Chapter 9

Temperature and Pressure Effects

In our search for favorable conditions for reaction we have considered how reactor type and size influence the extent of conversion and distribution of products. The reaction temperature and pressure also influence the progress of reactions, and it is the role of these variables that we now consider.

We follow a three-step procedure: First, we must find how equilibrium composition, rate of reaction, and product distribution are affected by changes in operating temperatures and pressures. This will allow us to determine the optimum temperature progression, and it is this that we strive to approximate with a real design. Second, chemical reactions are usually accompanied by heat effects, and we must know how these will change the temperature of the reacting mixture. With this information we are able to propose a number of favorable reactor and heat exchange systems—those which closely approach the optimum. Finally, economic considerations will select one of these favorable systems as the best.

So, with the emphasis on finding the optimum conditions and then seeing how best to approach them in actual design rather than determining what specific reactors will do, let us start with discussions of single reactions and follow this with the special considerations of multiple reactions.

9.1 SINGLE REACTIONS

With single reactions we are concerned with conversion level and reactor stability. Questions of product distribution do not occur.

Thermodynamics gives two important pieces of information, the first being the heat liberated or absorbed for a given extent of reaction, the second being the maximum possible conversion. Let us briefly summarize these findings. A justification of the expressions to follow can be found in any standard thermodynamics texts for chemical engineers.

Heats of Reaction from Thermodynamics

The heat liberated or absorbed during reaction at temperature T_2 depends on the nature of the reacting system, the amount of material reacting, and the

temperature and pressure of the reacting system, and is calculated from the heat of reaction ΔH_r, for the reaction in question. When this is not known, it can in most cases be calculated from known and tabulated thermochemical data on heats of formation ΔH_f or heats of combustion ΔH_c of the reacting materials. These are tabulated at some standard temperature, T_1, usually 25°C. As a brief reminder, consider the reaction

$$aA \rightarrow rR + sS$$

By convention we define the heat of reaction at temperature T as the heat transferred to the reacting system from the surroundings when a moles of A disappear to produce r moles of R and s moles of S with the system measured at the same temperature and pressure before and after the change. Thus

$$aA \rightarrow rR + sS, \qquad \Delta H_{rT} \begin{cases} \text{positive, endothermic} \\ \text{negative, exothermic} \end{cases} \tag{1}$$
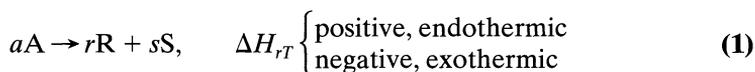
Heats of Reaction and Temperature. The first problem is to evaluate the heat of reaction at temperature T_2 knowing the heat of reaction at temperature T_1. This is found by the law of conservation of energy as follows:

$$\begin{pmatrix} \text{heat absorbed} \\ \text{during reaction} \\ \text{at temperature} \\ T_2 \end{pmatrix} = \begin{pmatrix} \text{heat added to} \\ \text{reactants to} \\ \text{change their} \\ \text{temperature} \\ \text{from } T_2 \text{ to } T_1 \end{pmatrix} + \begin{pmatrix} \text{heat absorbed} \\ \text{during reaction} \\ \text{at temperature} \\ T_1 \end{pmatrix} + \begin{pmatrix} \text{heat added to} \\ \text{products to} \\ \text{bring them} \\ \text{back to } T_2 \\ \text{from } T_1 \end{pmatrix} \tag{2}$$

In terms of enthalpies of reactants and products this becomes

$$\Delta H_{r2} = -(H_2 - H_1)_{\text{reactants}} + \Delta H_{r1} + (H_2 - H_1)_{\text{products}} \tag{3}$$

where subscripts 1 and 2 refer to quantities measured at temperatures T_1 and T_2, respectively. In terms of specific heats

$$\Delta H_{r2} = \Delta H_{r1} + \int_{T_1}^{T_2} \nabla C_p \, dT \tag{4}$$

where

$$\nabla C_p = rC_{pR} + sC_{pS} - aC_{pA} \tag{5}$$

When the molar specific heats are functions of temperatures as follows,

$$C_{pA} = \alpha_A + \beta_A T + \gamma_A T^2$$
$$C_{pR} = \alpha_R + \beta_R T + \gamma_R T^2 \tag{6}$$
$$C_{pS} = \alpha_S + \beta_S T + \gamma_S T^2$$

we obtain

$$\boxed{\begin{aligned} \Delta H_{r2} &= \Delta H_{r1} + \int_{T_1}^{T_2} (\nabla\alpha + \nabla\beta T + \nabla\gamma T^2)\, dT \\ &= \Delta H_{r1} + \nabla\alpha(T_2 - T_1) + \frac{\nabla\beta}{2}(T_2^2 - T_1^2) + \frac{\nabla\gamma}{3}(T_2^3 - T_1^3) \end{aligned}} \qquad (7)$$

where

$$\begin{aligned} \nabla\alpha &= r\alpha_R + s\alpha_S - a\alpha_A \\ \nabla\beta &= r\beta_R + s\beta_S - a\beta_A \qquad\qquad (8) \\ \nabla\gamma &= r\gamma_R + s\gamma_S - a\gamma_A \end{aligned}$$

Knowing the heat of reaction at any one temperature as well as the specific heats of reactants and products in the temperature range concerned allows us to calculate the heat of reaction at any other temperature. From this the heat effects of the reaction can be found.

EXAMPLE 9.1 ΔH_r AT VARIOUS TEMPERATURES

From the ΔH_c and ΔH_f tables, I've calculated that the standard heat of my gas-phase reaction at 25°C is as follows:

$$A + B \rightarrow 2R \cdots \Delta H_{r,298K} = -50\ 000\ J$$

At 25°C the reaction is strongly exothermic. But this doesn't interest me because I plan to run the reaction at 1025°C. What is the ΔH_r at that temperature, and is the reaction still exothermic at that temperature?

Data. Between 25°C and 1025°C the average C_p values for the various reaction components are

$$\overline{C_{pA}} = 35\ J/mol\cdot K \quad \overline{C_{pB}} = 45\ J/mol\cdot K \quad \overline{C_{pR}} = 70\ J/mol\cdot K$$

SOLUTION

First, prepare a reaction map as shown in Fig. E9.1. Then an enthalpy balance for 1 mol A, 1 mol B, and 2 mol R gives

$$\begin{aligned} \Delta H_1 &= \Delta H_2 + \Delta H_3 + \Delta H_4 \\ &= (n\overline{C}_p\Delta T)_{\substack{\text{reactants}\\ \text{1A + 1B}}} + \Delta H_{r,25°C} + (n\overline{C}_p\Delta T)_{\substack{\text{products}\\ \text{2R}}} \\ &= 1(35)(25 - 1025) + 1(45)(25 - 1025) + (-50\ 000) + 2(70)(1025 - 25) \end{aligned}$$
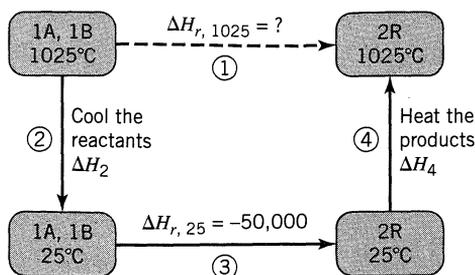
Figure E9.1

or

$$\Delta H_{r,1025°C} = 10\ 000\ \text{J}$$

The reaction is $\begin{cases} \underline{\underline{\text{exothermic at 25°C}}} \\ \underline{\underline{\text{endothermic at 1025°C}}} \end{cases}$

Equilibrium Constants from Thermodynamics

From the second law of thermodynamics equilibrium constants, hence equilibrium compositions of reacting systems, may be calculated. We must remember, however, that real systems do not necessarily achieve this conversion; therefore, the conversions calculated from thermodynamics are only suggested attainable values.

As a brief reminder, the standard free energy $\Delta G°$ for the reaction of Eq. 1 at temperature T is defined as

$$\Delta G° = rG_R^o + sG_S^o - aG_A^o = -\mathbf{R}T \ln K = -\mathbf{R}T \ln \frac{\left(\dfrac{f}{f°}\right)_R^r \left(\dfrac{f}{f°}\right)_S^s}{\left(\dfrac{f}{f°}\right)_A^a} \tag{9}$$

where f is the fugacity of the component at equilibrium conditions; $f°$ is the fugacity of the component at the arbitrarily selected standard state at temperature T, the same one used in calculating $\Delta G°$; $G°$ is the standard free energy of a reacting component, tabulated for many compounds; and K is the thermodynamic equilibrium constant for the reaction. Standard states at given temperature are commonly chosen as follows:

Gases—pure component at one atmosphere, at which pressure ideal gas behavior is closely approximated
Solid—pure solid component at unit pressure
Liquid—pure liquid at its vapor pressure
Solute in liquid—1 molar solution; or at such dilute concentrations that the activity is unity.

For convenience define

$$K_f = \frac{f_R^r f_S^s}{f_A^a}, \quad K_p = \frac{p_R^r p_S^s}{p_A^a}, \quad K_y = \frac{y_R^r y_S^s}{y_A^a}, \quad K_C = \frac{C_R^r C_S^s}{C_A^a} \tag{10}$$

and

$$\Delta n = r + s - a$$

Simplified forms of Eq. 9 can be obtained for various systems. For *gas reactions* standard states are usually chosen at a pressure of 1 atm. At this low pressure the deviation from ideality invariably is small; hence fugacity and pressure are identical and $f^\circ = p^\circ = 1$ atm. Thus

$$K = e^{-\Delta G^\circ / RT} = K_p \{p^\circ = 1 \text{ atm}\}^{-\Delta n} \tag{11}$$

The term in braces in this equation and in Eq. 13 is always unity but is retained to keep the equations dimensionally correct.

For any component i of an *ideal gas*

$$f_i = p_i = y_i \pi = C_i RT \tag{12}$$

Hence

$$K_f = K_p$$

and

$$K = \frac{K_p}{\{p^\circ = 1 \text{ atm}\}^{\Delta n}} = \frac{K_y \pi^{\Delta n}}{\{p^\circ = 1 \text{ atm}\}^{\Delta n}} = \frac{K_c (RT)^{\Delta n}}{\{p^\circ = 1 \text{ atm}\}^{\Delta n}} \tag{13}$$

For a *solid component* taking part in a reaction, fugacity variations with pressure are small and can usually be ignored. Hence

$$\left(\frac{f}{f^\circ}\right)_{\text{solid component}} = 1 \tag{14}$$

Equilibrium Conversion. The equilibrium composition, as governed by the equilibrium constant, changes with temperature, and from thermodynamics the rate of change is given by

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_r}{RT^2} \tag{15}$$

On integrating Eq. 15, we see how the equilibrium constant changes with temperature. When the heat of reaction ΔH_r can be considered to be constant in the temperature interval, integration yields

$$\boxed{\ln \frac{K_2}{K_1} = -\frac{\Delta H_r}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \tag{16}$$

When the variation of ΔH_r must be accounted for in the integration we have

$$\ln \frac{K_2}{K_1} = \frac{1}{\mathbf{R}} \int_{T_1}^{T_2} \frac{\Delta H_r}{T^2} dT \tag{17}$$

where ΔH_r is given by a special form of Eq. 4 in which subscript 0 refers to the base temperature

$$\Delta H_r = \Delta H_{r0} + \int_{T_0}^{T} \nabla C_p dT \tag{18}$$

Replacing Eq. 18 in Eq. 17 and integrating, while using the temperature dependency for C_p given by Eq. 8, gives

$$\mathbf{R} \ln \frac{K_2}{K_1} = \nabla\alpha \ln \frac{T_2}{T_1} + \frac{\nabla\beta}{2}(T_2 - T_1) + \frac{\nabla\gamma}{6}(T_2^2 - T_1^2)$$
$$+ \left(-\Delta H_{r0} + \nabla\alpha T_0 + \frac{\nabla\beta}{2}T_0^2 + \frac{\nabla\gamma}{3}T_0^3\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{19}$$

These expressions allow us to find the variation of the equilibrium constant, hence, equilibrium conversion, with temperature.

The following conclusions may be drawn from thermodynamics. These are illustrated in part by Fig. 9.1.

1. The thermodynamic equilibrium constant is unaffected by the pressure of the system, by the presence or absence of inerts, or by the kinetics of the reaction, but is affected by the temperature of the system.
2. Though the thermodynamic equilibrium constant is unaffected by pressure or inerts, the equilibrium concentration of materials and equilibrium conversion of reactants can be influenced by these variables.
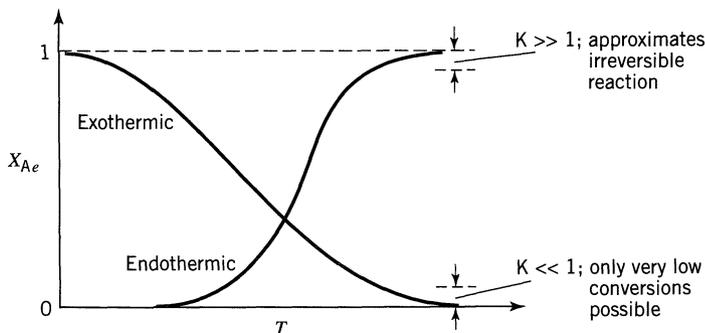
Figure 9.1 Effect of temperature on equilibrium conversion as predicted by thermodynamics (pressure fixed.)

3. $K \gg 1$ indicates that practically complete conversion may be possible and that the reaction can be considered to be irreversible. $K \ll 1$ indicates that reaction will not proceed to any appreciable extent.

4. For an increase in temperature, equilibrium conversion rises for endothermic reactions and drops for exothermic reactions.

5. For an increase in pressure in gas reactions, conversion rises when the number of moles decreases with reaction; conversion drops when the number of moles increases with reaction.

6. A decrease in inerts for all reactions acts in the way that an increase in pressure acts for gas reactions.

EXAMPLE 9.2   EQUILIBRIUM CONVERSION AT DIFFERENT TEMPERATURES

(a) Between 0°C and 100°C determine the equilibrium conversion for the elementary aqueous reaction

$$A \rightleftharpoons R \begin{cases} \Delta G^{0}_{298} = -14\,130 \text{ J/mol} \\ \Delta H^{0}_{298} = -75\,300 \text{ J/mol} \end{cases} \quad C_{pA} = C_{pR} = \text{constant}$$
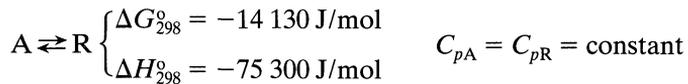
Present the results in the form of a plot of temperature versus conversion.

(b) What restrictions should be placed on the reactor operating isothermally if we are to obtain a conversion of 75% or higher?

