

The course of the reaction was followed by analyzing very small gas samples for CO and C₂H₆. In one run, for which the initial concentration of acetone, C₄₆, was 5.7 × 10⁻³ kmol/m³, the results were:

t, h†	1.25	2.25	3.25	4.25
C _{C₂H₆} , kmol/m ³	2.0 × 10 ⁻⁵	6.5 × 10 ⁻⁵	8.5 × 10 ⁻⁵	11.8 × 10 ⁻⁵

† These times were corrected for an induction period, of about 1.75 h.

Data for other runs at different initial concentrations gave the following results, reported as conversion of acetone x_A:

Time t, h	Initial acetone concn, C ₄₆ × 10 ³ kmol/m ³	
	4.62	1.99
	Conversion of acetone, 100x _A , %	
1.0	0.60	1.00
2.0	1.10	1.75
3.0	1.70	3.00
4.0	2.20	3.35
5.0	2.60	4.30

(a) Calculate values of the conversion per pass through the reactor. Does the system operate as a differential reactor?

(b) Using the stationary-state hypothesis, and with some assumptions about the reaction mechanism, the following rate expression for the photodecomposition of acetone can be derived:

$$r = \frac{k_1 C_A}{1 + k_2 C_A}$$

How do the data compare with a linearized form of the derived rate equation?

4-34 A first-order, irreversible reaction, A → B, is studied in a flow, recycle reactor (Fig. 4-19). Derive an equation for the reactor volume in terms of the conversion in the effluent stream, the rate constant, k, and the recycle ratio, R. The volumetric flow rates of the feed and effluent are equal (Q_f = Q_e). The recycle volumetric flow rate is Q_R = RQ_e. The fresh feed contains no product (B).

NONISOTHERMAL REACTORS

Nonuniform temperatures are common in tubular-flow or batch reactors. Also, continuous-flow tank reactors often operate at temperature levels different from the temperature of the feed or surroundings. The temperature may be varied deliberately (by heat exchange with the surroundings) in order to achieve maximum rates or selectivity. More frequently temperature changes arise because the inherent heat of reaction is significant and heat exchange with the surroundings is limited. Adiabatic operation results when the heat exchange is negligible. Large commercial reactors are more likely to approach adiabatic operation than isothermal conditions, except in those few cases, such as isomerization processes, where the heat of reaction itself is negligible. The design of nonisothermal reactors normally requires the simultaneous solution of an energy balance with the mass conservation equations developed in Chap. 3. The general form of the energy equation is discussed in Sec. 5-1. This is followed with illustrations of the design procedure for tank and for tubular-flow reactors in Secs. 5-2 to 5-4. In all cases ideal behavior is assumed: either well-stirred-tank or plug-flow, tubular reactors. When but one reaction is involved, the desired results of the calculations are the conversion and temperature vs. time or vs. reactor volume. For multiple reactions, selectivity as well as conversion is important. Both objectives are illustrated in Examples 5-1 to 5-3.

Multiple steady states in continuous-flow, stirred-tank reactors are discussed in Sec. 5-5. The particular steady state that is attained depends upon the initial state. Hence, Sec. 5-5 is closely related to the dynamic behavior during startup, a subject treated in the study of semibatch reactors in Sec. 5-6. Finally, optimum temperatures in reactors are discussed in the last part of the chapter, Sec. 5-7. The optimum-temperature question in tubular-flow reactors for reversible exothermic reactions is particularly interesting because the profile is not uniform.

As an introduction to the effect of temperature changes, it is instructive to consider the quantitative behavior of adiabatic flow reactors. Such reactors are simple to analyze since the energy balance can be solved, without reference to the mass balance, to obtain a relation between temperature and conversion. This eliminates the stepwise numerical procedure necessary for nonadiabatic and nonisothermal operation. Normally, heat exchange with the surroundings modifies rather than completely changes the temperature effects in adiabatic reactors. Therefore, the results for adiabatic conditions provide a helpful insight into temperature effects. Figure 5-1 illustrates the solution of the energy equation for endothermic and exothermic reactions. These nearly straight lines[†] express the fact that, for adiabatic operation, all the heat of reaction is reflected in a temperature change of the reaction mixture.

Consider now a single, irreversible reaction, first in a tubular-flow reactor. As the conversion increases with reactor length the temperature would also increase (for an exothermic reaction), as determined by the line in Fig. 5-1. Since the rate is a function of temperature as well as conversion, the nature of the temperature-length profile will depend upon the activation energy as well as the order of the reaction. Typical profiles of rate, conversion, and temperature for an exothermic reaction are shown in Fig. 5-2a. Note that the rate first increases due to the temperature rise, and then goes through a maximum. The rate approaches zero as the conversion approaches 100% because the reactant concentration is decreasing to zero. However, the volume required for a given conversion will be less for

[†] They would be exactly straight if the specific heat of the reaction mixture and heat of reaction are independent of temperature and composition [as shown in Sec. 5-3, Eq. (5-17)].

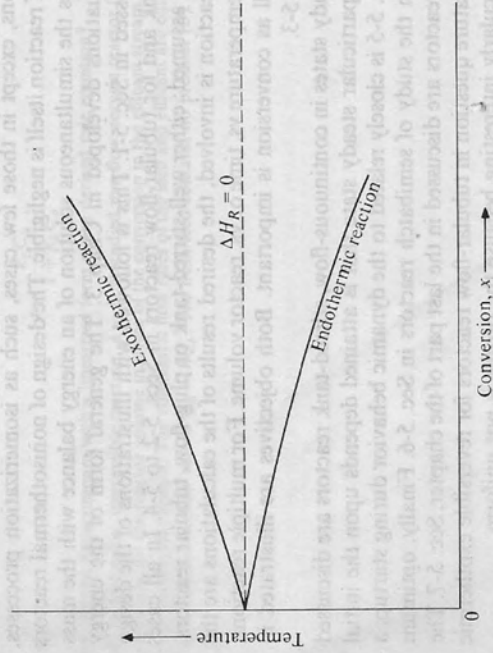


Figure 5-1 Temperature vs. conversion in adiabatic reactors.

