimes referred to as the “point” or temperature at which the reaction ignites. If the inlet temperature were lowered to 500 K, the corresponding equilibrium conversion is increased to 0.38; however, the reaction rate is slower at this lower temperature so that this conversion is not achieved until closer to the end of the reactor. If the entering temperature were lowered further to 350 K, the corresponding equilibrium conversion is 0.75, but the rate is so slow that a conversion of 0.05 is achieved for the specified catalyst weight in the reactor. At a very low feed temperature, the specific reaction rate will be so small that virtually all of the reactant will pass through the reactor without reacting. It is apparent that with conversions close to zero for both high and low feed temperatures there must be an optimum feed temperature that maximizes conversion. As the feed temperature is increased from a very low value, the specific reaction rate will increase, as will the conversion. The conversion will continue to increase with increasing feed temperature until the equilibrium conversion is approached in the reaction. Further increases in feed temperature for this exothermic reaction will only decrease the conversion due to the decreasing equilibrium conversion. This optimum inlet temperature is shown in Figure 8-11.

Optimum inlet temperature

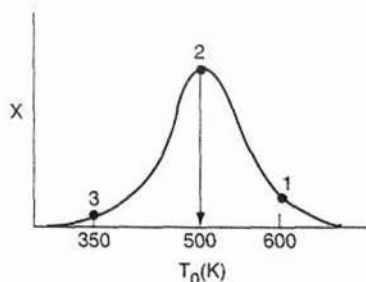


Figure 8-11 Finding the optimum feed temperature.

8.6 CSTR with Heat Effects

In this section we apply the general energy balance [Equation (8-22)] to the CSTR at steady state. We then present example problems showing how the mole and energy balances are combined to size reactors operating adiabatically and non-adiabatically.

Substituting Equation (8-26) into Equation (8-22), the steady-state energy balance becomes

$$\dot{Q} - \dot{W}_s - F_{A0} \sum \Theta_i C_{P_i} (T - T_{i0}) - [\Delta H_{R_x}^{\circ}(T_R) + \Delta C_P (T - T_R)] F_{A0} X = 0 \quad (8-27)$$

These are the forms of the steady-state balance we will use.

[Note: In many calculations the CSTR mole balance ($F_{A0}X = -r_A V$) will be used to replace the term following the brackets in Equation (8-27), that is, ($F_{A0}X$) will be replaced by ($-r_A V$).] Rearranging yields the steady-state balance

$$\dot{Q} - \dot{W}_s - F_{A0} \sum \Theta_i C_{P_i} (T - T_{i0}) + (r_A V)(\Delta H_{R_x}) = 0 \quad (8-42)$$

Although the CSTR is well mixed and the temperature is uniform throughout the reaction vessel, these conditions do not mean that the reaction is carried out isothermally. Isothermal operation occurs when the feed temperature is identical to the temperature of the fluid inside the CSTR.

The \dot{Q} Term in the CSTR

8.6.1 Heat Added to the Reactor, \dot{Q}

Figure 8-12 shows schematics of a CSTR with a heat exchanger. The heat transfer fluid enters the exchanger at a mass flow rate \dot{m}_c (e.g., kg/s) at a temperature T_{a1} and leaves at a temperature T_{a2} . The rate of heat transfer from the exchanger to the reactor is⁶

$$\dot{Q} = \frac{UA(T_{a1} - T_{a2})}{\ln[(T - T_{a1})/(T - T_{a2})]} \quad (8-43)$$

For exothermic reactions
($T > T_{a2} > T_{a1}$)

For endothermic reactions
($T_{1a} > T_{2a} > T$)

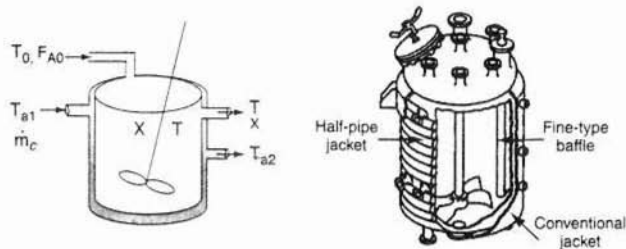


Figure 8-12 CSTR tank reactor with heat exchanger. [(b) Courtesy of Pfaunder, Inc.]