SOLUTION

(a) With all specific heats alike, $\nabla C_p = 0$. Then from Eq. 4 the heat of reaction is independent of temperature and is given by

$$\Delta H_r = \Delta H_{r,298} = -75\,300 \text{ J/mol} \tag{i}$$

From Eq. 9 the equilibrium constant at 25°C is given by

$$K_{298} = \exp(-\Delta G^{0}_{298}/\mathbf{R}T)$$

$$= \exp\left(\frac{14\,130 \text{ J/mol}}{(8.314 \text{ J/mol} \cdot \text{K})\,(298\text{K})}\right) = 300 \tag{ii}$$

Since the heat of reaction does not change with temperature, the equilibrium constant K at any temperature T is now found from Eq. 16. Thus

$$\ln\frac{K}{K_{298}} = -\frac{\Delta H_r}{8.314}\left(\frac{1}{T} - \frac{1}{298}\right)$$

Rearranging gives

$$K = K_{298} \exp\left[\frac{-\Delta H_r}{\mathbf{R}}\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

Replacing K_{298} and ΔH_r from Eqs. (i) and (ii) gives on rearranging,

$$K = \exp\left[\frac{75\,300}{\mathbf{R}T} - 24.7\right] \tag{iii}$$

But at equilibrium

$$K = \frac{C_R}{C_A} = \frac{C_{A0}X_{Ae}}{C_{A0}(1 - X_{Ae})} = \frac{X_{Ae}}{1 - X_{Ae}}$$

or

$$X_{Ae} = \frac{K}{K + 1} \tag{iv}$$

Putting T values into Eq. (iii), then K into Eq. (iv), as shown in Table E9.2 gives the changing equilibrium conversion as a function of temperature in the range of 0°C to 100°C. This result is displayed in Fig. E9.2.

(b) From the graph we see that the temperature must stay below 78°C if conversion of 75% or higher may be expected.

Table E9.2 Calculating $X_{Ae}(T)$ from Eqs. (iii) and (iv)

Selected Temperature		$K = \exp\left[\dfrac{75\,300}{\mathbf{R}T} - 24.7\right]$	X_{Ae}
°C	K	from Eq. (iii)	from Eq. (iv)
5	278	2700	0.999+
15	288	860	0.999
25	298	300	0.993
35	308	110	0.991
45	318	44.2	0.978
55	328	18.4	0.949
65	338	8.17	0.892
75	348	3.79	0.791
85	358	1.84	0.648
95	368	0.923	0.480
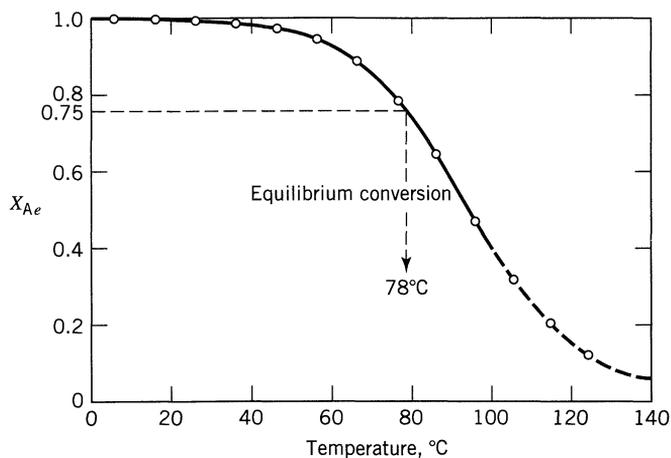
Figure E9.2

General Graphical Design Procedure

Temperature, composition, and reaction rate are uniquely related for any single homogeneous reaction, and this may be represented graphically in one of three ways, as shown in Fig. 9.2. The first of these, the composition-temperature plot, is the most convenient so we will use it throughout to represent data, to calculate reactor sizes, and to compare design alternatives.

For a given feed (fixed $C_{A0}, C_{B0}, \ldots$) and using conversion of key component as a measure of the composition and extent of reaction, the X_A versus T plot has the general shape shown in Fig. 9.3. This plot can be prepared either from a thermodynamically consistent rate expression for the reaction (the rate must be zero at equilibrium) or by interpolating from a given set of kinetic data in conjunction with thermodynamic information on the equilibrium. Naturally, the reliability of all the calculations and predictions that follow are directly dependent on the accuracy of this chart. Hence, it is imperative to obtain good kinetic data to construct this chart.
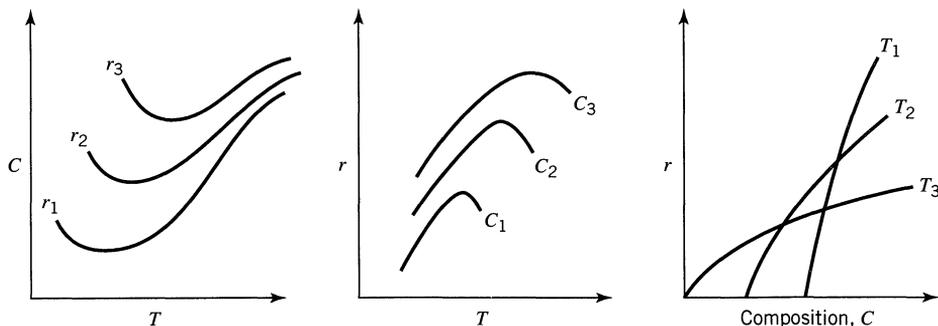
Figure 9.2 Different ways of representing the relationship of temperature, composition, and rate for a single homogeneous reaction.
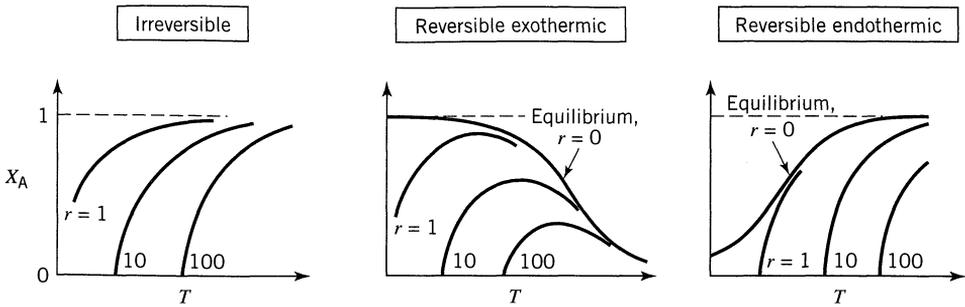
Figure 9.3 General shape of the temperature–conversion plot for different reaction types.

The size of reactor required for a given duty and for a given temperature progression is found as follows:

1. Draw the reaction path on the X_A versus T plot. This is the *operating line* for the operation.
2. Find the rates at various X_A along this path.
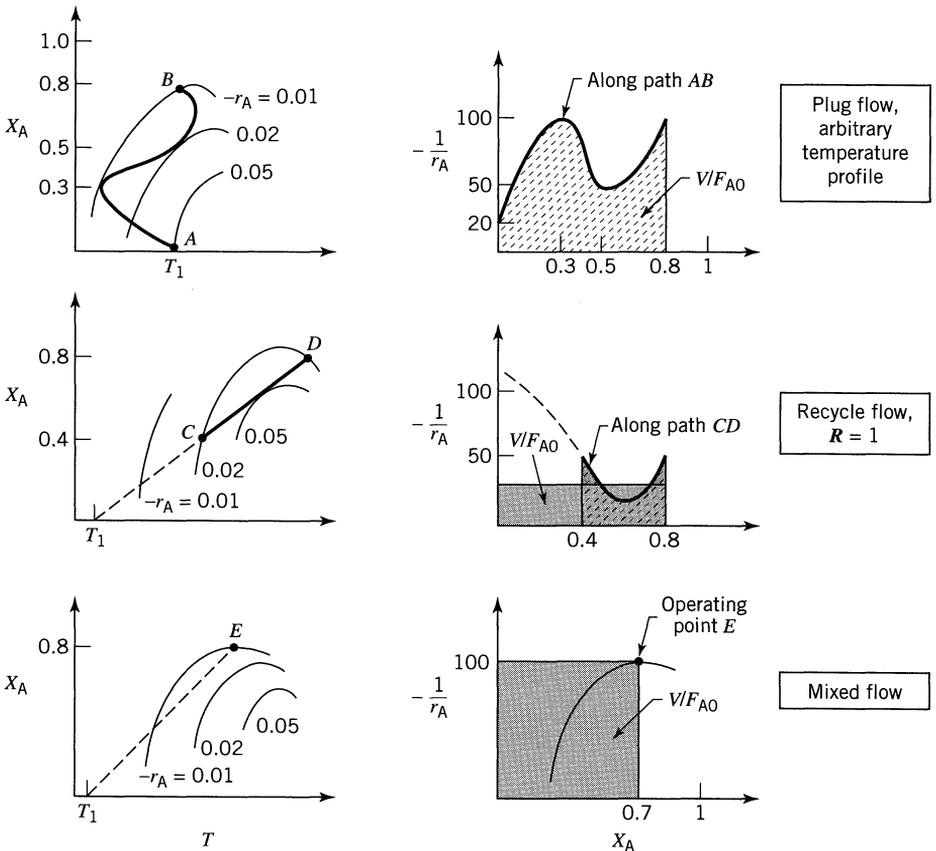
Figure 9.4 Finding the reactor size for different types of flow and for a feed temperature T_1.

3. Plot the $1/(-r_A)$ versus X_A curve for this path.
4. Find the area under this curve. This gives V/F_{A0}.

For exothermic reactions we illustrate this procedure in Fig. 9.4 for three paths: path AB for plug flow with an arbitrary temperature profile, path *CD* for nonisothermal plug flow with 50% recycle, and point E for mixed flow. Note that for mixed flow the operating line reduces to a single point.

This procedure is quite general, applicable for any kinetics, any temperature progression, and any reactor type or any series of reactors. So, once the operating line is known, the reactor size can be found.

EXAMPLE 9.3   CONSTRUCTION OF THE RATE-CONVERSION-TEMPERATURE CHART FROM KINETIC DATA

With the system of Example 9.2 and starting with an R-free solution, kinetic experiments in a batch reactor give 58.1% conversion in 1 min at 65°C, 60% conversion in 10 min at 25°C. Assuming reversible first-order kinetics, find the rate expression for this reaction and prepare the conversion-temperature chart with reaction rate as parameter.

SOLUTION

Integrate the Performance Equation.   For a reversible first-order reaction, the performance equation for a batch reactor is

$$t = C_{A0} \int \frac{dX_A}{-r_A} = C_{A0} \int \frac{dX_A}{k_1 C_A - k_2 C_R} = \frac{1}{k_1} \int_0^{X_A} \frac{dX_A}{1 - X_A/X_{Ae}}$$

According to Eq. 3.54 this integrates to give

$$\frac{k_1 t}{X_{Ae}} = -\ln\left(1 - \frac{X_A}{X_{Ae}}\right) \tag{i}$$

Calculate the Forward Rate Constant.   From the batch run at 65°C, noting from Example 9.2 that $X_{Ae} = 0.89$, we find with Eq. (i)

$$\frac{k_1 (1 \text{ min})}{0.89} = -\ln\left(1 - \frac{0.581}{0.89}\right)$$

or

$$k_{1, 338} = 0.942 \text{ min}^{-1} \tag{ii}$$

Similarly, for the batch run at 25°C we find

$$k_{1, 298} = 0.0909 \text{ min}^{-1} \tag{iii}$$

Assuming an Arrhenius temperature dependency, the ratio of forward rate constants at these two temperatures gives

$$\frac{k_{1,338}}{k_{1,298}} = \frac{0.942}{0.0909} = \frac{k_{10}e^{-\mathbf{E}_1/\mathbf{R}(338)}}{k_{10}e^{-\mathbf{E}_1/\mathbf{R}(298)}} \tag{iv}$$

from which the activation energy of the forward reaction can be evaluated, giving

$$\mathbf{E}_1 = 48\ 900\ \text{J/mol}$$

Note that there are two activation energies for this reaction, one for the forward reaction, another for the reverse.

Now for the complete rate constant for the forward reaction. From either the numerator or the denominator of Eq. (iv) first evaluate k_{10}, then use it as shown below:

$$k_1 = 34 \times 10^6 \exp\left[\frac{-48\ 900}{\mathbf{R}T}\right] = \exp\left[17.34 - \frac{48\ 900}{\mathbf{R}T}\right]$$

Noting that $K = \dfrac{k_1}{k_2}$, thus $k_2 = \dfrac{k_1}{K}$, where K is given by Eq. (iii) of Example 9.2, we can find the value of k_2.

Summary. For the reversible first-order reaction of Example 9.2 we have

$$A \underset{2}{\overset{1}{\rightleftarrows}} R; \qquad K = \frac{C_{Re}}{C_{Ae}}; \quad -r_A = r_R = k_1 C_A - k_2 C_R$$

$$\text{Equilibrium:} \qquad K = \exp\left[\frac{75\ 300}{\mathbf{R}T} - 24.7\right]$$

$$\text{Rate constants:} \quad k_1 = \exp\left[17.34 - \frac{48\ 900}{\mathbf{R}T}\right], \quad \text{min}^{-1}$$

$$k_2 = \exp\left[42.04 - \frac{124\ 200}{\mathbf{R}T}\right], \quad \text{min}^{-1}$$

From these values the X_A versus T chart for any specific C_{A0} can be prepared and for this purpose the electronic computer is a great timesaver. Figure E9.3 is such a plot prepared for $C_{A0} = 1$ mol/liter and $C_{R0} = 0$.

Since we are dealing with first-order reactions this plot can be used for any C_{A0} value by properly relabeling the rate curves. Thus, for $C_{A0} = 10$ mol/liter simply multiply all the rate values on this graph by a factor of 10.
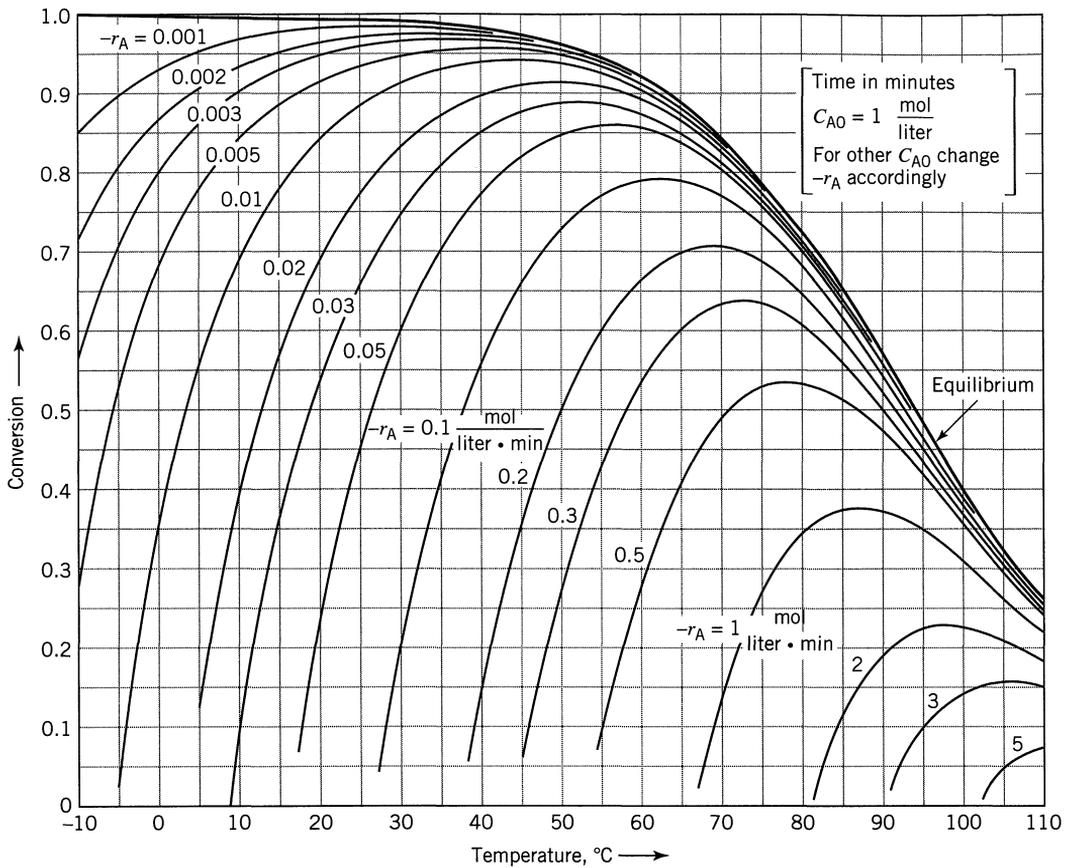
Figure E9.3

Optimum Temperature Progression

We define the optimum temperature progression to be that progression which minimizes V/F_{A0} for a given conversion of reactant. This optimum may be an isothermal or it may be a changing temperature: in time for a batch reactor, along the length of a plug flow reactor, or from stage to stage for a series of mixed flow reactors. It is important to know this progression because it is the ideal which we try to approach with a real system. It also allows us to estimate how far any real system departs from this ideal.