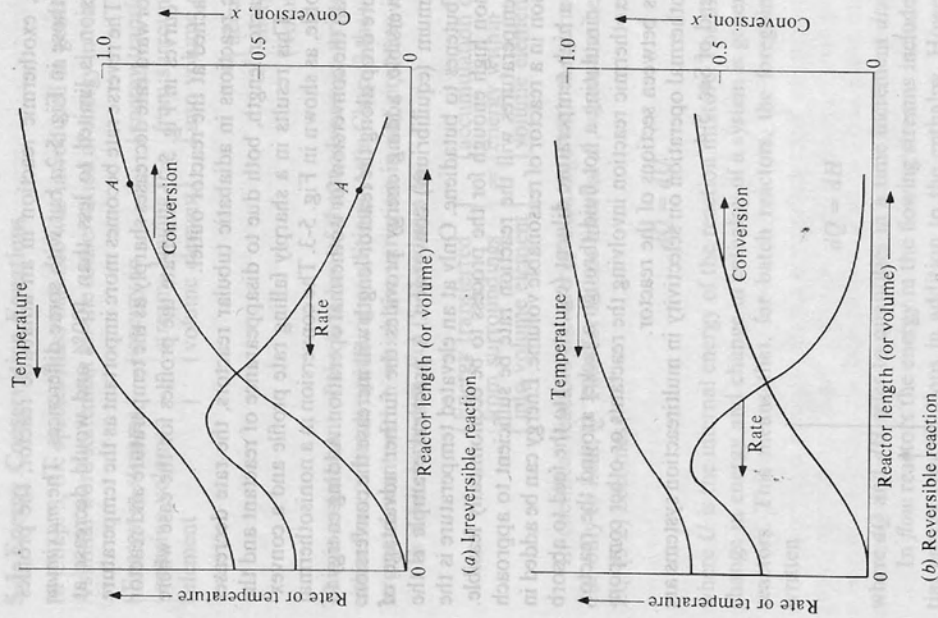


Figure 5-2 Rate, temperature, and conversion profiles for exothermic reactions in adiabatic flow reactors.

nonisothermal operation than in an isothermal reactor. Next, consider a stirred-tank reactor. The temperature and composition will be uniform throughout the vessel and this means that reactor behavior can be represented by a point on each of the profiles in Fig. 5-2. Suppose the desired conversion is high, for example corresponding to point *A*. The figure shows that the stirred-tank reactor would operate at a constant, lower rate than at any point (except at the outlet) in the tubular-flow reactor. The required volume would be larger for a stirred-tank unit. For either type, permissible temperatures may be limited by undesirable side reactions, or other factors. In these cases, effective design depends upon efficient removal of energy.

For a reversible, exothermic reaction in an adiabatic reactor, the profiles would be similar to those in Fig. 5-2a but with some differences. The *maximum* (equilibrium) conversion is limited to less than 100% and would decrease at higher temperatures. The reverse rate becomes more important as the temperature rises so that the net forward rate decreases sharply as the temperature and reactor length increase. The curves in Fig. 5-2b illustrate the profiles for the case where equilibrium is approached at the reactor outlet.

For endothermic reactions in adiabatic tubular reactors, the rate decreases continuously with reactor length, both due to disappearance of reactant and the drop in temperature. This results in a sharply falling rate profile and a convex rising conversion profile, as shown in Fig. 5-3. The conversion in a nonisothermal reactor will be less than the conversion for isothermal operation. Adding energy to reduce the temperature drop along the reactor length will increase the conversion. If the reaction is reversible, adding energy provides the further advantage of increasing the maximum (equilibrium) conversion. A practical example is the dehydrogenation of butenes to butadiene. Only at an elevated temperature is the equilibrium conversion high enough for the process to be economically feasible. Also, only at high temperatures will the reaction rate be sufficient to approach equilibrium conversion in a reactor of reasonable volume. Energy can be added in many ways: adding a high temperature diluent (e.g., steam) to the feed to absorb the heat of reaction, circulating a hot fluid through a jacket around the reactor, by a simultaneous exothermic reaction involving the reactants or other components, or from heaters between sections of the reactor.

Effects of nonisothermal operation on selectivity in multireaction systems are summarized at the end of Sec. 5-4.

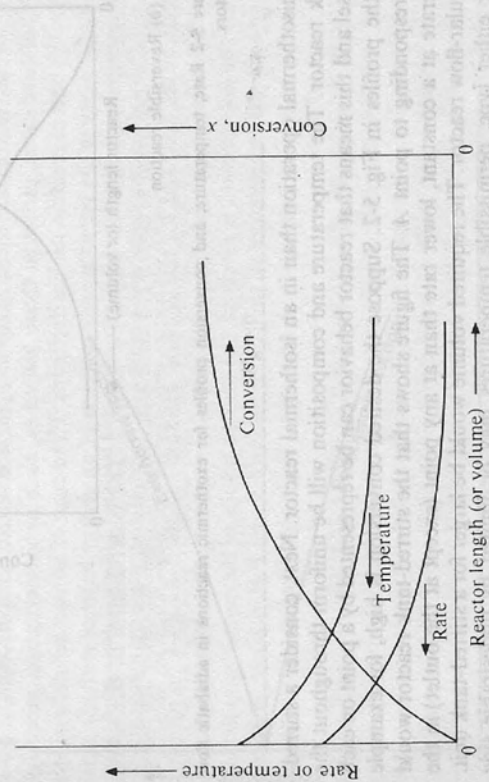


Figure 5-3 Rate, temperature, and conversion profiles for endothermic reactions in adiabatic flow reactors.

5-1 Energy Conservation Equations

In Chap. 3, the species mass balance was introduced in general form as Eq. (3-1). A similar word statement for the conservation of energy in reactors may be written:

$$\left\{ \begin{array}{l} \text{Energy in streams} \\ \text{entering volume} \\ \text{element} \end{array} \right\} - \left\{ \begin{array}{l} \text{energy in} \\ \text{streams leaving} \\ \text{volume element} \end{array} \right\} + \left\{ \begin{array}{l} \text{energy transferred} \\ \text{from surroundings} \\ \text{into volume element} \end{array} \right\} = \left\{ \begin{array}{l} \text{accumulation of} \\ \text{energy within} \\ \text{volume element} \end{array} \right\} \quad (5-1)$$

This is a statement of the first law of thermodynamics written so as to apply for either flow or batch operating conditions. As in Chap. 3 the volume element is the largest element within which the variation in any property is negligible.