⁶ Information on the overall heat-transfer coefficient may be found in C. J. Geankoplis, *Transport Processes and Unit Operations*, 3rd ed. Englewood Cliffs, N.J., Prentice Hall (2003), p. 268.

The following derivations, based on a coolant (exothermic reaction) apply also to heating mediums (endothermic reaction). As a first approximation, we assume a quasi-steady state for the coolant flow and neglect the accumulation term (i.e., $dT_a/dt = 0$). An energy balance on the coolant fluid entering and leaving the exchanger is

Energy balance on
heat exchanger

$$\left[\begin{array}{c} \text{Rate of} \\ \text{energy} \\ \text{in} \\ \text{by flow} \end{array} \right] - \left[\begin{array}{c} \text{Rate of} \\ \text{energy} \\ \text{out} \\ \text{by flow} \end{array} \right] - \left[\begin{array}{c} \text{Rate of} \\ \text{heat transfer} \\ \text{from exchanger} \\ \text{to reactor} \end{array} \right] = 0 \quad (8-44)$$

$$\dot{m}_c C_{p_c} (T_{a1} - T_R) - \dot{m}_c C_{p_c} (T_{a2} - T_R) - \frac{UA(T_{a1} - T_{a2})}{\ln(T - T_{a1})/(T - T_{a2})} = 0 \quad (8-45)$$

where C_{p_c} is the heat capacity of the coolant fluid and T_R is the reference temperature. Simplifying gives us

$$\dot{Q} = \dot{m}_c C_{p_c} (T_{a1} - T_{a2}) = \frac{UA(T_{a1} - T_{a2})}{\ln(T - T_{a1})/(T - T_{a2})} \quad (8-46)$$

Solving Equation (8-46) for the exit temperature of the coolant fluid yields

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

From Equation (8-46)

$$\dot{Q} = \dot{m}_c C_{p_c} (T_{a1} - T_{a2}) \quad (8-48)$$

Substituting for T_{a2} in Equation (8-48), we obtain

Heat transfer to a
CSTR

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

For large values of the coolant flow rate, the exponent will be small and can be expanded in a Taylor series ($e^{-x} = 1 - x + \dots$) where second-order terms are neglected in order to give

$$\dot{Q} = \dot{m}_c C_{p_c} (T_{a1} - T) \left[1 - \left(1 - \frac{UA}{\dot{m}_c C_{p_c}} \right) \right]$$

Then

Valid only for large
coolant flow rates!!

$$\dot{Q} = UA(T_a - T) \quad (8-50)$$

where $T_{a1} \cong T_{a2} = T_a$.

With the exception of processes involving highly viscous materials such as Problem P8-4c, the California P.E exam problem, the work done by the reactor can usually be neglected. Setting W_s in (8-27) to zero, neglecting ΔC_p , substituting for \dot{Q} and rearranging, we have the following relationship between conversion and temperature in a CSTR.

$$\frac{UA}{F_{A0}}(T_a - T) - \sum \Theta_i C_{p_i} (T - T_0) - \Delta H_{Rx}^\circ X = 0 \quad (8-51)$$

Solving for X

$$X = \frac{\frac{UA}{F_{A0}}(T - T_a) + \sum \Theta_i C_{p_i} (T - T_0)}{[-\Delta H_{Rx}^\circ(T_R)]} \quad (8-52)$$

Equation (8-52) is coupled with the mole balance equation

$$V = \frac{F_{A0} X}{-r_A(X, T)} \quad (8-53)$$

to size CSTRs.