The optimum temperature progression in any type of reactor is as follows: At any composition, it will always be at the temperature where the rate is a maximum. The locus of maximum rates is found by examining the $r(T, C)$ curves of Fig. 9.4; Fig. 9.5 shows this progression.

For irreversible reactions, the rate always increases with temperature at any composition, so the highest rate occurs at the highest allowable temperature. This
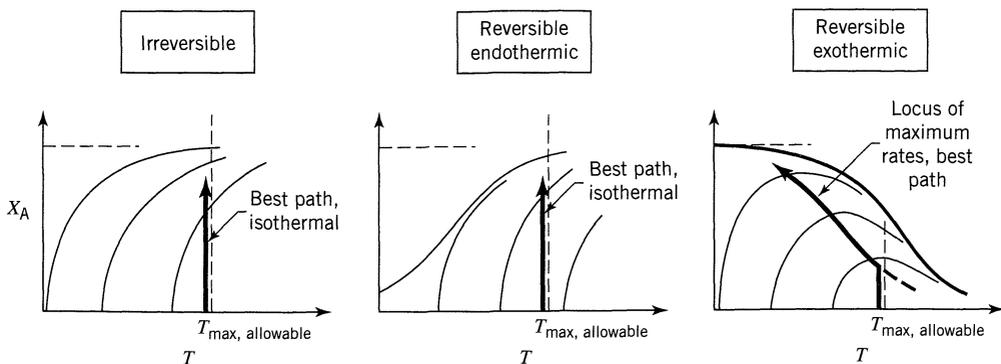
Figure 9.5 Operating lines for minimum reactor size.

temperature is set by the materials of construction or by the possible increasing importance of side reactions.

For endothermic reactions a rise in temperature increases both the equilibrium conversion and the rate of reaction. Thus, as with irreversible reactions, the highest allowable temperature should be used.

For exothermic reversible reactions the situation is different, for here two opposing factors are at work when the temperature is raised—the rate of forward reaction speeds up but the maximum attainable conversion decreases. Thus, in general, a reversible exothermic reaction starts at a high temperature which decreases as conversion rises. Figure 9.5 shows this progression, and its precise values are found by connecting the maxima of the different rate curves. We call this line the *locus of maximum rates*.

Heat Effects

When the heat absorbed or released by reaction can markedly change the temperature of the reacting fluid, this factor must be accounted for in design. Thus we need to use both the material and energy balance expressions, Eqs. 4.1 and 4.2, rather than the material balance alone, which was the starting point of all the analyses of isothermal operations of Chapters 5 through 8.

First of all, if the reaction is exothermic and if heat transfer is unable to remove all of the liberated heat, then the temperature of the reacting fluid will rise as conversion rises. By similar arguments, for endothermic reactions the fluid cools as conversion rises. Let us relate this temperature change with extent of conversion.

We start with adiabatic operations, later extending the treatment to account for heat interchange with the surroundings.

Adiabatic Operations

Consider either a mixed flow reactor, a plug flow reactor, or a section of plug flow reactor, in which the conversion is X_A, as shown in Fig. 9.6. In Chapters 5 and 6 one component, usually the limiting reactant, was selected as the basis for
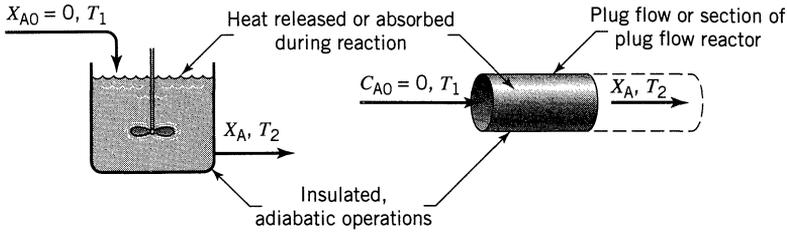
Figure 9.6 Adiabatic operations with large enough heat effect to cause a rise in temperature (exothermic) or drop in temperature (endothermic) in the reacting fluid.

all material balance calculations. The same procedure is used here, with limiting reactant A taken as the basis. Let

Subscripts 1, 2 refer to temperatures of entering and leaving streams.

C'_p, C''_p = Mean specific heat of unreacted feed stream and of *completely* converted product stream per mole of entering reactant A.

H', H'' = enthalpy of unreacted feed stream and of *completely* converted product stream per mole of entering reactant A.

ΔH_{ri} = heat of reaction per mole of entering reacting A, and at temperature T_i.

With T_1 as the reference temperature on which enthalpies and heats of reaction are based we have

Enthalpy of entering feed:

$$H'_1 = C'_p (T_1 - T_1) = 0 \text{ J/mol A}$$

Enthalpy of leaving stream:

$$H''_2 X_A + H'_2(1 - X_A) = C''_p (T_2 - T_1)X_A + C'_p(T_2 - T_1)(1 - X_A) \text{ J/mol A}$$

Energy absorbed by reaction:

$$\Delta H_{r1} X_A \text{ J/mol A}$$

Replacing these quantities in the energy balance,

input = output + accumulation + disappearance by reaction   (4.2)

we obtain at steady state

$$0 = [C''_p (T_2 - T_1)X_A + C'_p (T_2 - T_1)(1 - X_A)] + \Delta H_{r1} X_A \qquad (20)$$

By rearranging,

$$X_A = \frac{C'_p (T_2 - T_1)}{-\Delta H_{r1} - (C''_p - C'_p)(T_2 - T_1)} = \frac{C'_p \Delta T}{-\Delta H_{r1} - (C''_p - C'_p)\Delta T} \qquad (21)$$

or, with Eq. 18

$$X_A = \frac{C'_p \Delta T}{-\Delta H_{r2}} = \left(\frac{\text{heat needed to raise feed stream to } T_2}{\text{heat released by reaction at } T_2} \right) \qquad (22)$$

which for complete conversion becomes

$$-\Delta H_{r2} = C'_p \Delta T, \qquad \text{for } X_A = 1 \qquad (23)$$

The latter form of the equation simply states that the heat released by reaction just balances the heat necessary to raise the reactants from T_1 to T_2.

The relation between temperature and conversion, as given by the energy balances of Eq. 21 or 22, is shown in Fig. 9.7. The resulting lines are straight for all practical purposes since the variation of the denominator term of these equa-
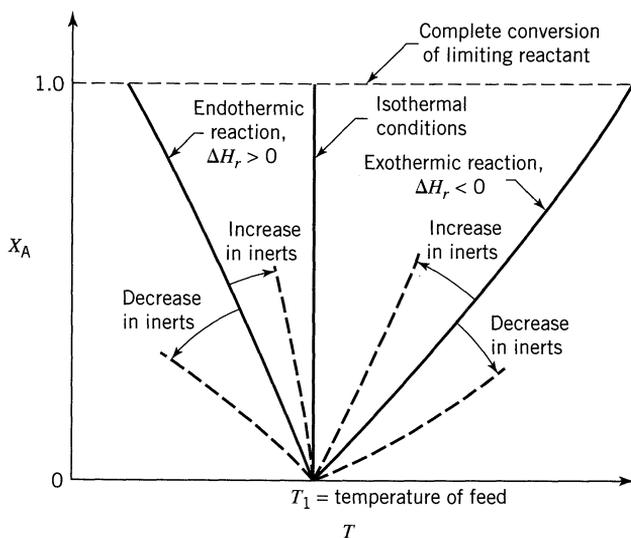
Figure 9.7 Graphical representation of energy balance equation for adiabatic operation. These are adiabatic operating lines.

tions is relatively small. When $C_p'' - C_p' = 0$, the heat of reaction is independent of temperature and Eqs. 21 and 22 reduce to

$$X_A = \frac{C_p \Delta T}{-\Delta H_r} \qquad (24)$$

which are straight lines in Fig. 9.7.

This figure illustrates the shape of the energy balance curve for both endothermic and exothermic reactions for both mixed flow and plug flow reactors. This representation shows that whatever is the conversion at any point in the reactor, the temperature is at its corresponding value on the curve. For plug flow the fluid in the reactor moves progressively along the curve, for mixed flow the fluid immediately jumps to its final value on the curve. These are the *adiabatic operating lines* for the reactor. With increased inerts C_p rises, and these curves become more closely vertical. A vertical line indicates that temperature is unchanged as reaction proceeds. This then is the special case of isothermal reactions treated in Chapters 5 through 7.

The *size of reactor* needed for a given duty is found as follows. For plug flow tabulate the rate for various X_A along this adiabatic operating line, prepare the $1/(-r_A)$ versus X_A plot and integrate. For mixed flow simply use the rate at the conditions within the reactor. Figure 9.8 illustrates this procedure.

The *best adiabatic operations* of a single plug flow reactor are found by shifting the operating line (changing the inlet temperature) to where the rates have the highest mean value. For endothermic operations this means starting at the highest allowable temperature. For exothermic reactions this means straddling the locus of maximum rates as shown in Fig. 9.9. A few trials will locate the best inlet temperature, that which minimizes V/F_{A0}. For mixed flow the reactor should operate on the locus of maximum rates, again shown in Fig. 9.9.

The *best reactor type,* that which minimizes V/F_{A0}, is found directly from this X_A versus T graph. If the rate progressively decreases with conversion, then use plug flow. This is the case for endothermic reactions (Fig. 9.8a) and close to isothermal exothermic reactions. For exothermic reactions that have a large temperature rise during reaction, the rate rises from a very low value to a maximum at some intermediate X_A, then falls. This behavior is characteristic of autocatalytic reactions, thus recycle operations are best. Figure 9.10 illustrates two situations, one where plug flow is best, the other where large recycle or mixed flow is best. The slope of the operating line, $C_p/-\Delta H_r$, will determine which case one has at hand. Thus

1. for small $C_p/-\Delta H_r$ (pure gaseous reactants) mixed flow is best.
2. for large $C_p/-\Delta H_r$ (gas with much inerts, or liquid systems) plug flow is best.

Nonadiabatic Operations

For the adiabatic operating line of Fig. 9.7 to more closely approach the ideals of Fig. 9.5, we may want deliberately to introduce or remove heat from the reactor. In addition, there are heat losses to the surroundings to account for.
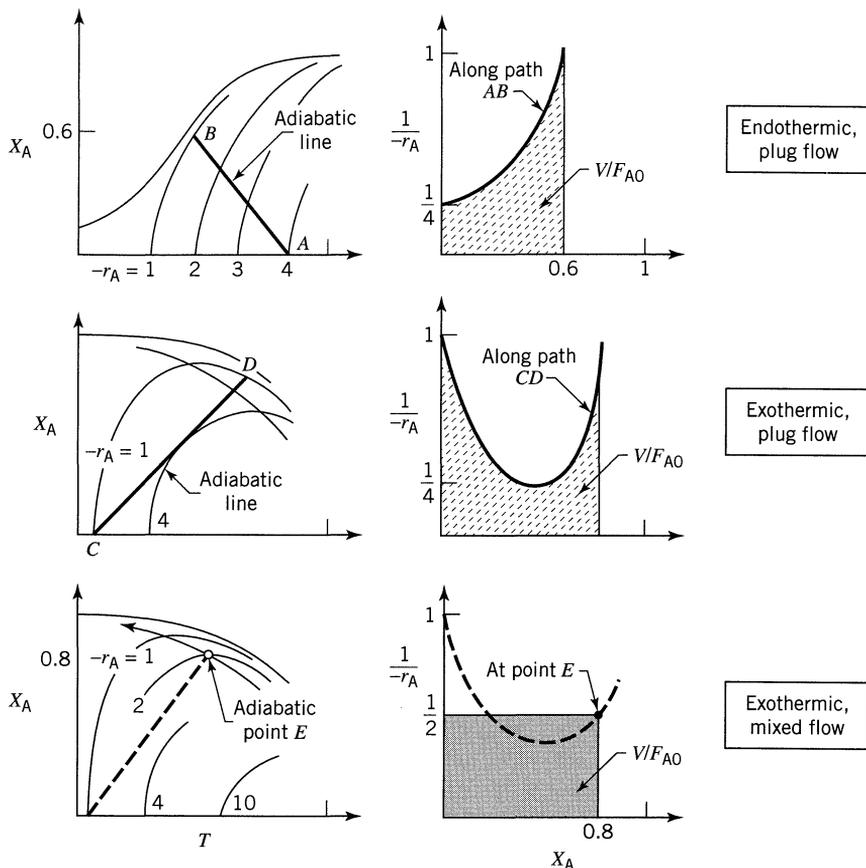
Figure 9.8 Finding reactor size for adiabatic operations of plug flow and mixed flow reactors.
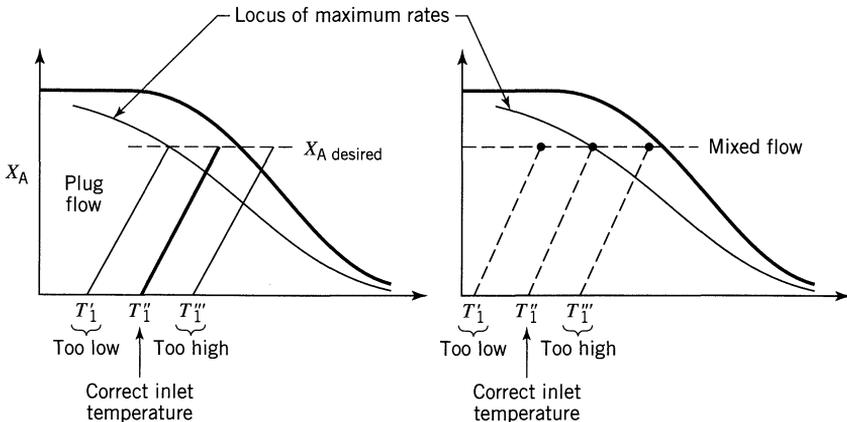
Figure 9.9 Best location for the adiabatic operating line. For plug flow, a trial and error search is needed to find this line; for mixed flow, no search is needed.
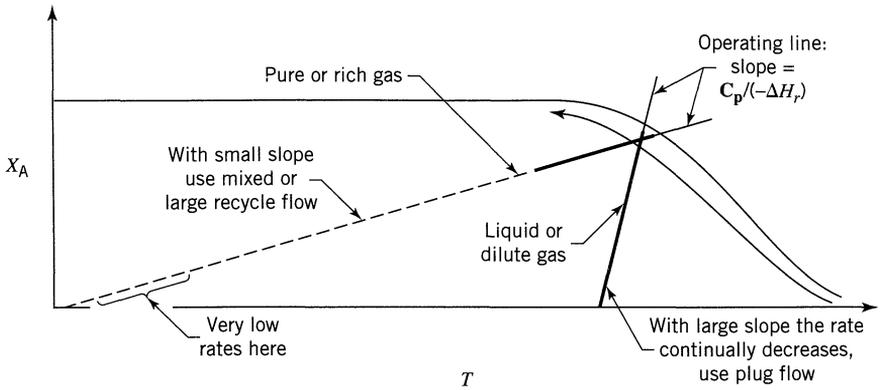
Figure 9.10 For exothermic reactions mixed flow is best where the temperature rise is large; plug flow is best for close to isothermal systems.