In a *batch* process, Eq. (5-1) reduces to

$$\left\{ \begin{array}{l} \text{Energy transferred} \\ \text{from surroundings} \\ \text{into volume element} \end{array} \right\} = \left\{ \begin{array}{l} \text{accumulation of} \\ \text{energy within} \\ \text{volume element} \end{array} \right\} \quad (5-2)$$

In chemical reactors the energy exchange with the surroundings is normally due only to heat, Q . Then for a time interval dt , where the heat transferred is dQ , Eq. (5-2) becomes[†]

$$dQ = dU$$

where U is the internal energy of the reaction mixture. The difference between the change in energy and change in enthalpy of a system is generally unimportant in reactors. This means that, for batch reactors, the foregoing equation may be written

$$dQ = dH \quad (5-3)$$

where dQ and dH refer to quantities in a time increment dt .

In *flow* reactors the energy in the flowing streams includes kinetic and potential energy contributions in addition to the enthalpy. However, when reactions occur these two contributions are normally unimportant. Then for *steady-state* operation of a flow reactor, Eq. (5-1) becomes

$$H'_f - H'_e + Q' = 0 \quad (5-4)^\ddagger$$

where H' and Q' refer to energy *rates* and subscripts f and e designate feed and effluent streams for the appropriate volume element of the reactor. For a tank

[†] In thermodynamics the first law for a batch process is expressed as $\Delta U = Q - W$. If $W \rightarrow 0$, $Q = \Delta U$. (For example see "Introduction to Chemical Engineering Thermodynamics" by J. M. Smith and H. G. Van Ness, 3d ed., p. 25, McGraw-Hill Book Company, New York, 1975.)

[‡] The first law of thermodynamics for a steady-state process is written $(H + P.E. + K.E.)_e - (H + P.E. + K.E.)_f = Q' - W'$. The terms $P.E.$ and $K.E.$ refer to potential and kinetic energy. If $W' \rightarrow 0$, $\Delta(P.E.) \rightarrow 0$ and $\Delta(K.E.) \rightarrow 0$, this expression is the same as Eq. (5-4).

reactor the volume element is the entire volume of the reactor while for a tubular flow form a differential volume must be used (see Secs. 3-3 and 3-4).

For semibatch reactors, all four terms of Eq. (5-1) may be important. If kinetic and potential energy contributions are neglected as well as any energy transferred as work, the energy balance for a time dt is

$$(H'_r - H'_c) dt + dQ = dH \quad (5-5)$$

Here, as in Eq. (5-3) dQ and dH refer to quantities of energy rather than rates. In writing Eq. (5-5) the accumulation of energy in the reaction has been assumed to be equal to the accumulation of enthalpy, ΔH , as was done in writing Eq. (5-3) for batch reactors.

Equations (5-3), (5-4), and (5-5) are the starting expressions for treating heat effects in nonisothermal reactors operating as batch, continuous flow, or semibatch processes. In the following sections these expressions are employed, along with mass balances, for calculating reactor performance (temperature, conversions, selectivity vs. reactor volume, or time).

5-2 Batch, Stirred-Tank Reactors

Equations (3-7) [or Eq. (3-8) for constant volume] and (5-3) are the mass-and-energy-conservation equations applicable for batch operation of stirred-tank reactors. For the energy equation to be useful, the enthalpy change dH needs to be expressed in terms of temperature and reaction rate (or conversion). This is primarily a thermodynamic procedure. Suppose the total mass and constant-pressure specific heat of the reaction mixture are m and c_p . In an increment of time dt , the mixture undergoes a temperature change dT and also a composition change determined by the amount of reaction. We wish to evaluate the enthalpy change in this time increment. Since enthalpy is a state property, any sequence of states may be used to determine dH , without regard to the actual process (path). Heats of reaction are more likely to be available, and accurately known, at a reference temperature, $T_r = 298$ K. Therefore, the preferable path will involve the reaction at T_r and consist of the following three steps:

1. Cool the reaction mixture at constant pressure from T to T_r . The enthalpy change is

$$\Delta H_1 = m_i \int c_p dT \approx m_i c_p (T_r - T)$$

The second equality requires that c_p be independent of temperature. Also, c_p is the specific heat for the composition of the mixture at time t .

2. Carry out the reaction at T_r . The amount of reaction will be $(\mathbf{r}V) dt$ moles per unit time, where \mathbf{r} is the molal rate of disappearance of reactant (the same reactant as used to formulate the mass balance). If ΔH_R is the molal heat of reaction at T_r , the enthalpy change for this constant temperature and constant pressure process is

$$dH_2 = \Delta H_R(\mathbf{r}V) dt$$

3. Heat the reaction mixture from T_r to $T + dT$, the temperature at the end of the time increment. For this third step:

$$\Delta H_3 \approx m_i c_p (T + dT - T_r)$$

The required enthalpy change is the sum of ΔH_1 , dH_2 , and ΔH_3 . If we neglect changes in c_p with composition as well as with temperature, the sum is

$$dH = m_i c_p dT + \Delta H_R(\mathbf{r}V) dt \quad (5-6)$$

The heat exchange with the surroundings may be expressed in terms of an overall heat transfer coefficient h_o , surroundings temperature† T_s , and heat transfer area A_n . Thus, the amount of energy transferred to the reactor in time dt is

$$dQ = h_o A_n (T_s - T) dt \quad (5-7)$$

Finally, we substitute Eqs. (5-6) and (5-7) in (5-3) to obtain an energy equation in terms of temperature and rate of disappearance of reactant:

$$h_o A_n (T_s - T) = \Delta H_R(\mathbf{r}V) + m_i c_p \frac{dT}{dt} \quad (5-8)$$

Many assumptions regarding c_p and the relationship between dH and dU have been made in obtaining Eq. (5-8). However, the errors introduced are nearly always negligible with respect to uncertainties in the reaction rate and the magnitude of the remaining terms.