We now will further rearrange Equation (8-51) after letting $\sum \Theta_i C_{p_i} = C_{p_0}$

$$\boxed{\sum \Theta_i C_{p_i} = C_{p_0}} \quad C_{p_0} \left(\frac{UA}{F_{A0} C_{p_0}} \right) T_a + C_{p_0} T_0 - C_{p_0} \left(\frac{UA}{F_{A0} C_{p_0}} + 1 \right) T - \Delta H_{Rx}^\circ X = 0$$

Let

$$\boxed{\kappa = \frac{UA}{F_{A0} C_{p_0}} \text{ and } T_c = \frac{\kappa T_a + T_0}{1 + \kappa}}$$

Then

$$-X \Delta H_{Rx}^\circ = C_{p_0} (1 + \kappa) (T - T_c) \quad (8-54)$$

The parameters κ and T_c are used to simplify the equations for non-adiabatic operation. Solving Equation (8-54) for conversion

$$X = \frac{C_{p_0} (1 + \kappa) (T - T_c)}{-\Delta H_{Rx}^\circ} \quad (8-55)$$

Solving Equation (8-54) for the reactor temperature

$$T = T_c + \frac{(-\Delta H_{Rx}^\circ)(X)}{C_{p_0} (1 + \kappa)} \quad (8-56)$$

Forms of the energy balance for a CSTR with heat exchange

Figure 8-13 and Table 8-4 show three ways to specify the sizing of a CSTR. This procedure for nonisothermal CSTR design can be illustrated considering a first-order irreversible liquid-phase reaction. The algorithm working through either case A (X specified), B (T specified), or C (V specified) is shown in Table 8-4. Its application is illustrated in the following example.

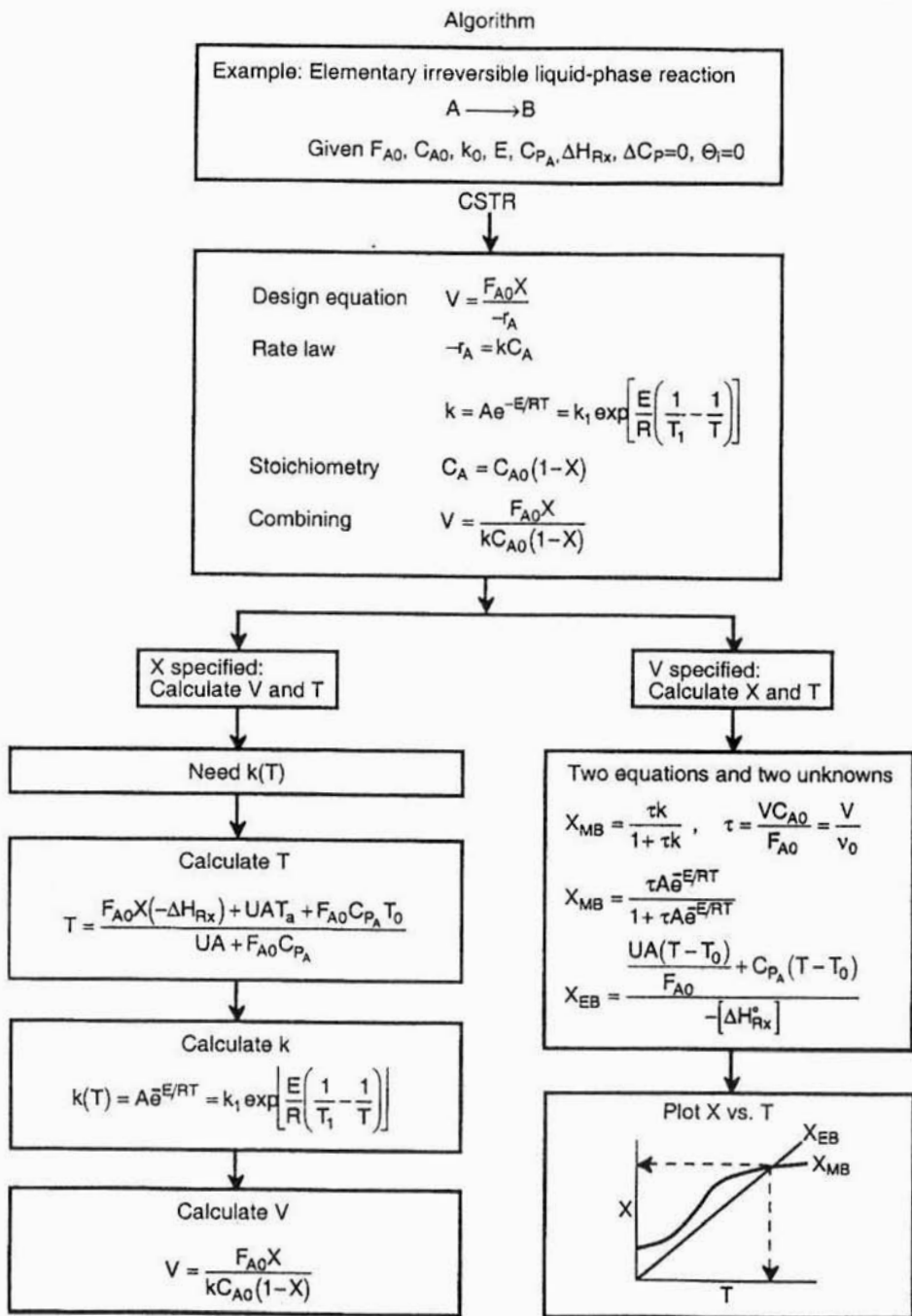
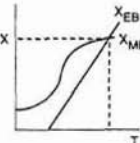