Let us see how these forms of heat interchange modify the shape of the adiabatic operating line.

Let Q be the total heat *added* to a reactor *per mole* of entering reactant A, and let this heat also include the losses to the surroundings. Then Eq. 20, the energy balance about the system, is modified to

$$Q = \mathbf{C_p''}(T_2 - T_1)X_A + \mathbf{C_p'}(T_2 - T_1)(1 - X_A) + \Delta H_{r1} X_A$$

which on rearrangement and with Eq. 18 gives

$$X_A = \frac{\mathbf{C_p'}\Delta T - Q}{-\Delta H_{r2}} = \left(\frac{\begin{array}{c}\text{net heat still needed after heat} \\ \text{transfer to raise feed to } T_2\end{array}}{\text{heat released by reaction at } T_2}\right) \qquad (25)$$

and for $\mathbf{C_p''} = \mathbf{C_p'}$, which often is a reasonable approximation

$$\boxed{X_A = \frac{\mathbf{C_p}\Delta T - Q}{-\Delta H_r}} \qquad (26)$$

With heat input proportional to $\Delta T = T_2 - T_1$ the energy balance line rotates about T_1. This change is shown in Fig. 9.11. Other modes of heat addition or removal yield corresponding shifts in the energy balance line.

Using this modified operating line, the procedure for finding the reactor size and optimum operations follows directly from the discussion on adiabatic operations.

Comments and Extensions

Adiabatic operations of an exothermic reaction give a rising temperature with conversion. However, the desired progression is one of falling temperature. Thus,
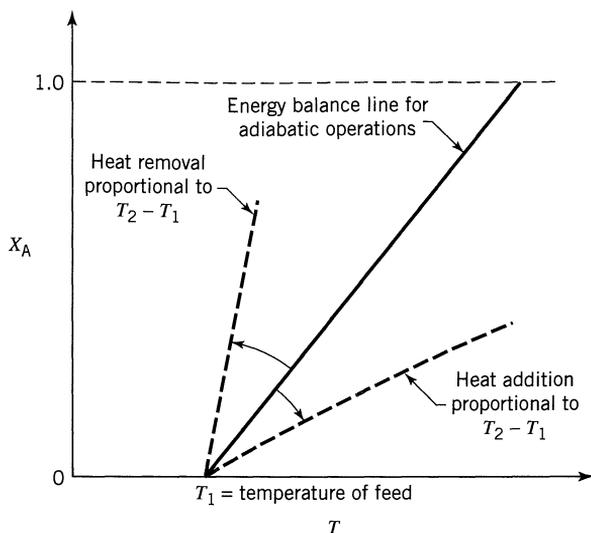
Figure 9.11 Sketch of the energy balance equation showing the shift in adiabatic line caused by heat exchange with surroundings.

very drastic heat removal may be needed to make the operating line approach the ideal, and many schemes may be proposed to do this. As an example, we may have heat exchange with the incoming fluid (see Fig. 9.12a), a case treated by van Heerden (1953, 1958). Another alternative is to have multistage operations with interstage cooling between adiabatic sections (see Fig. 9.12b). In general multistaging is used when it is impractical to effect the necessary heat exchange within the reactor itself. This is usually the case with gas-phase reactions with their relatively poor heat transfer characteristics. For endothermic reactions, multistaging with reheat between stages is commonly used to keep the temperature from dropping too low (see Fig. 9.12c).

Since the main use of these and many other forms of multistage operations is with solid catalyzed gas-phase reactions we discuss these operations in Chapter 19. Design for homogeneous reactions parallels that for catalytic reactions, so the reader is referred to Chapter 19 for the development.

Exothermic Reactions in Mixed Flow Reactors—A Special Problem

For exothermic reactions in mixed flow (or close to mixed flow) an interesting situation may develop in that more than one reactor composition may satisfy the governing material and energy balance equations. This means that we may not know which conversion level to expect. van Heerden (1953, 1958) was the first to treat this problem. Let us examine it.

First, consider reactant fluid fed at a given rate (fixed τ or V/F_{A0}) to a mixed flow reactor. At each reactor temperature there will be some particular conversion which satisfies the material balance equation, Eq. 5.11. At low temperature the rate is low so this conversion is low. At higher temperature the conversion
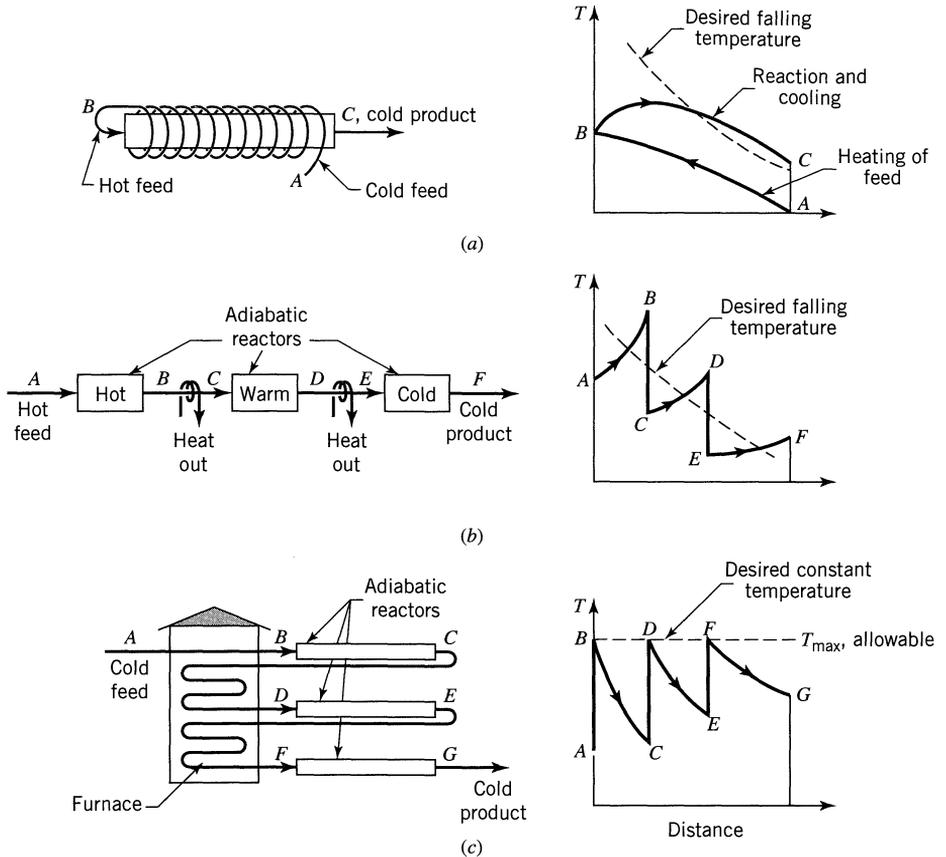
Figure 9.12 Ways of approaching the ideal temperature profile with heat exchange: (*a*) and (*b*) exothermic reaction; (*c*) endothermic reaction.

rises and approaches the equilibrium. At a still higher temperature we enter the region of falling equilibrium so the conversion for given τ will likewise fall. Figure 9.13 illustrates this behavior for different τ values. Note that these lines do not represent an operating line or a reaction path. Actually any point on these curves represents a particular solution of the material balance equations; thus, it represents an operating point for the mixed flow reactor.

Now, for a given feed temperature T_1 the intersection of the energy balance line with the S-shaped material balance line for the operating τ gives the conditions within the reactor. Here three cases may be distinguished. These are shown in Fig. 9.14 for *irreversible reactions*.

First, the energy balance line T_1A represents the situation where insufficient heat is liberated by reaction to raise the temperature to a high enough level for the reaction to be self-sustaining. Hence, conversion is negligible. At the other extreme, if we have more than enough heat liberated, the fluid will be hot and conversion essentially complete. This is shown as line T_1B. Finally, line T_1C indicates an intermediate situation which has three solutions to the material and
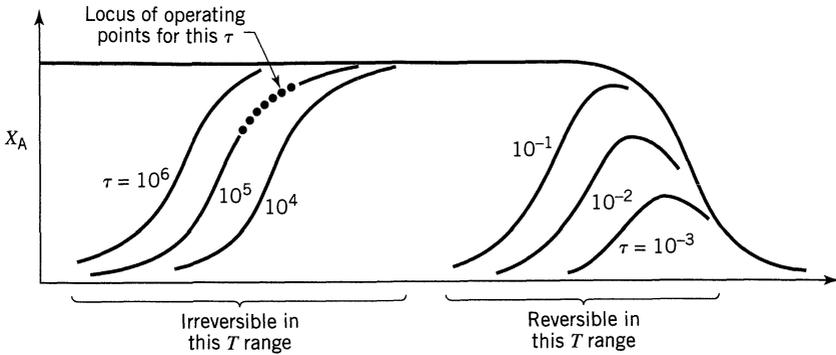
Figure 9.13 Conversion in a mixed flow reactor as a function of T and τ, from the material balance equation, Eq. 5.11.

energy balance equations, points M', M'', and M'''. However, point M'' is an unstable state because with a small rise in temperature the heat produced (with the rapidly rising material balance curve) is greater than the heat consumed by the reacting mixture (energy balance curve). The excess heat produced will make the temperature rise until M''' is reached. By similar reasoning, if the temperature drops slightly below M'' it will continue to drop until M' is reached. Thus, we look upon M'' as the ignition point. If the mixture can be raised above this temperature, then the reaction will be self-sustaining.

For *reversible exothermic reactions* the same three cases occur, as shown in Fig. 9.15. However, it can be seen that here there is an optimum operating temperature for the given τ value where conversion is maximized. Above or below this temperature the conversion drops; thus, proper control of heat removal is essential.

The type of behavior described here occurs in systems where the slope of the energy balance line, $C_p/-\Delta H_r$, is small; thus, large liberation of heat and pure reactants which leads to far from isothermal operations. van Heerden (1953, 1958) discusses and gives examples of this type of reacting system. In addition, though it is a much more complex situation, a gas flame illustrates well the
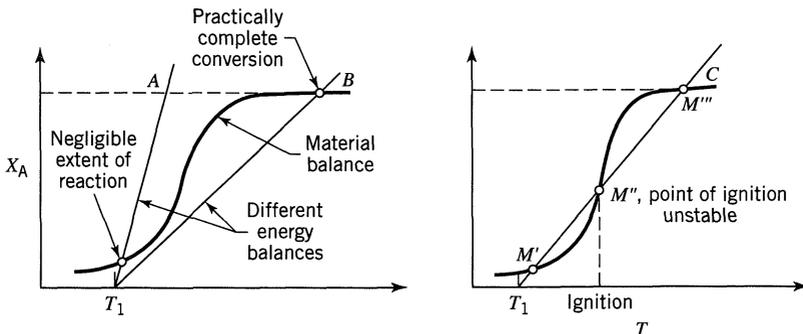
Figure 9.14 Three types of solutions to the energy and material balances for exothermic irreversible reactions.
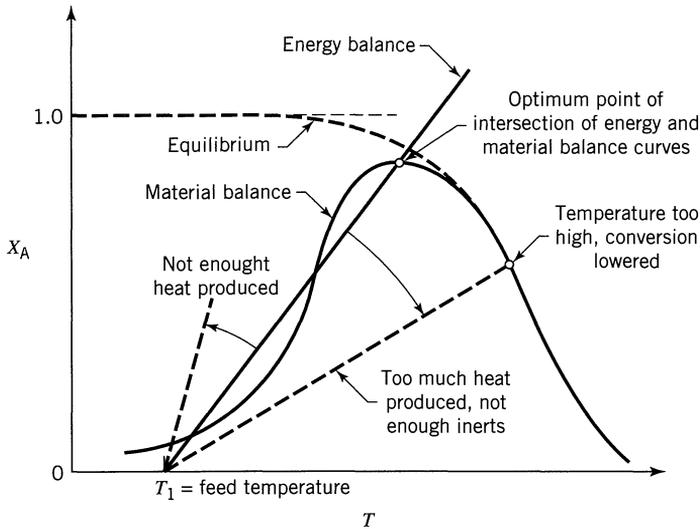
Figure 9.15 Solution of energy and material balances for reversible exothermic reaction.

multiple solutions discussed here: the unreacted state, the reacted state, and the ignition point.

Reactor dynamics, stability, and start-up procedures are particularly important for auto-induced reactions such as these. For example, a small change in feed rate (τ value), feed composition or temperature, or heat transfer rate may cause the reactor output to jump from one operating point to the other.

<div style="border:1px solid">EXAMPLE 9.4</div> **PERFORMANCE FOR THE OPTIMAL TEMPERATURE PROGRESSION**

Using the optimal temperature progression in a plug flow reactor for the reaction of Examples 9.2 and 9.3,

  (a) calculate the space time and volume needed for 80% conversion of a feed of $F_{A0} = 1000$ mol/min where $C_{A0} = 4$ mol/liter.
  (b) plot the temperature and conversion profile along the length of the reactor.

Let the maximum allowable operating temperature be 95°C.
Note that Fig. E9.3 was prepared for $C_{A0} = 1$ mol/liter, not 4 mol/liter.