Equation (5-8) and the mass balance, along with an expression for the reaction rate, are sufficient to calculate the composition and temperature of the reaction mixture as a function of time. A stepwise numerical solution of the two differential equations is usually required because of the exponential effect of temperature in the rate equation.

The energy balance can be expressed in terms of conversion by combining the mass balance, Eq. (3-7),‡ with Eq. (5-8) to eliminate \mathbf{r} :

$$h_o A_n (T_s - T) = \Delta H_R(V_0 C_{A_0}) \frac{dx_A}{dt} + m_i c_p \frac{dT}{dt} \quad (5-9)$$

where x_A is the conversion of reactant A . This form is advantageous for adiabatic operation. Thus, when $dQ = 0$, Eq. (5-9) reduces to a form not involving time:

$$m_i c_p dT = -\Delta H_R(V_0 C_{A_0}) dx_A \quad (5-10)$$

If again, c_p is assumed to be independent of temperature and composition, Eq. (5-10) can be integrated immediately to give a relationship between temperature and conversion:

$$T - T_0 = -\frac{\Delta H_R(V_0 C_{A_0})}{m_i c_p} (x - 0) \quad (5-11)$$

† For example, the temperature in the internal cooling (or heating) coils or jacket surrounding the reactor.

‡ The negative sign in Eq. (3-7) disappears if \mathbf{r}_A is the rate of disappearance of reactant A .

where T_0 is the initial temperature in the reactor and $x_i = 0$. Note that ($V_0 C_{A_0}$) is initial moles of reactant A . For adiabatic operation Eq. (5-11) eliminates the need for simultaneous stepwise solution of the mass and energy balances. Both adiabatic and nonadiabatic design calculations are illustrated in the following example.

Example 5-1 In a study of the production of drying oils by the decomposition of acetylated castor oil, Grummitt and Fleming[†] were able to correlate decomposition data on the basis of a first-order reaction written as



where r is rate of decomposition, in kg of acetic acid produced per second per cubic meter, and C is concentration of acetic acid, in kg per m³, equivalent to acetylated castor oil. Data obtained over the temperature range 295 to 340°C indicated an activation energy of 44,500 cal/g mol in accordance with the following expression for the specific-reaction-rate constant k :

$$\ln k = -\frac{44,500}{R_g T} + 35.2$$

where T is in degrees Kelvin.

If a batch reactor initially contains 227 kg of acetylated castor oil at 340°C (density 0.90) and the operation is adiabatic, plot curves of conversion (fraction of the acetylated oil that is decomposed) and temperature vs. time. It is estimated that the endothermic heat effect for this reaction is 62,760 J/mol of acetic acid vapor. The acetylated oil charged to the reactor contains 0.156 kg of equivalent acetic acid per kg of oil; i.e., complete decomposition of 1 kg of the oil would yield 0.156 kg of acetic acid. Assume that the specific heat of the liquid reaction mixture is constant and equal to 2.51×10^3 J/(kg)(K). Also assume that the acetic acid vapor produced leaves the reactor at the temperature of the reaction mixture.

SOLUTION The applicable mass conservation expression, assuming no change in volume, is Eq. (3-8):

$$\frac{dx}{dt} = \frac{1}{C_0} r$$

$$\frac{dt}{dx} = \frac{C_0}{r} \quad (A)$$

or

where C_0 and r are measured in terms of equivalent acetic acid.[†] The concentration-conversion relation is

$$C = C_0(1 - x)$$

If we replace r with the rate equation expressed in terms of conversion and temperature Eq. (A) becomes

$$\frac{dt}{dx} = \frac{C_0}{(k/60)C_0(1-x)}$$

$$\frac{dt}{dx} = f(T, x) = \frac{60}{[\exp(35.2 - 44500/R_g T)](1-x)} \quad (B)$$

Since the reactor operates adiabatically, Eq. (5-11) is applicable. If we take 1 kg of oil as a basis, the initial moles of equivalent acetic acid is $V_0 C_{A_0} = 0.156/60$. Substituting numbers in Eq. (5-11) yields

$$T - T_0 = -\frac{62,760}{2.51 \times 10^3} \left(\frac{0.156/60}{10^{-3}} \right) (x - 0) \quad (C)$$

or

$$T = T_0 - 65x = (340 + 273) - 65x \quad (D)$$

The right-hand side of Eq. (B) can now be expressed in terms of x only by substituting Eq. (D) for the temperature. Hence, Eq. (B) can be solved numerically, for example, by the Runge-Kutta procedure described in Examples 4-7 and 4-15. The working equations for this, one dependent-variable problem are:

$$k_0 = (\Delta x) f(x_n, T_n)$$

$$k_1 = (\Delta x) f\left(x_n + \frac{\Delta x}{2}, T_{(x_n + \Delta x/2)}\right)$$

$$k_2 = (\Delta x) f\left(x_n + \frac{\Delta x}{2}, T_{(x_n + \Delta x/2)}\right)$$

$$k_3 = (\Delta x) f(x_n + \Delta x, T_{(x_n + \Delta x)})$$

$$t_{n+1} = t_n + \frac{1}{6}(k_0 + 2k_1 + 2k_2 + k_3)$$

where Eqs. (B) and (D) give $f(T, x)$ and n represents the number of increments of Δx .

[†] The reaction rate used in mass or energy conservation equations can be expressed either in mass or moles. This is the first example in which we have used mass. Of course, the conservation equations must be consistent. If r in Eq. (3-8) is expressed in terms of mass, the concentration must also be so expressed.