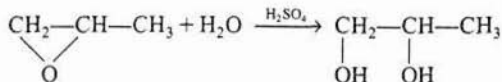
Figure 8-13 Algorithm for adiabatic CSTR design.

TABLE 8-4. WAYS TO SPECIFY THE SIZING A CSTR

A	B	C
Specify X Find V and T	Specify T Find X and V	Specify V Find X and T
↓ Calculate T From Eqn. (8-56)	↓ Calculate X From Eqn. (8-55)	↓ Use Eqn. (8-55) to plot X_{EB} vs. T
↓ Calculate k $k = Ae^{-E/RT}$	↓ Calculate k $k = Ae^{-E/RT}$	↓ Solve Eqn. (8-53) for $X_{MB} = f(T)$ to find X_{MB} vs. T (e.g., $X_{MB} =$
(e.g., $-r_A = kC_{A0}(1 - X)$)	(e.g., $-r_A = kC_{A0}(1 - X)$)	$\frac{\tau A \exp[-E/(RT)]}{1 + \tau A \exp[-E/(RT)]}$)
↓	↓	↓ Plot X_{EB} and X_{MB} as a function of T
Calculate $-r_A(X, T)$	Calculate $-r_A(X, T)$	↓ 
↓ Calculate V	↓ Calculate V	
$V = \frac{F_{A0}X}{-r_A}$	$V = \frac{F_{A0}X}{-r_A}$	
X_{MB} = conversion calculated from the mole balance X_{EB} = conversion calculated from the energy balance		

Example 8-8 Production of Propylene Glycol in an Adiabatic CSTR

Propylene glycol is produced by the hydrolysis of propylene oxide:



Over 800 million pounds of propylene glycol were produced in 2004 and the selling price was approximately \$0.68 per pound. Propylene glycol makes up about 25% of the major derivatives of propylene oxide. The reaction takes place readily at room temperature when catalyzed by sulfuric acid.

You are the engineer in charge of an adiabatic CSTR producing propylene glycol by this method. Unfortunately, the reactor is beginning to leak, and you must replace it. (You told your boss several times that sulfuric acid was corrosive and that mild steel was a poor material for construction.) There is a nice-looking overflow CSTR of 300-gal capacity standing idle; it is glass-lined, and you would like to use it.