SOLUTION

  (a) *Minimum Space-Time.* On the conversion-temperature graph (Fig. E9.3) draw the locus of maximum rates. Then, remembering the temperature restriction, draw the optimum path for this system (line *ABCDE* in Fig E9.4a) and
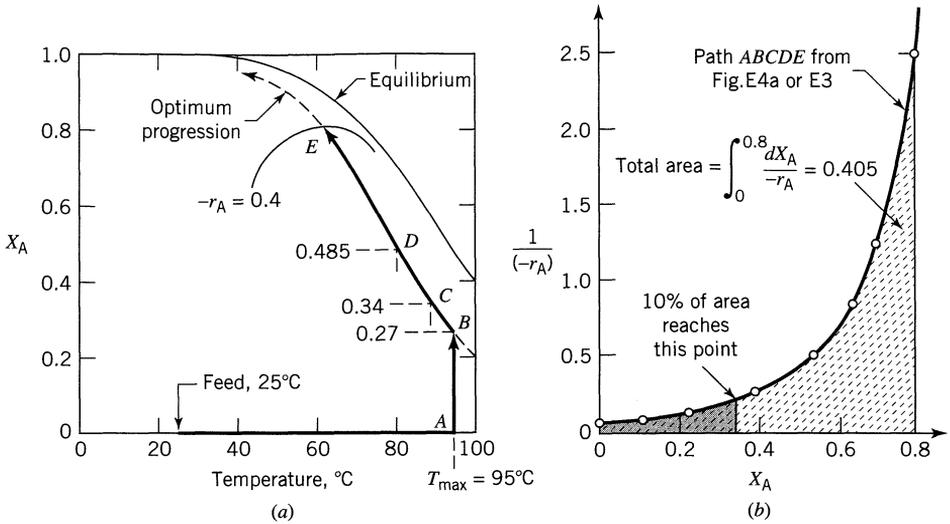
Figure E9.4a
Figure E9.4b

integrate graphically along this path to obtain

$$\frac{\tau}{C_{A0}} = \frac{V}{F_{A0}} = \int_0^{0.8} \frac{dX_A}{(-r_A)_{\text{optimum path ABCDE}}} = \left(\begin{array}{c}\text{shaded area}\\ \text{of Fig. E9.4}b\end{array}\right) = 0.405 \text{ liter/mol} \cdot \text{min}$$

Therefore

$$\tau = C_{A0} \text{ (area)} = (4 \text{ mol/liter}) (0.405 \text{ liter} \cdot \text{min/mol}) = \underline{\underline{1.62 \text{ min}}}$$

and

$$V = F_{A0} \text{ (area)} = (1000 \text{ mol/min}) (0.405 \text{ liter} \cdot \text{min/mol}) = \underline{\underline{405 \text{ liters}}}$$

(b) *T and X_A Profiles Through the Reactor.* Let us take 10% increments through the reactor by taking 10% increments in area under the curve of Fig. E9.4b. This procedure gives $X_A = 0.34$ at the 10% point, $X_A = 0.485$ at the 20% point, etc. The corresponding temperatures are then 362 K at $X_A = 0.34$ (point C), 354 K at $X_A = 0.485$ (point D), etc.

In addition we note that the temperature starts at 95°C, and at $X_A = 0.27$ (point B) it drops. Measuring areas in Fig. E9.4b we see that this happens after the fluid has passed 7% of the distance through the reactor.

In this manner the temperature and conversion profiles are found. The result is shown in Fig. E9.4c.
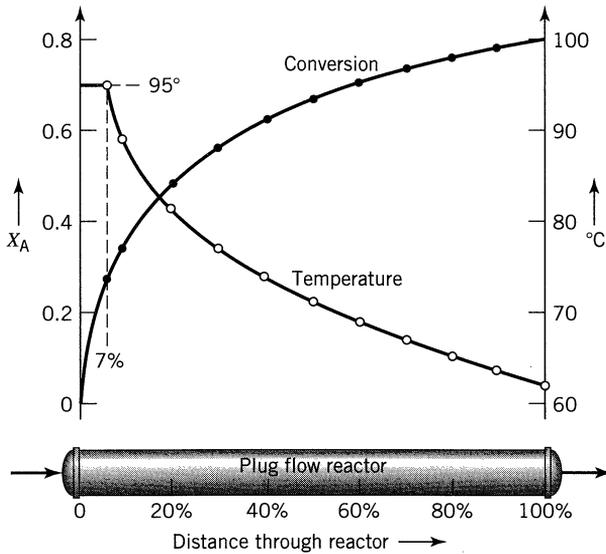
Figure E9.4c

■

EXAMPLE 9.5   *OPTIMUM MIXED FLOW REACTOR PERFORMANCE*

A concentrated aqueous A-solution of the previous examples ($C_{A0} = 4$ mol/liter, $F_{A0} = 1000$ mol/min) is to be 80% converted in a mixed flow reactor.

(a) What size of reactor is needed?

(b) What is the heat duty if feed enters at 25°C and product is to be withdrawn at this temperature?

Note that

$$C_{pA} = \frac{1000 \text{ cal}}{\text{kg} \cdot \text{K}} \cdot \frac{1 \text{ kg}}{1 \text{ liter}} \cdot \frac{1 \text{ liter}}{4 \text{ mol A}} = 250 \frac{\text{cal}}{\text{mol A} \cdot \text{K}}$$

SOLUTION

(a) *Reactor Volume.* For $C_{A0} = 4$ mol/liter we may use the X_A versus T chart of Fig. E9.3 as long as we multiply all rate values on this chart by 4.

Following Fig. 9.9 the mixed flow operating point should be located where the locus of optima intersects the 80% conversion line (point C on Fig. E9.5a). Here the reaction rate has the value

$$-r_A = 0.4 \text{ mol A converted/min} \cdot \text{liter}$$

From the performance equation for mixed flow reactors, Eq. 5.11, the volume required is given by

$$\underline{\underline{V}} = \frac{F_{A0} X_A}{(-r_A)} = \frac{(1000 \text{ mol/min}) (0.80)}{0.4 \text{ mol/min} \cdot \text{liter}} = \underline{\underline{2000 \text{ liters}}}$$
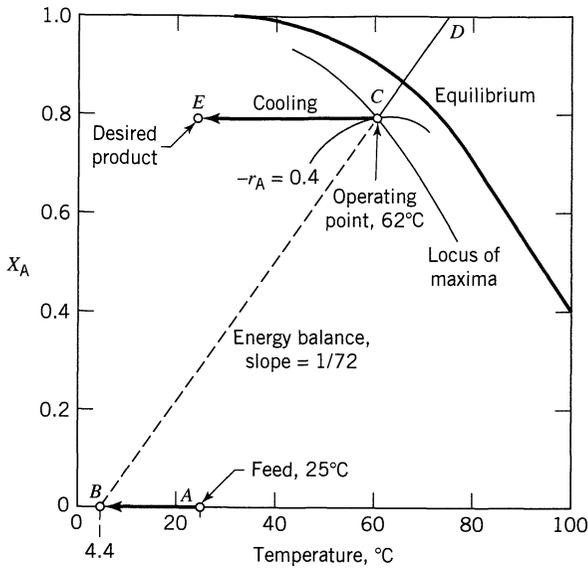
Figure E9.5*a*

(b) *Heat Duty.* Of course we can use joules in our calculations; however, since we are dealing with aqueous solutions it is simpler to use calories. Let us use calories. Then the slope of the energy balance line is

$$\text{slope} = \frac{\mathbf{C_p}}{-\Delta H_r} = \frac{(250\,\text{cal/mol A} \cdot \text{K})}{18\,000\,\text{cal/mol A})} = \frac{1}{72}\,\text{K}^{-1}$$

Drawing this line through point *C* (line *BCD*) we see that the feed must be cooled 20° (from point *A* to point *B*) before it enters and reacts adiabatically. Also, the product must be cooled 37°C (from point *C* to point *E*). Thus the heat duty is

Precooler: Q_{AB} = (250 cal/mol A · K)(20 K) = 5000 cal/mol A fed

$\qquad$ = (5000 cal/mol A)(1000 molA/min) = 5000 000 cal/min

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ = 348.7 kW

Postcooler: Q_{CE} = (250)(37) = 9250 cal/mol A fed

$\qquad$ = (9250)(1000) = 9250 000 cal/min

$\qquad\qquad\qquad$ = 645.0 kW

Figure E9.5*b* shows two reasonable arrangements for the coolers.
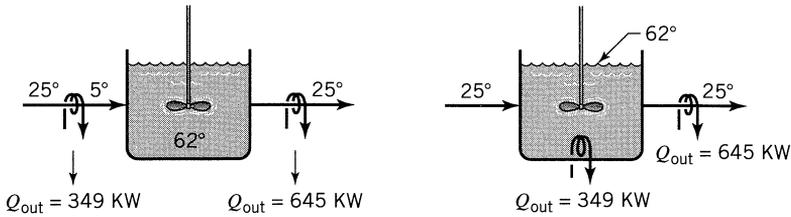
Figure E9.5*b*

EXAMPLE 9.6 *ADIABATIC PLUG FLOW REACTOR PERFORMANCE*

Find the size of adiabatic plug flow reactor to react the feed of Example 9.5 (F_{A0} = 1000 mol/min and C_{A0} = 4 mol/liter) to 80% conversion.

SOLUTION

Following the procedure of Fig. 9.9 draw trial operating lines (see Fig. E9.6*a*) with a slope of $\frac{1}{72}$ (from Example 9.5), and for each evaluate the integral

$$\int_0^{0.8} \frac{dX_A}{-r_A}$$

to find which is smallest. Figures E9.6*a* and *b* show this procedure for lines *AB* and *CD*. Line *CD* has the smaller area, is in fact closer to the minimum, and is
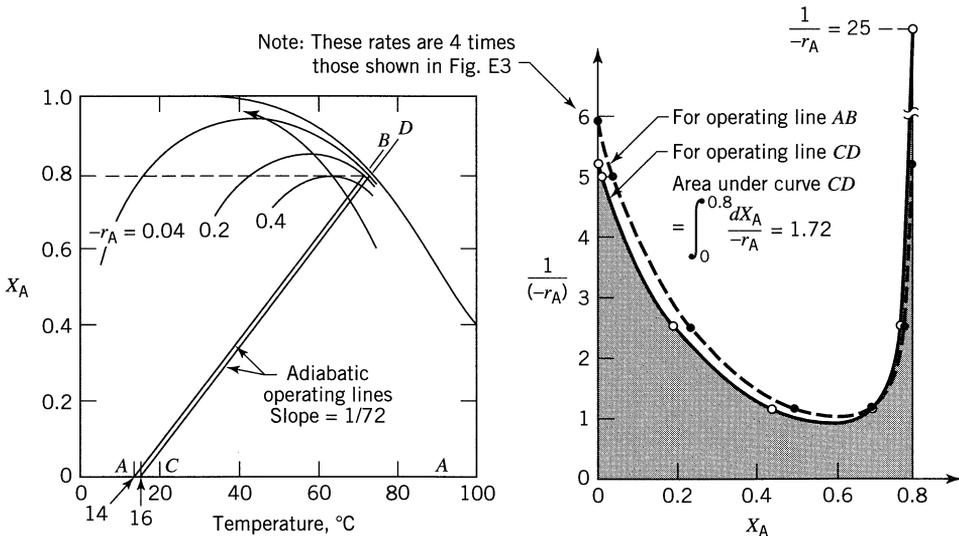
Figure E9.6

therefore the desired adiabatic operating line. So

$$\underline{\underline{V}} = F_{A0} \int_0^{0.8} \frac{dX_A}{-r_A} = F_{A0} \text{ (area under curve } CD)$$

$$= (1000 \text{ mol/min})(1.72 \text{ liter} \cdot \text{min/mol})$$

$$= \underline{\underline{1720 \text{ liters}}}$$

This volume is somewhat smaller than the volume of mixed flow reactor (from Example 9.5) but it is still four times as large as the minimum possible (405 liters, from Example 9.4).

Regarding temperatures: Figure E6a shows that the feed must first be cooled to 16.0°C, it then passes through the adiabatic reactor and leaves at 73.6°C and 80% conversion.

EXAMPLE 9.7 *ADIABATIC PLUG FLOW REACTOR WITH RECYCLE*

Repeat Example 9.6 but now allow recycle to product stream.

SOLUTION

For operating line CD of Example 9.6 we find an optimum recycle area, shown in Fig. E9.7 as rectangle $EFGH$.

$$\text{Area} = (0.8 - 0)(15 \text{ liter} \cdot \text{min/mol}) = 1.2 \text{ liter} \cdot \text{min/mol}$$

$$\underline{\underline{V}} = F_{A0} \text{ (area)} = (1000 \text{ mol/min})(1.2 \text{ liter/mol} \cdot \text{min}) = \underline{\underline{1200 \text{ liter}}}$$
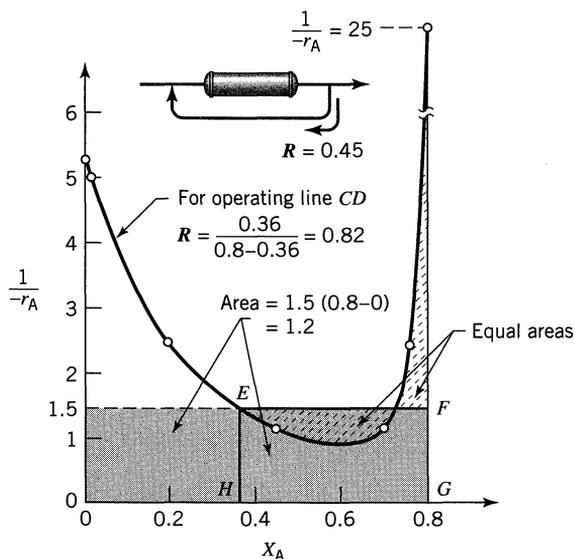
Figure E9.7

To summarize the results of these four examples, all of which are performing the same duty with the same feed

for the plug flow with optimal T progression	$V = 405$ liter (Example 4)
for the mixed flow reactor	$V = 2000$ liter (Example 5)
for the adiabatic plug flow reactor	$V = 1720$ liter (Example 6)
for the adiabatic recycle reactor	$V = 1200$ liter (Example 7)

9.2 MULTIPLE REACTIONS

As pointed out in the introduction to Chapter 7, in multiple reactions both reactor size and product distribution are influenced by the processing conditions. Since the problems of reactor size are no different in principle than those for single reactions and are usually less important than the problems connected with obtaining the desired product material, let us concentrate on the latter problem. Thus, we examine how to manipulate the temperature so as to obtain, first, a desirable product distribution, and second, the maximum production of desired product in a reactor with given space-time.

In our development we ignore the effect of concentration level by assuming that the competing reactions are all of the same order. This effect is studied in Chapter 7.

Product Distribution and Temperature

If two competing steps in multiple reactions have rate constants k_1 and k_2, then the relative rates of these steps are given by

$$\frac{k_1}{k_2} = \frac{k_{10}e^{-E_1/RT}}{k_{20}e^{-E_2/RT}} = \frac{k_{10}}{k_{20}} e^{(E_2 - E_1)/RT} \propto e^{(E_2 - E_1)/RT} \tag{27}$$

This ratio changes with temperature depending on whether E_1 is greater or smaller than E_2, so

$$\text{when } T \text{ rises} \begin{cases} k_1/k_2 \text{ increases if } E_1 > E_2 \\ k_1/k_2 \text{ decreases if } E_1 < E_2 \end{cases}$$

Thus the reaction with larger activation energy is the more temperature-sensitive of the two reactions. This finding leads to the following general rule on the influence of temperature on the relative rates of competing reactions:

> *A high temperature favors the reaction of higher activation energy, a low temperature favors the reaction of lower activation energy.*

Let us apply this rule to find the proper temperature of operations for various types of multiple reactions.