For the first increment choose $\Delta x = 0.1$. Since $x = 0$ at $t = 0$, Eq. (D) gives $T = T_0 = 613$ K. Then from Eq. (B),

$$f(x_0, T_{x_0}) = f(0, 613^\circ) = \frac{60}{\left[\exp \left(\frac{35.2 - 44500}{1.98(613)} \right) \right] (1 - 0)} = 259 \text{ s}$$

The k values are

$$(k_0) = 0.1 f(0, 613^\circ) = 0.1 (259) = 25.9 \text{ s}$$

$$k_1 = 0.1 f(0 + 0.1/2, T_{0+0.1/2})$$

$$= 0.1 f(0.05, 610^\circ)^\dagger = 0.1(32.7) = 32.7 \text{ s}$$

$$k_2 = 0.1 f(0 + 0.1/2, T_{0+0.1/2}) = 32.7 \text{ s}$$

$$k_3 = 0.1 f(0 + 0.1, T_{0,1}) = f(0.1, 606.5^\circ) = 42.7 \text{ s}$$

and

$$t_1 = t_0 + \frac{1}{2}(25.9 + 2(32.7) + 42.7) + (42.7) \\ = 0 + 33 = 33 \text{ s}$$

Results for subsequent increments are given in Table 5-1 and in Fig. 5-4.

The curves of temperature and conversion vs. time show the necessity of supplying energy (as heat) to a highly endothermic reaction if large conversions are desired. In the present case, where no energy was supplied, the temperature decreased so rapidly that the reaction essentially stopped after a conversion of 50% was reached. If, instead of operating adiabatically, a constant rate of energy $Q' = 52,700$ J/s had been added to the reactor, the energy balance, according to Eqs. (5-9) and (5-7), would have been

$$m_t c_p \frac{dT}{dt} = -\Delta H_R (V_0 C_{A0}) \frac{dx_A}{dt} + \frac{dQ}{dt}$$

or, numerically

$$227(2.51 \times 10^3) \frac{dT}{dt} = -62760 \left(\frac{0.156/60}{10^{-3}} \right) 227 \frac{dx}{dt} + Q'$$

[†] The temperature of 610 K is obtained from Eq. (D) with $x = 0.10/2$.

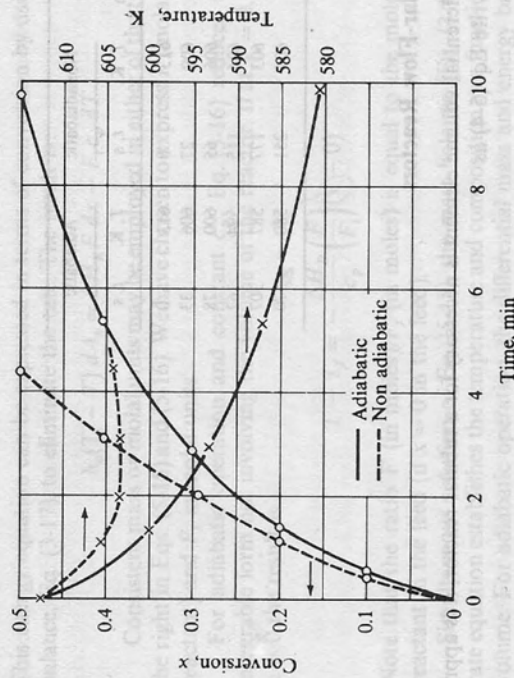


Figure 5-4 Temperature and conversion vs. time.

Integrating from $x = 0$, $T = T_0$ at $t = 0$, this expression becomes

$$T = T_0 + 1.75 \times 10^{-6} Q'(t - 0) - 65(x - 0) \quad (D')$$

Equation (B) is still applicable for this nonadiabatic case and can be integrated numerically. However, Eq. (D') must be used to determine the temperature. The working equations for the Runge-Kutta method are:

$$k_0 = (\Delta x) f(x_n, T_{x_n, t_n})$$

$$k_1 = (\Delta x) f \left(x_n + \frac{\Delta x}{2}, T_{x_n + \Delta x/2, t_n + k_0/2} \right)$$

$$k_2 = (\Delta x) f \left(x_n + \frac{\Delta x}{2}, T_{x_n + \Delta x/2, t_n + k_1/2} \right)$$

$$k_3 = (\Delta x) f(x_n + \Delta x, T_{x_n + \Delta x, t_n + k_2})$$

The subscripts on T indicate the values of x and t to use in Eq. (D') to evaluate the temperature.

The temperatures and times obtained by these numerical calculations for various conversions are given in Table 5-2 and are also shown in Fig. 5-4. Comparison of the results for adiabatic and nonadiabatic operation demonstrates the advantage of adding heat. For example, a conversion of 30% is obtained in about one-third less time when 52,700 J/s. (3000 Btu/min) are added continuously to the reactor.

Table 5-1

Conversion	T , K	t , s
0	613	0
0.10	606	33
0.20	600	78
0.30	594	162
0.40	587	307

Table 5-2

Conversion	Nonadiabatic		Adiabatic	
	T, K	t, s	T, K	t, s
0.0	613	0	613	0
0.10	609	27	606	33
0.20	606	65	600	78
0.30	604	115	594	162
0.40	603	177	587	307
0.50	604	251	580	570

5-3 Tubular-Flow Reactors

Since a differential volume element is necessary for a tubular reactor, it is appropriate to write Eq. (5-4) as

$$dQ' = dH' \quad (5-12)$$

where the differentials refer to a change over a volume element rather than an element of time as in Eq. (5-3). That is, dH' is the change in energy rate between the streams entering and leaving the volume element and dQ' is the rate of energy transfer into the differential volume element.† The enthalpy difference will again be due to the temperature change dT and a composition change associated with the reaction. Hence the procedure used in Sec. 5-2 for deriving an expression for dH is applicable here. If F_i is the total molar feed flow rate through the reactor, and c_p is the molar heat capacity (assumed constant) of the reaction mixture,

$$dH' = F_i c_p dT + \Delta H_R(\mathbf{r} dV) \quad (5-13)$$

where $\mathbf{r} dV$ is the moles of reactant disappearing per unit time in the reactor volume dV , and ΔH_R is the molar heat of reaction.

If the heat transfer rate can be expressed in terms of an overall coefficient h_o and the surrounding temperature, T_s ,

$$dQ' = h_o(T_s - T) dA_h \quad (5-14)$$

Here dA_h is the effective heat transfer area in the volume element.