You are feeding 2500 lb/h (43.04 lb mol/h) of propylene oxide (P.O.) to the reactor. The feed stream consists of (1) an equivolometric mixture of propylene oxide (46.62 ft³/h) and methanol (46.62 ft³/h), and (2) water containing 0.1 wt % H₂SO₄. The volumetric flow rate of water is 233.1 ft³/h, which is 2.5 times the methanol-P.O. flow rate. The corresponding molar feed rates of methanol and water are 71.87 and 802.8 lb mol/h, respectively. The water-propylene oxide-methanol mixture undergoes a slight decrease in volume upon mixing

(approximately 3%), but you neglect this decrease in your calculations. The temperature of both feed streams is 58°F prior to mixing, but there is an immediate 17°F temperature rise upon mixing of the two feed streams caused by the heat of mixing. The entering temperature of all feed streams is thus taken to be 75°F (Figure E8-8.1).

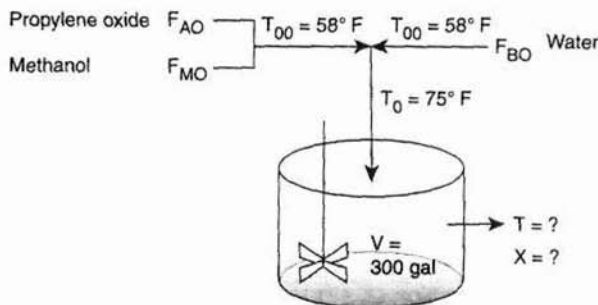


Figure E8-8.1

Furusawa et al.⁷ state that under conditions similar to those at which you are operating, the reaction is first-order in propylene oxide concentration and apparent zero-order in excess of water with the specific reaction rate

$$k = Ae^{-E/RT} = 16.96 \times 10^{12} (e^{-32,400/RT}) \text{ h}^{-1}$$

The units of E are Btu/lb mol.

There is an important constraint on your operation. Propylene oxide is a rather low-boiling substance. With the mixture you are using, you feel that you cannot exceed an operating temperature of 125°F, or you will lose too much oxide by vaporization through the vent system.

Can you use the idle CSTR as a replacement for the leaking one if it will be operated adiabatically? If so, what will be the conversion of oxide to glycol?

Solution

(All data used in this problem were obtained from the *Handbook of Chemistry and Physics* unless otherwise noted.) Let the reaction be represented by



where

A is propylene oxide ($C_{p_A} = 35 \text{ Btu/lb mol} \cdot ^\circ\text{F}$)⁸

B is water ($C_{p_B} = 18 \text{ Btu/lb mol} \cdot ^\circ\text{F}$)

⁷ T. Furusawa, H. Nishimura, and T. Miyauchi, *J. Chem. Eng. Jpn.*, 2, 95 (1969).

⁸ C_{p_A} and C_{p_C} are estimated from the observation that the great majority of low-molecular-weight oxygen-containing organic liquids have a mass heat capacity of $0.6 \text{ cal/g} \cdot ^\circ\text{C} \pm 15\%$.

C is propylene glycol ($C_{p_C} = 46 \text{ Btu/lb mol} \cdot ^\circ\text{F}$)

M is methanol ($C_{p_M} = 19.5 \text{ Btu/lb mol} \cdot ^\circ\text{F}$)

In this problem neither the exit conversion nor the temperature of the adiabatic reactor is given. By application of the material and energy balances we solve two equations with two unknowns (X and T). Solving these coupled equations we determine the exit conversion and temperature for the glass-lined reactor to see if it can be used to replace the present reactor.

1. Mole Balance and design equation:

$$F_{A0} - F_A + r_A V = 0$$

The design equation in terms of X is

$$V = \frac{F_{A0} X}{-r_A} \quad (\text{E8-8.4})$$

2. Rate Law:

$$-r_A = k C_A \quad (\text{E8-8.5})$$

3. Stoichiometry (liquid phase, $v = v_0$):

$$C_A = C_{A0}(1 - X) \quad (\text{E8-8.6})$$

4. Combining yields

$$V = \frac{F_{A0} X}{k C_{A0}(1 - X)} = \frac{v_0 X}{k(1 - X)} \quad (\text{E8-8.7})$$

Solving for X as a function of T and recalling that $\tau = V/v_0$ gives

$$X_{\text{MB}} = \frac{\tau k}{1 + \tau k} = \frac{\tau A e^{-E/RT}}{1 + \tau A e^{-E/RT}} \quad (\text{E8-8.8})$$

This equation relates temperature and conversion through the mole balance.