For *parallel reactions*

$$A \begin{array}{c} \nearrow^{1} R_{desired} \\ \searrow_{2} S_{unwanted} \end{array}$$
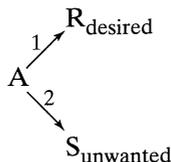
Step 1 is to be promoted, step 2 depressed, so k_1/k_2 is to be made as large as possible. Thus, from the above rule

$$\left. \begin{array}{l} \text{if } \mathbf{E}_1 > \mathbf{E}_2 \text{ use high } T \\ \text{if } \mathbf{E}_1 < \mathbf{E}_2 \text{ use low } T \end{array} \right\} \tag{28}$$

For *reactions in series*

$$A \xrightarrow{1} R_{desired} \xrightarrow{2} S \tag{29}$$

the production of R is favored if k_1/k_2 is increased. Thus

$$\left. \begin{array}{l} \text{if } \mathbf{E}_1 > \mathbf{E}_2 \text{ use high } T \\ \text{if } \mathbf{E}_1 < \mathbf{E}_2 \text{ use low } T \end{array} \right\} \tag{30}$$

For the general series-parallel reaction we introduce two additional considerations. First of all for *parallel steps* if one requirement is for a high temperature and another is for a low temperature, then a particular intermediate temperature is best in that it gives the most favorable product distribution. As an example, consider the reactions

$$A \begin{array}{c} \nearrow^{1} R_{desired} \\ \xrightarrow{2} S \\ \searrow_{3} \\ T \end{array} \qquad \text{where } \mathbf{E}_1 > \mathbf{E}_2, \mathbf{E}_1 < \mathbf{E}_3 \tag{31}$$
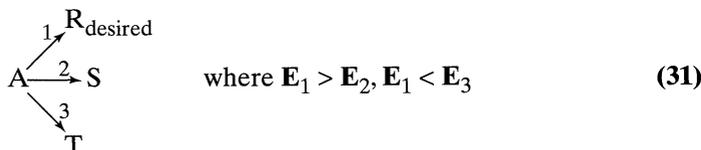
Now, $\mathbf{E}_1 > \mathbf{E}_2$ requires a high T, $\mathbf{E}_1 < \mathbf{E}_3$ requires a low T, and it can be shown that the most favorable product distribution is obtained when the temperature satisfies the following condition

$$\frac{1}{T_{opt}} = \frac{\mathbf{R}}{\mathbf{E}_3 - \mathbf{E}_2} \ln \left[\frac{\mathbf{E}_3 - \mathbf{E}_1}{\mathbf{E}_1 - \mathbf{E}_2} \frac{k_{30}}{k_{20}} \right] \tag{32}$$

Second, for *steps in series* if an early step needs a high temperature and a later step needs a low temperature, then a falling progression of temperatures should be used. Analogous arguments hold for other progressions.

The problems at the end of this chapter verify some of the qualitative findings on T_{opt} and also show some possible extension.

Comments

This discussion of multiple reactions shows that the relative size of the activation energies will tell which temperature level or progression is favored, just as Chapter 7 showed what concentration level or progression and what state of mixing is best. Although the general pattern of low, high, falling, or rising temperature can usually be determined without much difficulty, calculation of the optimum is not easy.

In experimentation we usually meet with the inverse of the situation outlined here in that we observe product distributions from experiment, and from this we wish to find the stoichiometry, kinetics, and the most favorable operating conditions. The generalizations of this chapter should be helpful in this inductive search.

Finally, when the reactions are of different order and of different activation energies, we must combine the methods of Chapters. 7, 8, and 9. Jackson et al. (1971) treat a particular system of this type and find that the optimum policy requires adjusting only one of the two factors, temperature or concentration, while keeping the other at its extreme. Which factor to adjust depends on whether the change in product distribution is more temperature dependent or concentration dependent. It would be interesting to know whether this finding represents a general conclusion.

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van Heerden, C., *Ind. Eng. Chem.,* **45,** 1242 (1953).
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PROBLEMS

Examples 9.4 through 9.7 illustrate the approach to problems dealing with nonisothermal reactors. Chapter 19 extends this approach to multistage operations of solid catalyzed reactions.

To reinforce these concepts, Problems 9.1 through 9.9 ask the reader to redo these examples with one or more changes. In many of these problems there is no need to redo the whole problem, just indicate where changes are needed in text and graphs.

9.1. For the reaction system of Example 9.4
(a) find τ needed for 60% conversion of reactant using the optimal temperature progression in the plug flow reactor.
(b) also find the exit temperature of fluid from the reactor.
Use whatever information you need from Example 9.4.

9.2. For the mixed flow reactor system of Example 9.5, we wish to get 70% conversion in the smallest size of reactor. Sketch your recommended system and on it indicate the temperature of the flowing stream entering and leaving the reactor as well as τ, the space time needed.

9.3. For the optimum temperature progression in a plug flow reactor in Example 9.4 (C_{A0} = 4 mol/liter, F_{A0} = 1000 mol A/min, X_A = 0.8, T_{min} = 5°C, T_{max} = 95°C) and feed and product both at 25°C, how much heating and cooling would be needed
(a) for the feed stream?
(b) in the reactor itself?
(c) for the stream leaving the reactor?

9.4. We plan to run the reaction of Example 9.4 (C_{A0} = 4 mol/liter, F_{A0} = 1000 mol/min) in a plug flow reactor kept at 40°C throughout to 90% conversion. Find the volume of reactor needed.

9.5. Redo Example 9.4⎤

9.6. Redo Example 9.5⎬ where C_{A0} = 4 mol/liter is replaced by C_{A0} = 1 mol/liter, and

9.7. Redo Example 9.6⎨ where F_{A0} remains unchanged at 1000 mol A/min.

9.8. Redo Example 9.7⎭

9.9. We wish to run the reaction of Example 9.4 in a mixed flow reactor to 95% conversion for a feed concentration C_{A0} = 10 mol/liter and feed rate of v = 100 liter/min. What size of reactor would we need?

9.10. Qualitatively find the optimum temperature progression to maximize C_S for the reaction scheme

$$A \xrightarrow{1} R \xrightarrow{3} S_{desired} \xrightarrow{5} T$$
$$\quad \searrow^{2} \quad \searrow^{4} \quad \quad \searrow^{6}$$
$$\quad U \quad\quad V \quad\quad\quad W$$
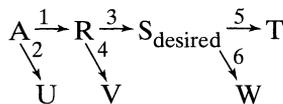
Data: E_1 = 10, E_2 = 25, E_3 = 15, E_4 = 10, E_5 = 20, E_6 = 25

9.11. The first-order reactions

$$A \xrightarrow{1} R \xrightarrow{3} S_{\text{desired}}$$
$$\searrow{2} \quad \searrow{4}$$
$$T \qquad U$$

$$k_1 = 10^9 e^{-6000/T}$$
$$k_2 = 10^7 e^{-4000/T}$$
$$k_3 = 10^8 e^{-9000/T}$$
$$k_4 = 10^{12} e^{-12,000/T}$$
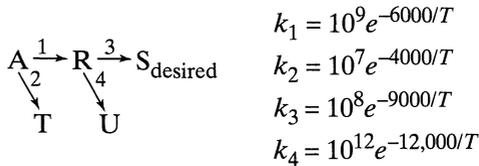
are to be run in two mixed flow reactors in series anywhere between 10 and 90°C. If the reactors may be kept at different temperatures, what should these temperatures be for maximum fractional yield of S? Find this fractional yield.

9.12. The reversible first-order gas reaction

$$A \underset{2}{\overset{1}{\rightleftharpoons}} R$$
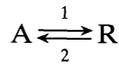
is to be carried out in a mixed flow reactor. For operations at 300 K the volume of reactor required is 100 liters for 60% conversion of A. What should be the volume of the reactor for the same feed rate and conversion but with operations at 400 K?

Data: $k_1 = 10^3 \exp[-2416/T]$

$\Delta C_p = C_{pR} - C_{pA} = 0$

$\Delta H_r = -8000$ cal/mol at 300 K

$K = 10$ at 300 K

Feed consists of pure A

Total pressure stays constant

Choosing the Right Kind of Reactor

So far we have concentrated on homogeneous reactions in ideal reactors. The reason is two-fold; because this is the simplest of systems to analyze and is the easiest to understand and master; also because the rules for good reactor behavior for homogeneous systems can often be applied directly to heterogeneous systems.

The important lessons learned in the first nine chapters of this book should guide us right away, or with a very minimum of calculations, to the optimum reactor system. Previously we have come up with six general rules. Let us present them and then practice using them.

Rule 1. For Single Reactions

To minimize the reactor volume, keep the concentration as high as possible for a reactant whose order is $n > 0$. For components where $n < 0$ keep the concentration low.

Rule 2. For Reactions in Series

Consider reactions in series, as shown:

$$A \rightarrow R \rightarrow S \rightarrow \cdots Y \rightarrow Z$$
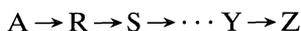
To maximize any intermediate, do not mix fluids that have different concentrations of the active ingredients—reactant or intermediates. See Fig. 10.1.

Rule 3. For Parallel Reactions

Consider the parallel reactions with reaction orders n_i

$n_1 \cdots$ low order

$n_2 \cdots$ intermediate

$n_3 \cdots$ high order
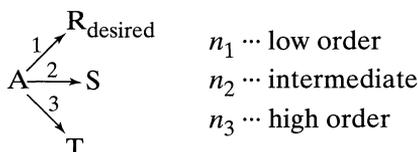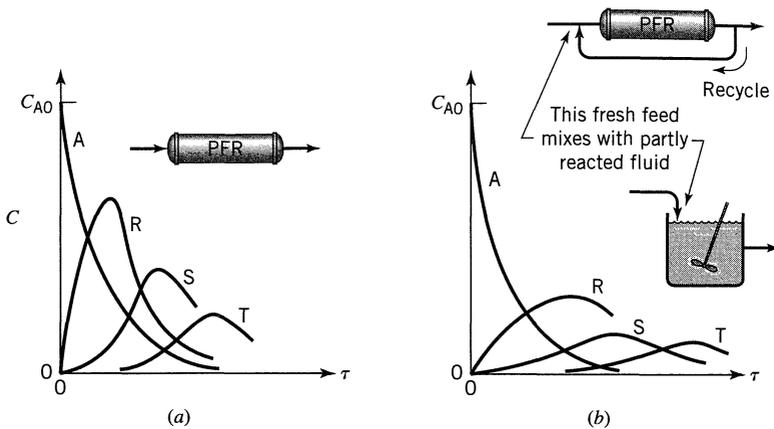
Figure 10.1 (*a*) Plug flow (no intermixing) gives the most of all the intermediates. (*b*) Intermixing depresses the formation of all intermediates.

To get the best product distribution,

- low C_A favors the reaction of lowest order
- high C_A favors the reaction of highest order
- If the desired reaction is of intermediate order then some intermediate C_A will give the best product distribution.
- For reactions all of the same order the product distribution is not affected by the concentration level.

Rule 4. Complex Reactions

These networks can be analyzed by breaking them down into their simple series and simple parallel components. For example, for the following elementary reactions, where R is the desired product, the breakdown is as follows:

$$\left.\begin{array}{c} A + B \rightarrow R \\ \\ R + B \rightarrow S \end{array}\right\} \quad \rightarrow \quad \begin{array}{c} A \rightarrow R \rightarrow S \\ \quad\quad R \\ B \begin{array}{c} \nearrow \\ \searrow \end{array} \\ \quad\quad S \end{array}$$
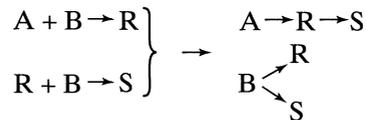
This breakdown means that A and R should be in plug flow, without any recycle, while B can be introduced as you wish, at any concentration level, since it will not affect the product distribution.

Rule 5. Continuous versus Noncontinuous Operations

Any product distribution that can be obtained in continuous steady-state flow operations can be gotten in a non-flow operation and vice versa. Figure 10.2 illustrates this.
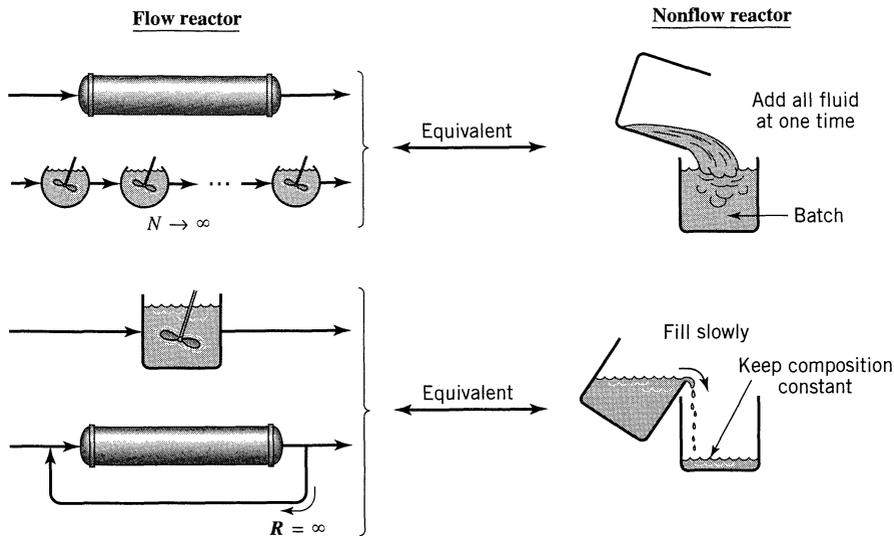
Figure 10.2 Correspondence between the residence time distribution of steady flow and either non-flow, batch or semibatch systems.

Rule 6. Effect of Temperature on Product Distribution

Given

$$A \xrightarrow{1} R \xrightarrow{2} S \qquad A \begin{smallmatrix} 1 \nearrow R \\ \\ 2 \searrow S \end{smallmatrix} \qquad \text{with} \qquad \begin{aligned} k_1 &= k_{10}e^{-E_1/RT} \\ \\ k_2 &= k_{20}e^{-E_2/RT} \end{aligned}$$
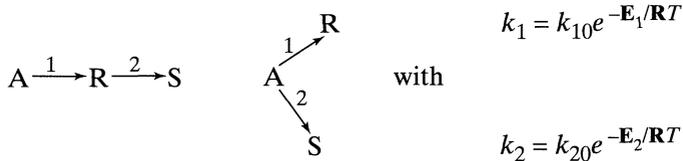
a high temperature favors the reaction with larger **E**, while a low temperature favors the reaction with smaller **E**.

Let us now see how these six rules can be used to guide us to the optimum.

Optimum Operation of Reactors

In reactor operations the word "optimum" can have different meanings. Let us look at two definitions which are particularly useful.

Feed a stream containing reactant A to a reactor and let R, S, T, ... be formed, with R being the desired product. Then by optimum

1. we could mean maximizing the overall fractional yield of R, or

$$\Phi\left(\frac{R}{A}\right) = \left(\frac{\text{moles R formed}}{\text{moles of A consumed}}\right)_{\text{max}} \tag{1}$$

2. we could mean running the reactor system so that the production of R is maximized, or

$$(\text{Prod R})_{\text{max}} = \left(\frac{\text{moles of R formed}}{\text{moles of A fed to the system}}\right)_{\text{max}} \tag{2}$$

For reactions in series we calculate the maximum production rate of R directly, as shown in Chapter 8. However, for reactions in parallel we find it useful to first evaluate the instantaneous fractional yield of R, or

$$\varphi\left(\frac{R}{A}\right) = \left(\frac{\text{moles R formed}}{\text{moles A consumed}}\right) \tag{3}$$

and then proceed to find the optimum. This procedure is shown in Chapter 7.