Substituting Eqs. (5-13) and (5-14) into (5-12) yields

$$h_o(T_s - T) dA_h = \Delta H_R(\mathbf{r} dV) + F_i c_p dT \quad (5-15)$$

† For nonideal reactors (where the plug flow assumption is not justified) axial dispersion contributions to the energy entering and leaving the reactor may be important. This is most likely to be significant in heterogeneous catalytic reactions and is considered in Chap. 13. In the present chapter the assumptions of a plug-flow reactor, no axial mixing, and no radial gradients, are retained.

This energy equation can be expressed in terms of conversion by using the mass balance, Eq. (3-17), to eliminate the rate. The result is:

$$h_o(T_s - T) dA_h = \Delta H_R F dx + F_i c_p dT \quad (5-16)$$

Consistent mass or molar units may be employed in either of the two terms on the right in Eqs. (5-15) and (5-16). We have chosen to express F (molar feed rate of reactant) and F_i in molar units.

For adiabatic operation and constant c_p , Eq. (5-16) reduces to an easily integrable form not involving the volume of the reactor. If at $V = 0$, $T = T_f$ and $x = 0$ the result is

$$T - T_f = - \frac{\Delta H_R}{c_p} \left(\frac{F}{F_i} \right) (x - 0) \quad (5-17)$$

Note that the ratio F (in moles)/ F_i (in moles) is equal to the mole fraction of reactant in the feed (if $x = 0$ in the feed).

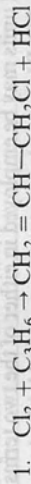
Simultaneous solution of Eq. (5-15), the mass balance [Eq. (3-17)], and the rate equation establishes the temperature and composition as a function of reactor volume. For adiabatic operation, the differential mass and energy balances need not be solved simultaneously. Equation (5-17) can be used in the rate equation to eliminate temperature as a variable. Then, this modified rate equation can be substituted in the mass balance to give a single differential equation (see Prob. 5-3). For the nonadiabatic case the calculations are the same as those for batch reactors (Example 5-1), except that the reactor volume replaces time as the independent variable. The procedure is not repeated here for single reactions; instead the treatment for multiple-reaction systems is illustrated. The most significant point is the effect of temperature on the product distribution (selectivity) in the effluent stream. Example 5-2 concerns a nonisothermal reactor in which two parallel reactions occur.† The desired reaction has the higher activation energy. After the example, a case of consecutive reactions with different activation energies is considered.

Example 5-2 It is proposed to design a pilot plant for the production of allyl chloride. The reactants consist of 4 moles propylene/mole chlorine and enter the reactor at 392°F. The reactor will be a vertical tube of 2 in. ID. If the combined feed rate is 0.85 lb mol/h, determine the conversion to allyl chloride as a function of tube length. The pressure may be assumed constant and equal to 29.4 lb/in.² abs.

The reactants will be preheated separately to 392°F and mixed at the entrance to the reactor. At this low temperature explosion difficulties on mixing are not serious. The reactor will be jacketed with boiling ethylene glycol, so that the inside-wall temperature will be constant and equal to 392°F. The inside-heat-transfer coefficient may be taken as 5.0 Btu/(h)(ft²)(°F).

† Kinetics data and selectivity for an important set of homogeneous reactions, the thermal cracking of light hydrocarbons, have been analyzed by C. F. Froment et al. in *AIChE J.* 23, 93 (1977).

Additional data and notes The basic development of the allyl chloride process has been reported by Groll and Hearne[†] and Fairbairn, Cheney, and Cherniavsky.[‡] It was found that the three chief reactions were allyl chloride formation,



the parallel addition reaction giving 1,2-dichloropropane,



and consecutive chlorination of allyl chloride to give 1,3-dichloro-1-propene



To simplify the kinetic treatment of the problem we shall consider only the first two reactions. The heats of reaction are shown in Table 5-3. The molal heat capacities c_p will be assumed constant and equal to the values given in Table 5-4.

No information is published for the rate-of-reaction equations, although it is known that reaction 2 takes place at temperatures as low as 212°F, while reaction 1 has an insignificant rate below 392°F. As the temperature increases above 392°F, the rate of reaction 1 increases rapidly, until at 932°F it is several times as fast as that of reaction 2. From this general information and some published data on the effect of residence time and temperature on the conversion, the proposed rate equations are

$$\mathbf{r}_1 = 206,000e^{-27,200/R_4 T} p_{\text{C}_3\text{H}_6} p_{\text{Cl}_2}; \quad (T, \text{ }^\circ\text{R})$$

$$\mathbf{r}_2 = 11.7e^{-6,860/R_4 T} p_{\text{C}_3\text{H}_6} p_{\text{Cl}_2}; \quad (T, \text{ }^\circ\text{R})$$

where \mathbf{r}_1 and \mathbf{r}_2 are in lb moles of Cl_2 disappearing per hour per cubic foot, T is in degrees Rankine, and the partial pressure p is in atmospheres.

SOLUTION: Since there will be heat transfer from the reaction gases to the glycol jacket, the temperature in the reactor will depend on the length z , and the design calculations have to be carried out by the stepwise integration of the mass and energy conservation equations. One mass balance may be written for each reaction. It is convenient in this problem to define the conversion

[†] H. P. A. Groll and G. Hearne, *Ind. Eng. Chem.*, **31**, 1530 (1939).

[‡] A. W. Fairbairn, H. A. Cheney, and A. J. Cherniavsky, *Chem. Eng. Progr.*, **43**, 280 (1947).

Table 5-3

ΔH Btu/lb mole	298 K
Reaction 1	-48,000
Reaction 2	-79,200

Table 5-4

Component	c_p , Btu/(lb mol)(°R)
Propylene (g)	25.3
Chlorine (g)	8.6
Hydrogen chloride (g)	7.2
Allyl chloride (g)	28.0
1,2-Dichloropropane (g)	30.7

as moles of chlorine reacted per mole of total feed rather than per mole of chlorine in the feed. If this conversion is $(x_1)_1$ for reaction 1 and $(x_1)_2$ for 2, the mass-balance equations, Eq. (3-17), are

$$\mathbf{r}_1 dV = F_1 d(x_1)_1 \quad (\text{A})$$

$$\mathbf{r}_2 dV = F_1 d(x_1)_2 \quad (\text{B})$$

where F_1 is the total molal feed rate.