5. The energy balance for this adiabatic reaction in which there is negligible energy input provided by the stirrer is

$$X_{\text{EB}} = \frac{\sum \Theta_i C_{p_i} (T - T_{i0})}{-[\Delta H_{\text{Rx}}^\circ(T_R) + \Delta C_p (T - T_R)]} \quad (\text{E8-8.9})$$

This equation relates X and T through the energy balance. We see that Equations [Equations (E8-8.5) and (E8-8.6)] must be solved with $X_{\text{MB}} = X_{\text{EB}} = X$ for the two unknowns, X and T .

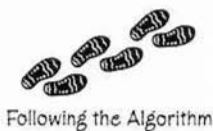
6. Calculations:

a. Heat of reaction at temperature T :⁹

$$\Delta H_{\text{Rx}}(T) = \Delta H_{\text{Rx}}^\circ(T_R) + \Delta C_p (T - T_R) \quad (\text{E8-8.10})$$

$$H_A^\circ(68^\circ\text{F}) : -66,600 \text{ Btu/lb mol}$$

⁹ H_A° and H_C° are calculated from heat-of-combustion data.



Following the Algorithm

Two equations,
two unknown

Calculating the parameter values

$$\begin{aligned} &\Delta H_{R_x} \\ &\Delta \hat{C}_p \\ &v_0 \\ &\tau \\ &C_{A0} \\ &\theta_M \\ &\theta_B \\ &\sum_{i=1}^n C_{p_i} \theta_i \end{aligned}$$

$$H_B^{\circ}(68^{\circ}\text{F}) : -123,000 \text{ Btu/lb mol}$$

$$H_C^{\circ}(68^{\circ}\text{F}) : -226,000 \text{ Btu/lb mol}$$

$$\Delta H_{R_x}^{\circ}(68^{\circ}\text{F}) = -226,000 - (-123,000) - (-66,600) \quad (\text{E8-8.7})$$

$$= -36,400 \text{ Btu/lb mol propylene oxide}$$

$$\Delta C_p = C_{p_C} - C_{p_B} - C_{p_A}$$

$$= 46 - 18 - 35 = -7 \text{ Btu/lb mol} \cdot ^{\circ}\text{F}$$

$$\Delta H_{R_x}^{\circ}(T) = -36,400 - (7)(T - 528) \quad T \text{ is in } ^{\circ}\text{R}$$

b. *Stoichiometry* (C_{A0} , Θ_i , τ): The total liquid volumetric flow rate entering the reactor is

$$\begin{aligned} v_0 &= v_{A0} + v_{M0} + v_{B0} \\ &= 46.62 + 46.62 + 233.1 = 326.3 \text{ ft}^3/\text{h} \end{aligned} \quad (\text{E8-8.8})$$

$$V = 300 \text{ gal} = 40.1 \text{ ft}^3$$

$$\tau = \frac{V}{v_0} = \frac{40.1 \text{ ft}^3}{326.3 \text{ ft}^3/\text{h}} = 0.123 \text{ h}$$

$$\begin{aligned} C_{A0} &= \frac{F_{A0}}{v_0} = \frac{43.0 \text{ lb mol/h}}{326.3 \text{ ft}^3/\text{h}} \\ &= 0.132 \text{ lb mol/ft}^3 \end{aligned} \quad (\text{E8-8.9})$$

$$\text{For methanol: } \Theta_M = \frac{F_{M0}}{F_{A0}} = \frac{71.87 \text{ lb mol/h}}{43.0 \text{ lb mol/h}} = 1.67$$

$$\text{For water: } \Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{802.8 \text{ lb mol/h}}{43.0 \text{ lb mol/h}} = 18.65$$

c. *Evaluate mole balance terms*: The conversion calculated from the mole balance, X_{MB} , is found from Equation (E8-8.5).