If unused reactant can be separated from the exit stream, reconcentrated to feed conditions and then recycled, then

$$(\text{Prod R})_{\text{max}} = \Phi(\text{R/A})_{\text{opt}} \tag{4}$$

EXAMPLE 10.1   *THE TRAMBOUZE REACTIONS (1958).*

The elementary reactions

$$A \begin{array}{c} \nearrow^{0} R \\ \xrightarrow{1} S_{\text{desired}} \\ \searrow_{2} T \end{array} \qquad \begin{array}{l} r_R = k_0 \\ r_S = k_1 C_A \\ r_T = k_2 C_A^2 \end{array} \qquad \begin{array}{l} k_0 = 0.025 \\ k_1 = 0.2 \text{ min}^{-1} \\ k_2 = 0.4 \text{ liter/mol·min} \end{array}$$
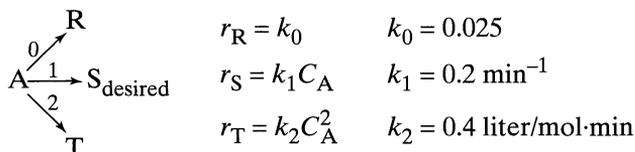
are to be run in four equal-size MFR's (mixed flow reactors), connected any way you wish. The feed is $C_{A0} = 1$, the feed flow rate is $v = 100$ liters/min.

The best scheme that the computer could come up with to maximize the fractional yield of S, or $\Phi(\text{S/A})$ [see problem 5, *Chem. Eng. Sci.*, **45**, 595–614 (1990)], is shown in Fig. E10.1a.

(a) How would you arrange a four-MFR system?
(b) With your best system what should be the volume of your four reactors?

$C_{A0} = 1$ 38.903   2.081
$v = 100$ 25.000   25.000   25.000   25.000
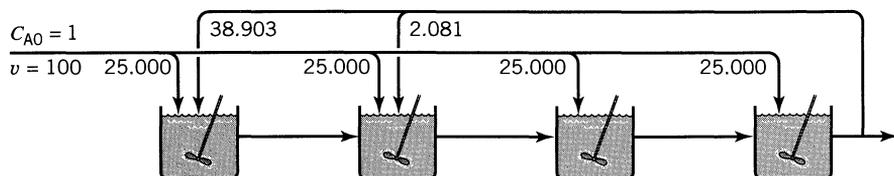
Figure E10.1a

SOLUTION

(a) First of all, the computer solution looks somewhat complicated from the engineering point of view. But never mind, let us proceed with our calculations. The instantaneous fractional yield, $\varphi(S/A)$, is

$$\varphi(S/A) = \frac{k_1 C_A}{k_0 + k_1 C_A + k_2 C_A^2} = \frac{0.2\, C_A}{0.025 + 0.2\, C_A + 0.4\, C_A^2} \qquad \textbf{(i)}$$

To maximize $\varphi(S/A)$ put

$$\frac{d\varphi}{dC_A} = 0 = \frac{0.2(0.025 + 0.2\, C_A + 0.4\, C_A^2) - 0.2\, C_A\,(0.2 + 0.8\, C_A)}{(---)^2}$$

Solving gives

$$\underline{\underline{C_{A\,opt} = 0.25}}$$

So from Eq. (i), at C_{Aopt},

$$\underline{\underline{C_{S\,opt} = \Phi(S/A)(C_{A0} - C_{A\,opt}) = 0.5(1 - 0.25) = 0.375}}$$

Thus the best way of running these four reactors is to keep the conditions at the optimum in all four units. One such design is shown in Fig. E10.1b. Problem P20 shows another design, and so does Fig. E10.1a.

$C_{A\,opt} = 0.25$
$C_{S\,opt} = 0.37$

$C_{A0} = 1$ mol/liter
$v_0 = 100$ liters/min

$C_{A\,opt}$
$C_{S\,opt}$
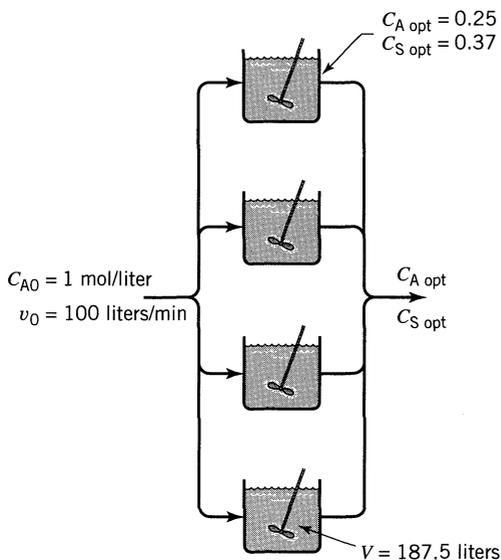
$V = 187.5$ liters

Figure E10.1b

(b) The volume per MFR comes from the performance equation

$$\tau = \frac{V}{v} = \frac{C_{A0} - C_A}{-r_A}$$

or

$$V = \frac{v(C_{A0} - C_A)}{-r_A} = \frac{(100/4)(1.00 - 0.25)}{0.025 + 0.2(0.25) + 0.4(0.25)^2}$$
$$= 187.5 \text{ liters}$$

Therefore, for the four reactor system

$$\underline{V}_{\text{total}} = 187.5 \times 4 = \underline{\underline{750 \text{ liters}}}$$

EXAMPLE 10.2   **TEMPERATURE PROGRESSION FOR MULTIPLE REACTIONS**

Consider the following scheme of elementary reactions:

$$A \underset{2}{\overset{1}{\rightleftarrows}} \begin{matrix} R \overset{3}{\to} U \\ \downarrow 5 \\ T \overset{4}{\to} S \end{matrix} \quad \left\{ \begin{matrix} E_1 = 79 \text{ kJ/mol} \\ E_2 = 113 \text{ kJ/mol} \\ E_3 = 126 \text{ kJ/mol} \\ E_4 = 151 \text{ kJ/mol} \\ E_5 = 0 \end{matrix} \right.$$
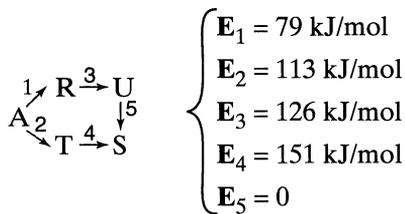
What temperature progression would you recommend if the desired product is:

(a) R, **(b)** S, **(c)** T, **(d)** U

and if reactor size is not important?

This industrially important reaction scheme is reported by Binns et al. (1969) and is used by Husain and Gangiah (1976, p. 245). In this problem we interchanged two of the reported **E** values to make the problem more interesting.

SOLUTION

(a) *Intermediate* **R** *is Desired.*   We want step 1 fast compared to step 2, and we want step 1 fast compared to step 3.

Since $E_1 < E_2$ and $E_1 < E_3$ use a <u>low temperature and plug flow.</u>

(b) *Final Product* **S** *is Desired.* Here speed is all that matters.

So use a <u>high temperature and plug flow</u>.

(c) *Intermediate* **T** *is Desired.* We want step 2 fast compared to step 1, and we want step 2 fast compared to step 4.

Since $E_2 > E_1$ and $E_2 < E_4$ use a <u>falling temperature and plug flow</u>

(d) *Intermediate* **U** *is Desired.* We want step 1 fast compared to step 2, and step 3 fast compared to step 5.

Since $E_1 < E_2$ and $E_3 > E_5$ use a <u>rising temperature and plug flow</u> ∎

REFERENCES

Binns, D.T., Kantyka, T.A., and Welland, R.C., *Trans. I. Chem. E.*, **47**, T53 (1969).
Husain, A., and Gangiah, K., *Optimization Techniques for Chemical Engineers*, Macmillan of India, Delhi (1976).
Trambouze, P.J., and Piret, E.L., *AIChE J,* **5,** 384 (1959).
van der Vusse, J.G., *Chem. Eng. Sci.,* 19, 994 (1964).

PROBLEMS

10.1. Given the two reactions

$$A + B \xrightarrow{1} R \qquad -r_1 = k_1 C_A C_B$$
$$R + B \xrightarrow{2} S \qquad -r_2 = k_2 C_A C_B$$

where R is the desired product and is to be maximized. Rate the four schemes shown in Fig. P10.1—either "good" or "not so good," Please, no complicated calculations, just reason it out.
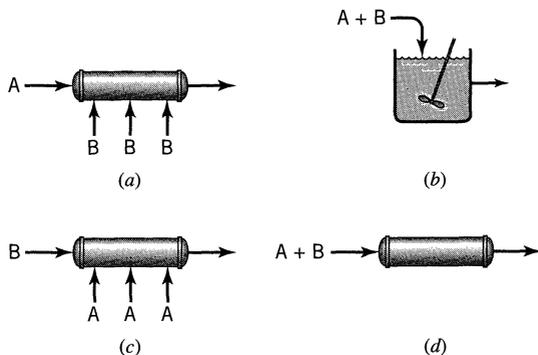
Figure P10.1

10.2. Repeat Problem 1 with just one change

$$-r_2 = k_2 C_R C_B^2$$

10.3. Repeat Problem 1 with just one change

$$-r_2 = k_1 C_R^2 C_B$$

10.4. For the reactions

$$A + B \rightarrow R \qquad -r_1 = k_1 C_A C_B$$
$$R + B \rightarrow S \qquad -r_2 = k_2 C_R C_B^2$$
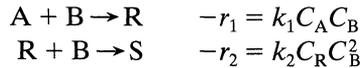
where R is the desired product, which of the following ways of running a batch reactor is favorable, which is not? See Fig. P10.4.
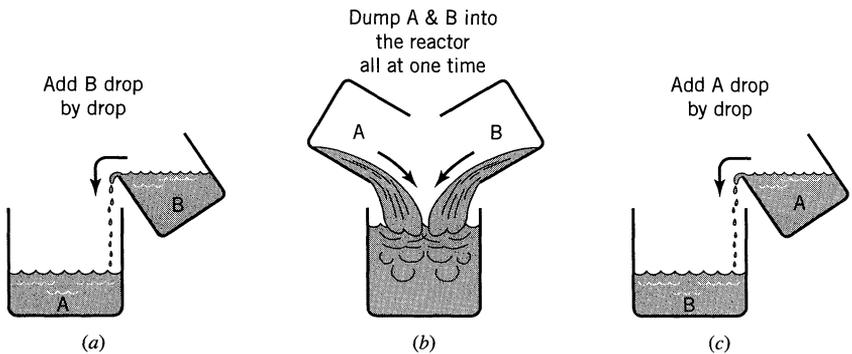
Figure P10.4

10.5. *The Oxydation of Xylene.* The violent oxidation of xylene simply produces CO_2 and H_2O; however, when oxidation is gentle and carefully controlled, it can also produce useful quantities of valuable phthalic anhydride as shown in Fig. P10.5. Also, because of the danger of explosion, the fraction
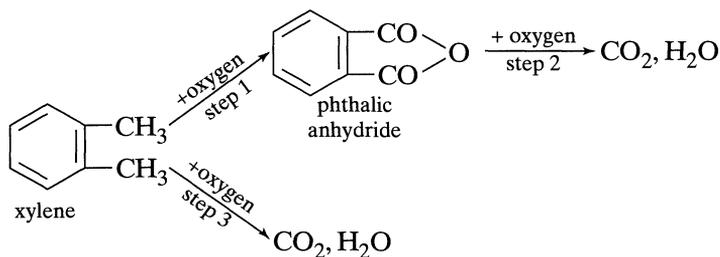
Figure P10.5

of xylene in the reacting mixture must be kept below 1%. Naturally, the problem in this process is to obtain a favorable product distribution.

(a) In a plug flow reactor what values of the three activation energies would require that we operate at the maximum allowable temperature?

(b) Under what circumstances should the plug flow reactor have a falling temperature progression?

10.6. *The Trambouze Reactions*—Reactions in parallel. Given the set of elementary reactions with a feed of $C_{A0} = 1$ mol/liter and $v = 100$ liters/min we wish to maximize the fractional yield, not the production of S, in a reactor arrangement of your choice.

$$
\begin{array}{lll}
\text{R}_{\text{desired}} & \cdots \quad r_R = k_0 & k_0 = 0.025 \text{ mol/liter·min} \\
\text{A} \xrightarrow{\;} \text{S} & \cdots \quad r_S = k_1 C_A & k_1 = 0.2 \text{ min}^{-1} \\
\text{T} & \cdots \quad r_T = k_2 C_A^2 & k_2 = 0.4 \text{ liter/mol·min}
\end{array}
$$
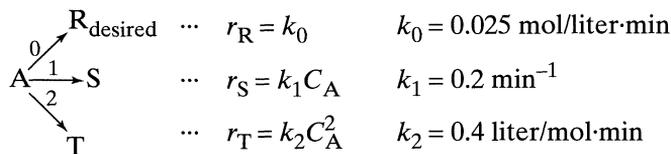
The computer, going through a multidimensional search [see problem 3, *Chem. Eng. Sci.*, **45**, 595–614 (1990)] came up with the arrangement of Fig. P10.6, which the authors claim is a LOCAL optimum, or a STATIONARY POINT. We are not interested in LOCAL optima, if such things exist. We are interested in finding the GLOBAL optimum. So with this in mind,

(a) do you judge that the arrangement of Fig. P10.6 is the best set up?

(b) if not, suggest a better scheme. Sketch your scheme and calculate the volume of the reactors you plan to use.
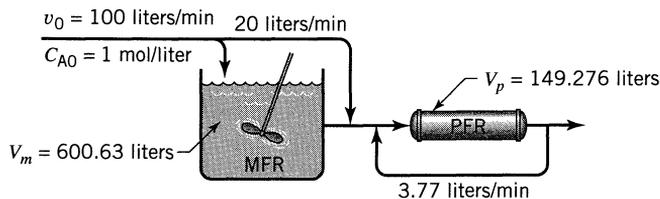
Figure P10.6

10.7. For the set of elementary reactions of Problem 10.6, with a feed of $C_{A0} = 1$ mol/liter and $v = 100$ liters/min we now wish to maximize the production rate of intermediate S (not the fractional yield) in a reactor arrangement of your choice. Sketch your chosen reactor scheme and determine $C_{S,max}$ obtainable.

10.8. *Automobile Antifreeze.* Ethylene glycol and diethylene glycol are used as automobile antifreeze, and are produced by the reactions of ethylene oxide with water, as follows:

$$H_2O + \underset{CH_2-CH_2}{\overset{O}{\diagup\diagdown}} \rightarrow O\diagdown\underset{\underline{}}{\overset{CH_2-CH_2OH}{\diagup}}_H$$

ethylene glycol

$$O\diagdown\underset{H}{\overset{CH_2-CH_2OH}{\diagup}} + \underset{CH_2-CH_2}{\overset{O}{\diagup\diagdown}} \rightarrow O\diagdown\underset{\underline{}}{\overset{CH_2-CH_2OH}{\diagup}}_{CH_2-CH_2OH}$$
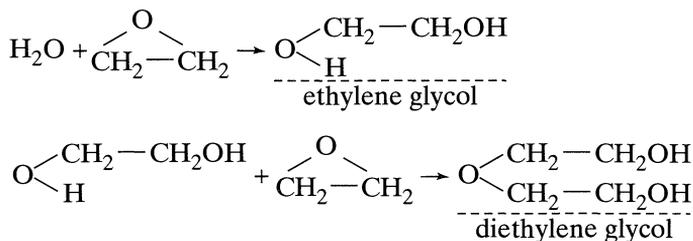
diethylene glycol

A mole of either glycol in water is as effective as the other in reducing the freezing point of water; however, on a molar basis the diethylene glycol is twice as expensive as the ethylene glycol. So we want to maximize ethylene glycol, and minimize the diethylene glycol in the mixture.