The appropriate energy balance is Eq. (5-15).

$$h_0(T_s - T) dA_h = (\mathbf{r}_1 \Delta H_{R_1} + \mathbf{r}_2 \Delta H_{R_2}) dV + F_1 c_p dT$$

If z is the reactor length and d is its diameter,

$$dV = \frac{\pi d^2}{4} dz$$

$$dA_h = \pi d dz$$

Using these relations in the previous expression gives

$$(F_1 c_p) dT = \pi d h_0(T_s - T) dz - (\mathbf{r}_1 \Delta H_{R_1} + \mathbf{r}_2 \Delta H_{R_2}) \left(\frac{\pi d^2}{4} \right) dz$$

or

$$\frac{dT}{dz} = \frac{\pi d h_0(T_s - T) - (\mathbf{r}_1 \Delta H_{R_1} + \mathbf{r}_2 \Delta H_{R_2}) \frac{\pi d^2}{4}}{(F_1 c_p)} \quad (\text{C})$$

Equations (A) to (C) and the expressions for the rates \mathbf{r}_1 and \mathbf{r}_2 can be solved numerically for $(x_1)_1$ and $(x_1)_2$ and for T as a function of reactor length z . To accomplish this we first express Eqs. (A) and (B) in terms of z :

$$\frac{d(x_1)_1}{dz} = \frac{\pi d^2}{4F_1} \mathbf{r}_1 \quad (\text{D})$$

$$\frac{d(x_1)_2}{dz} = \frac{\pi d^2}{4F_1} \mathbf{r}_2 \quad (\text{E})$$

Also the equations for \mathbf{r}_1 and \mathbf{r}_2 need to be written in terms of $(x_1)_1$, $(x_1)_2$ and T . If 4 moles of propylene per mole of chlorine enter the reactor, at an axial

position where the conversions are $(x_1)_1$ and $(x_1)_2$, the moles of each component are:

$$\text{Chlorine}^\dagger = 1 - 5(x_1)_1 - 5(x_1)_2$$

$$\text{Propylene} = 4 - 5(x_1)_1 - 5(x_1)_2$$

$$\text{Allyl chloride} = 5(x_1)_1$$

$$\text{Dichloropropane} = 5(x_1)_2$$

$$\text{Hydrogen chloride} = 5(x_1)_1$$

$$\text{Total moles} = 5[1 - (x_1)_2]$$

If we assume that all the components behave as ideal gases at $p_i = 29.4 \text{ lb/in.}^2$ abs, the partial pressures of chlorine and propylene, in atmospheres, are given by

$$p_{\text{C}_2\text{H}_4} = \frac{29.4}{14.7} \left[\frac{4 - 5(x_1)_1 - 5(x_1)_2}{5[1 - (x_1)_2]} \right] = 2 \frac{0.8 - (x_1)_1 - (x_1)_2}{1 - (x_1)_2}$$

$$p_{\text{C}_1} = \frac{29.4}{14.7} \left[\frac{1 - 5(x_1)_1 - 5(x_1)_2}{5[1 - (x_1)_2]} \right] = 2 \frac{0.2 - (x_1)_1 - (x_1)_2}{1 - (x_1)_2}$$

These expressions can be substituted in the proposed rate equations to relate the rates to the conversions and the temperature. The results are

$$\mathbf{r}_1 = 824,000 e^{-13,700/T} \frac{[0.8 - (x_1)_1 - (x_1)_2][0.2 - (x_1)_1 - (x_1)_2]}{[1 - (x_1)_2]^2} \quad (\text{F})$$

$$\mathbf{r}_2 = 46.8 e^{-3,460/T} \frac{[0.8 - (x_1)_1 - (x_1)_2][0.2 - (x_1)_1 - (x_1)_2]}{[1 - (x_1)_2]^2} \quad (\text{G})$$

Substituting Eqs. (F) and (G) for \mathbf{r}_1 and \mathbf{r}_2 allows Eqs. (C), (D), and (E) to be expressed in terms of the three dependent variables T , $(x_1)_1$, and $(x_1)_2$, and the independent variable z .

Values of d , h_o , T_s , ΔH_{R_1} , and ΔH_{R_2} are given. The heats of reaction do not change significantly with temperature. Assuming ideal gases, the term $(F_i c_p)$ in Eq. (C) is given by

$$(F_i c_p) = \sum_i F_i c_{pi} = \underbrace{F_1[0.2 - (x_1)_1 - (x_1)_2]}_{\text{chlorine}} + \underbrace{F_1[0.8 - (x_1)_1 - (x_1)_2]}_{\text{propylene}} c_{p_{\text{C}_2\text{H}_4}}$$

At a location where the conversions are $(x_1)_1$ and $(x_1)_2$

[†] The coefficient 5 appears in this equation because x_1 is the conversion based on 1 mole of total feed. Note that the maximum value for the sum of $(x_1)_1$ and $(x_1)_2$ is 0.2, which corresponds to complete conversion of the chlorine to either allyl chloride or dichloropropane.

For example, entering the reactor $(x_1)_1 = (x_1)_2 = 0$ so that

$$(F_i c_p) = 0.85(0.2)(8.6) + 0.85(0.8)(25.3) \\ = 18.5 \text{ Btu/(h)}(^{\circ}\text{F})$$

These results establish numerical values for all the coefficients in Eqs. (C), (D), and (E).

The numerical procedure is somewhat different from that used in Examples 4-7, 4-15, and 5-1 since we need to solve three coupled differential equations with three dependent variables. The modified Euler method will be used first to obtain approximate results for the first increment. By doing this the physical aspects of the problem and method of solution are clearly displayed. Then, more accurate results from the fourth-order Runge-Kutta procedure are presented.