$$X_{MB} = \frac{(16.96 \times 10^{12} \text{ h}^{-1})(0.1229 \text{ h}) \exp(-32,400/1.987T)}{1 + (16.96 \times 10^{12} \text{ h}^{-1})(0.1229 \text{ h}) \exp(-32,400/1.987T)} \quad (\text{E8-8.10})$$

$$X_{MB} = \frac{(2.084 \times 10^{12}) \exp(-16,306/T)}{1 + (2.084 \times 10^{12}) \exp(-16,306/T)}, \quad T \text{ is in } ^{\circ}\text{R}$$

d. *Evaluate energy balance terms*:

$$\begin{aligned} \sum \Theta_i C_{p_i} &= C_{p_A} + \Theta_B C_{p_B} + \Theta_M C_{p_M} \\ &= 35 + (18.65)(18) + (1.67)(19.5) \\ &= 403.3 \text{ Btu/lb mol} \cdot ^{\circ}\text{F} \end{aligned}$$

$$\begin{aligned} T_0 &= T_{00} + \Delta T_{\text{mix}} = 58^{\circ}\text{F} + 17^{\circ}\text{F} = 75^{\circ}\text{F} \\ &= 535^{\circ}\text{R} \end{aligned} \quad (\text{E8-8.11})$$

$$T_R = 68^{\circ}\text{F} = 528^{\circ}\text{R}$$

Plot X_{MB} as a function of temperature.

The conversion calculated from the energy balance, X_{EB} , for an adiabatic reaction is given by Equation (8-29):

$$X_{EB} = -\frac{\sum \Theta_i C_{p_i} (T - T_{i0})}{\Delta H_{R_x}^{\circ} (T_R) + \Delta C_p (T - T_R)} \quad (8-29)$$

Substituting all the known quantities into the energy balances gives us

$$X_{EB} = \frac{(403.3 \text{ Btu/lb mol} \cdot ^{\circ}\text{F})(T - 535)^{\circ}\text{F}}{-[-36,400 - 7(T - 528)] \text{ Btu/lb mol}}$$

$$\boxed{X_{EB} = \frac{403.3(T - 535)}{36,400 + 7(T - 528)}} \quad (\text{E8-8.12})$$

7. **Solving.** There are a number of different ways to solve these two simultaneous equations. The easiest way is to use the Polymath nonlinear equation solver. However, to give insight into the functional relationship between X and T for the mole and energy balances, we shall obtain a graphical solution. Here X is plotted as a function of T for the mole and energy balances, and the intersection of the two curves gives the solution where both the mole and energy balance solutions are satisfied. In addition, by plotting these two curves we can learn if there is more than one intersection (i.e., multiple steady states) for which both the energy balance and mole balance are satisfied. If numerical root-finding techniques were used to solve for X and T , it would be quite possible to obtain only one root when there are actually more than one. If Polymath were used, you could learn if multiple roots exist by changing your initial guesses in the nonlinear equation solver. We shall discuss multiple steady states further in Section 8.7. We choose T and then calculate X (Table E8-8.1). The calculations are plotted in Figure E8-8.2. The virtually straight line corresponds to the energy balance [Equation (E8-8.12)] and the curved line corresponds to the mole balance [Equation (E8-8.10)]. We observe from this plot that the only intersection point is at 85% conversion and 613°R. At this point, both the energy balance and mole balance are satisfied. Because the temperature must remain below 125°F (585°R), we cannot use the 300-gal reactor as it is now.

TABLE E8-8.1

T (°R)	X_{MB} [Eq. (E8-8.10)]	X_{EB} [Eq. (E8-8.12)]
535	0.108	0.000
550	0.217	0.166
565	0.379	0.330
575	0.500	0.440
585	0.620	0.550
595	0.723	0.656
605	0.800	0.764
615	0.860	0.872
625	0.900	0.980

Don't give up! Head back to the storage shed to check out the heat exchange equipment!