One of the country's largest suppliers produced millions of kilograms of antifreeze annually in reactors shown in Fig. P10.8*a*. One of the company's engineers suggested that they replace their reactors with one of the type shown in Fig. P10.8*b*. What do you think of this suggestion?

(a) (b)
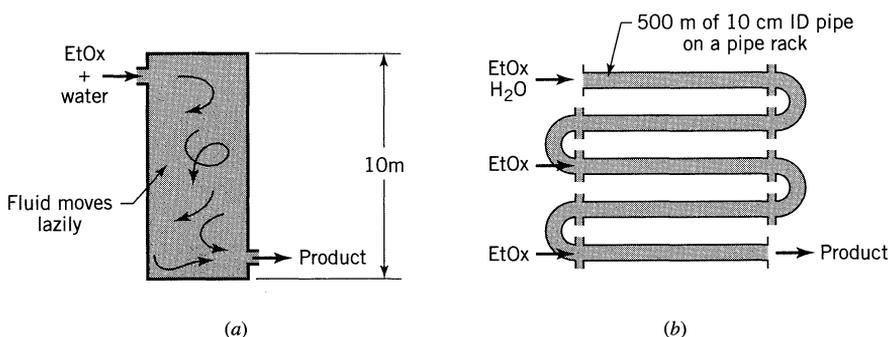
Figure P10.8*a* & P10.8*b*

10.9. *The Homogeneous Catalytic Reaction.* Consider the elementary reaction

$$A + B \xrightarrow{\ k\ } 2B, \quad -r_A = kC_A C_B \quad \text{with} \quad k = 0.4 \text{ liter/mol} \cdot \text{min}$$

For the following feed and reactor space time

$$\text{Flow rate} \qquad v = 100 \text{ liters/min}$$

$$\text{Feed composition} \qquad \begin{cases} C_{A0} = 0.45 \text{ mol/liter} \\ C_{B0} = 0.55 \text{ mol/liter} \end{cases}$$

$$\text{Space time} \qquad \tau = 1 \text{ min}$$

we want to maximize the concentration of B in the product stream. Our clever computer [see problem 8, *Chem. Eng. Sci.*, **45**, 595–614 (1990)] gives the design of Fig. P10.9 as its best try.

$C_{A0} = 0.45$ mol/liter
$C_{B0} = 0.55$ mol/liter
$v = 100$ liters/min
$V_p = 100$ liters
PFR
R
$v_R = 7.85$ liters/min
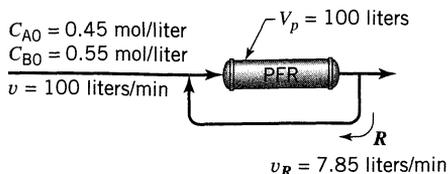
Figure P10.9

Do you think that this is the best way to run this reaction? If not, suggest a better scheme. Do not bother to calculate reactor size, recycle rate, etc. Just indicate a better scheme.

10.10. ***To Color Cola Drinks.*** When viscous corn syrup is heated it caramelizes (turns a deep dark brown). However, if it is heated a bit too long it transforms into carbon

$$\begin{array}{ccc} \text{corn} \\ \text{syrup} \end{array} \xrightarrow[]{\text{heat}} \text{caramel} \xrightarrow[\text{heat}]{\text{more}} \begin{array}{c} \text{carbon} \\ \text{particles} \end{array}$$
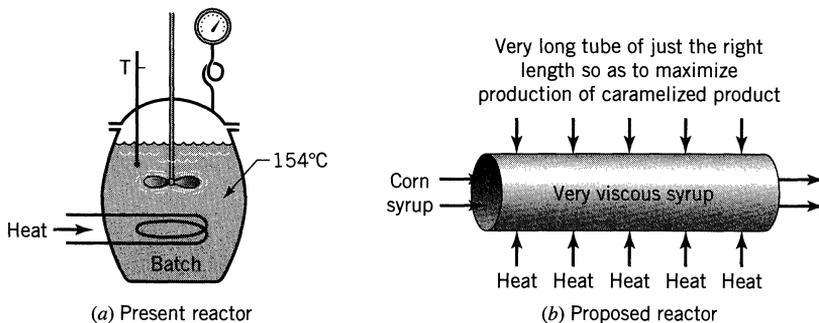
Figure P10.10 (*a*) Present reactor; (*b*) Proposed design.

The caramelized liquid is sent by railroad tank cars to the cola syrup formulators, who then test the solution for quality. If it is too light in color—penalty; if it has too many carbon particles per unit volume, then the whole tank car is rejected. There is thus a delicate balance between underreacting and overreacting.

At present a batch of corn syrup is heated at 154°C in a vat for a precise time. Then it is rapidly discharged and cooled, the vat is thoroughly cleaned (very labor intensive), and then is recharged.

The company wants to reduce costs and replace this costly labor intensive batch operation with a continuous flow system. Of course it will be a tubular reactor (rule 2). What do you think of their idea? Comment please, as you sit and sip your Coke or Pepsi.

10.11. *The Denbigh Reactions.* We intend to run the reactions below:

$$A \xrightarrow{1} R \xrightarrow{3} S$$

with the side reactions $A \xrightarrow{2} T$ and $R \xrightarrow{4} U$

$k_1 = 1.0$ liter/mol·s	2nd order
$k_2 = k_3 = 0.6 \text{ s}^{-1}$	1st order
$k_4 = 0.1$ liter/mol·s	2nd order
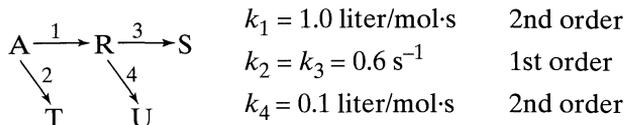
in a flow system under the following conditions

Feed flow rate $\quad v = 100$ liters/s

Feed composition $\quad \begin{cases} C_{A0} = 6 \text{ mol/liter} \\ C_{R0} = 0.6 \text{ mol/liter} \end{cases}$

We want to maximize the concentration ratio of C_R/C_T in the product stream.

As reported [see problem 7, *Chem. Eng. Sci.*, **45**, 595–614 (1990)], the attack on this problem used 2077 continuous variables, 204 integer variables, 2108 constraints, and gave as an optimal solution the design shown in Fig. P10.11.

(a) Do you think you could do better? If so, what reactor design would you suggest we use, and what C_R/C_T would you expect to obtain?
(b) If you wished to minimize the ratio of C_R/C_T, how would you go about it?

$C_{A0} = 6.0$ mol/liter
$C_{R0} = 0.6$ mol/liter
$v = 100$ liters/hr
$V_p = 20.706$ liters
PFR
$\left(\dfrac{C_R}{C_T}\right)$ is maximized ?
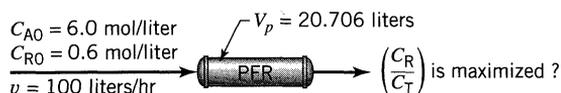
Figure P10.11

10.12. For the homogeneous catalytic reaction

$$A + B \rightarrow B + B, \qquad -r_A = kC_A C_B$$
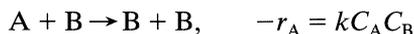
and with a feed of $C_{A0} = 90 \text{ mol/m}^3$, $C_{B0} = 10 \text{ mol/m}^3$ we want about 44% conversion of reactant A. What flow reactor or combination of flow reactors is best in that it gives the smallest total volume of reactors needed? There is no need to try to calculate the size of reactors needed; just determine the type of reactor system that is best and the type of flow that should be used.

10.13. Repeat Problem 12 with just one change. We need 90% conversion of reactant A.

10.14. Repeat Problem 12 with just one change. We only want about 20% conversion of reactant A.

10.15. We want to produce R from A in a batch reactor with a run time no greater than 2 hours and at a temperature somewhere between 5 and 90°C. The kinetics of this liquid first-order reaction system is as follows:

$$A \xrightarrow{1} R \xrightarrow{2} S, \begin{cases} k_1 = 30 \, e^{-20\,000/RT} & k = [\text{min}^{-1}] \\ k_2 = 1.9 \, e^{-15\,000/RT} & R = 8.314 \, \text{J/mol} \cdot \text{K} \end{cases}$$
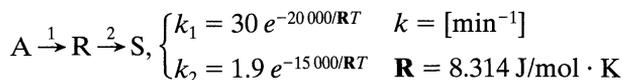
Determine the optimum temperature (to give C_{Rmax}) and run time to use, and the corresponding conversion of A to R.

10.16. *Reactor-Separator-Recycle System—Benzene Chlorination.* Here the elementary reactions are

$$C_6H_6 + Cl_2 \xrightarrow{1} C_6H_5Cl + HCl \qquad k_1 = 0.412 \text{ liter/kmol} \cdot \text{hr}$$
$$C_6H_5Cl + Cl_2 \xrightarrow{2} C_6H_4Cl_2 + HCl \qquad k_2 = 0.055 \text{ liter/kmol} \cdot \text{hr}$$
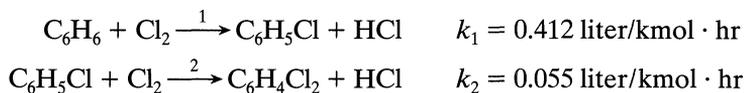
The desired product is monochlorobenzene. Also assume that any unreacted benzene in the product stream can be cleanly separated and reused as desired.

With the requirement that we only use PFRs, a minimum of three, in any arrangement, plus separator and recycle of unused reactant, the best of which was determined by the computer [see case 3, *Chem. Eng. Sci.*, **46**, 1361–1383 (1991)] is shown in Fig. P10.16.

Can you do better? There is no need to calculate volumes and flow rates. Just come up with an improved scheme.
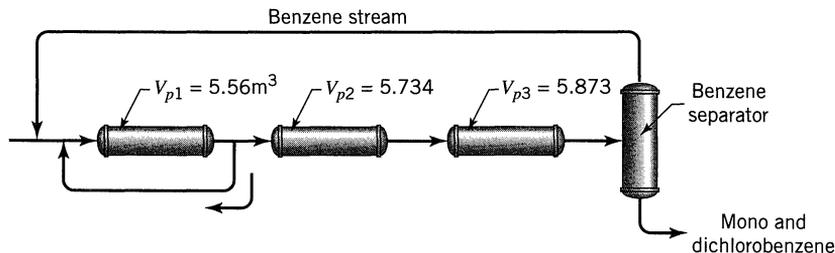
Figure P10.16

10.17. *Acrolein Production.* Adams et al. [*J. Catalysis*, **3**, 379 (1964)] studied the catalytic oxidation of propylene on bismuth molybdate catalyst to form acrolein. With a feed of propylene and oxygen and reaction at 460°C, the following three reactions occur.

$$C_3H_6 + O_2 \xrightarrow{1} C_3H_4O + H_2O$$

$$C_3H_6 + 4.5O_2 \xrightarrow{2} 3CO_2 + 3H_2O$$

$$C_3H_4O + 3.5O_2 \xrightarrow{3} 3CO_2 + 2H_2O$$
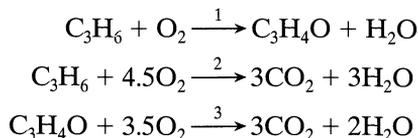
The reactions are all of first order in olefin and independent of oxygen and of reaction products, and with reaction rate ratios

$$\frac{k_2}{k_1} = 0.1, \qquad \frac{k_3}{k_1} = 0.25$$

If no cooling is needed to keep the reaction close to 460°C and if no separation and recycle of unused C_3H_6 is allowed, what kind of contactor would you suggest be used and what should be the maximum expected production rate of acrolein from this reactor?

10.18. *Nonisothermal van der Vusse Reactions (1964).* Consider the following reactions:

$$A \xrightarrow{1} R \xrightarrow{2} S \qquad \text{with} \qquad \begin{cases} k_1 = 5.4 \times 10^8 \exp(-66275/\mathbf{R}T) & [s^{-1}] \\ k_2 = 3.6 \times 10^3 \exp(-33137/\mathbf{R}T) & [s^{-1}] \\ k_3 = 1.6 \times 10^{10} \exp(-99412/\mathbf{R}T) & [\text{liter/mol·s}] \end{cases}$$

$$\begin{array}{c} \downarrow 3 \\ \tfrac{1}{2}T \end{array}$$
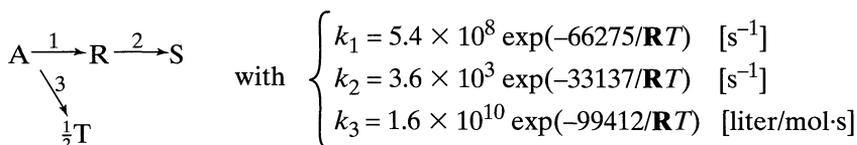
where the Arrhenius activation energy is given in units of J/mol, C_R is to be maximized and $C_{A0} = 1$ mol/liter.

Insisting on using three MFR's with τ_i between 0.1 and 20 s [see example 2, *AIChE J*, **40**, 849 (1994)], with possible intercooling and a temperature range between 360 K and 396 K, the best scheme calculated by the computer is shown in Fig. P10.18.

(a) Do you like this design? If not, what do you suggest we do with this three-reactor system? Please retain the three MFR's.
(b) What C_R/C_{A0} could be obtained and what τ should be used with the best reactor scheme (plug, mixed, or combined) and with ideal heat transfer?

Figure P10.18

10.19. *Phthalic Anhydride from Naphthalene.* The accepted mechanism for the highly exothermic solid catalyzed oxidation of naphthalene to produce phthalic anhydride is

$$
\begin{cases}
k_1 = k_2 = 2 \times 10^{13} \exp(-159000/\mathbf{R}T) & [\text{hr}^{-1}] \\
k_3 = 8.15 \times 10^{17} \exp(-209000/\mathbf{R}T) & [\text{hr}^{-1}] \\
k_4 = 2.1 \times 10^5 \exp(-83600/\mathbf{R}T) & [\text{hr}^{-1}]
\end{cases}
$$

where the reaction network is

$$A \xrightarrow{2} S \xrightarrow{4} T$$

with R formed via path 1 and 3.

and where

A = naphthalene (reactant)
R = naphthaquinone (postulated intermediate)
S = phthalic anhydride (desired product)
T = CO_2 + H_2O (waste products)

and the Arrenhius activation energy is given in units of J/mol. This reaction is to be run somewhere between 900 K and 1200 K.

A local optimum reactor setup discovered by the computer [see example 1, *Chem. Eng. Sci.*, **49**, 1037–1051 (1994)] is shown in Fig. P10.19.

Figure P10.19

(a) Do you like this design? Could you do better? If so, how?
(b) If you could keep the whole of your reactors at whatever temperature and τ value desired, and if recyle is allowed, how much phthalic anhydride could be produced per mole of naphthalene reacted?
Suggestion: Why not determine the values of k_1, k_2, k_3, and k_4 for both extremes of temperature, look at the values, and then proceed with the solution?

10.20. Professor Turton dislikes using reactors in parallel, and he cringed when he saw my recommended "best" design for Example 10.1. He much prefers using reactors in series, and so for that example he suggests using the design of Figure E10.1a, *but without any recycle* of fluid.

Determine the fractional yield of S, Φ (S/A), obtainable with Turton's design, and see if it matches that found in Example 10.1.