Modified Euler method Equations (C), (D), and (E) are first written in difference form:

$$F_i c_p \Delta T = \left[\pi d h_o (T_s - T)_{av} - \mathbf{r}_1 (\Delta H_{R_1} + \mathbf{r}_2 \Delta H_{R_2}) \right] \frac{\pi d^2}{4} (\Delta z) \quad (\text{C}')^\dagger$$

$$\Delta(x_1)_1 = \bar{\mathbf{r}}_1 \frac{\pi d^2}{4 F_1} (\Delta z) \quad (\text{D}')$$

$$\Delta(x_1)_2 = \bar{\mathbf{r}}_2 \frac{\pi d^2}{4 F_2} (\Delta z) \quad (\text{E}')$$

A solution procedure is as follows:

1. From the known initial conversion $[(x_1)_1 = 0 \text{ and } (x_1)_2 = 0]$ and temperature (200°C), \mathbf{r}_1 and \mathbf{r}_2 entering the reactor are computed.
2. An arbitrary increment of reactor length Δz is chosen. The smaller this increment, the more accurate the solution (and the more time consuming the calculations).
3. For the chosen Δz , first estimates of the conversion occurring within the increment are obtained from Eqs. (D') and (E'). It is convenient to assume that the average values of \mathbf{r}_1 and \mathbf{r}_2 are equal to the initial values evaluated in step 1.
4. The change in temperature within the increment ΔT is determined from Eq. (C'). An estimate of the average temperature difference $(T_s - T)_{av}$ in the increment is required in order to evaluate the heat-loss term. Once ΔT has been computed, the estimate of $(T_s - T)_{av}$ can be checked. Hence a trial-and-error calculation is necessary to evaluate ΔT .
5. From the conversion and temperature at the end of the first increment, as determined in steps 3 and 4, the rate of reaction is computed at this

[†] Since the inside-wall temperature is known, the heat transfer with the surroundings can be evaluated from $h_o(T_s - T)_{av} \pi d \Delta z$, where h_o is the inside-film coefficient and T_s is the inside-wall surface temperature. The overall coefficient U is not necessary in this case.

position in the reactor. Then steps 3 and 4 are repeated, using for \bar{r}_1 and \bar{r}_2 the arithmetic average of the values at the beginning and end of the increment. This, in turn, will give more precise values of the conversion and temperature at the end of the first increment and permit a third estimate of the average values of the rates. If this third estimate agrees with the second, the next increment of reactor length is chosen and the procedure is repeated.

The calculations according to these steps are as follows:

Step 1 The rates of reaction at the reactor entrance are given by Eqs. (E) and (F), with $T = (200 + 273)(1.8) = 852^\circ\text{R}$ and $(x_1)_1 = (x_1)_2 = 0$:

$$r_1 = 824,000e^{-16.1(0.16)} = 0.0135 \text{ lb mol/(h)(ft}^3\text{)}$$

$$r_2 = 46.8e^{-4.06(0.16)} = 0.129 \text{ lb mol/(h)(ft}^3\text{)}$$

Step 2 An increment of reactor length is chosen as $\Delta z = 4.0 \text{ ft}$.

Step 3 Assuming that the rates computed in step 1 are average values for the increment, the first estimates of the conversion in the increment are given by Eqs. (D') and (E'):

$$\frac{\pi d^2}{4} = \frac{\pi \left(\frac{2}{12}\right)^2}{4} = 0.0218 \text{ ft}^2$$

$$\frac{\pi d^2}{4F_1} = \frac{0.0218}{0.85} = 0.0257$$

$$\Delta(x_1)_1 = 0.0135(0.0257)(4.0) = 0.0014$$

$$(x_1)_1 = 0 + 0.0014 = 0.0014$$

Similarly, for the second reaction we obtain

$$\Delta(x_1)_2 = 0.129(0.0257)(4.0) = 0.0133$$

$$(x_1)_2 = 0 + 0.0133 = 0.0133$$

Step 4 If the average temperature difference $(T_s - T)_{av}$ for the first increment is estimated to be -20°F , substitution in Eq. (C') gives

$$18.5 \Delta T = \pi_2^2(5)(-20)(4) - [0.0135(-48,000) + 0.129(-79,200)](0.0218)(4)$$

$$\Delta T = \frac{946 - 210}{18.5} = 40^\circ\text{F}$$

$$T_1 = 852 + 40 = 892^\circ\text{R} \quad \text{temperature at end of first increment}$$

$$T_s - T \text{ at entrance} = 0$$

$$T_s - T \text{ at end of increment} = 852 - 892 = -40^\circ\text{F}$$

$$(T_s - T)_{av} = \frac{0 + (-40)}{2} = -20^\circ \quad \text{vs. } -20^\circ \text{ assumed}$$

Step 5 At the end of the first increment the first estimate of the conversions and temperature is

$$(x_1)_1 = 0.0014$$

$$(x_1)_2 = 0.0133$$

$$T_1 = 852 + 40 = 892^\circ\text{R}$$

Substitution of these conditions in rate equations (F) and (G) yields

$$r_1 = 0.0256 \quad r_2 = 0.143$$

A second, and more accurate, estimate of the average values of the rates for the first increment can now be made:

$$\bar{r}_1 = \frac{0.0135 + 0.0256}{2} = 0.0195$$

$$\bar{r}_2 = \frac{0.129 + 0.143}{2} = 0.136$$

The second estimate of the conversion in the increment, obtained from these rates and Eqs. (C') and (D'), is

$$\Delta(x_1)_1 = 0.0195(0.0257)(4.0) = 0.0020$$

$$(x_1)_1 = 0 + 0.0020 = 0.0020$$

$$\Delta(x_1)_2 = 0.136(0.0257)(4.0) = 0.0140$$

$$(x_1)_2 = 0 + 0.0140 = 0.0140$$

The second estimate of ΔT , determined from Eq. (C'), is

$$\Delta T = 41^\circ\text{F}$$

$$T_1 = 852 + 41 = 893^\circ\text{R}$$

At the revised values of $(x_1)_1$, $(x_1)_2$, and T (at the end of the first increment) the rates are

$$r_1 = 0.0258$$

$$r_2 = 0.144$$

Since these values are essentially unchanged from the previous estimate, the average rates will also be the same, and no further calculations for this increment are necessary.

The same calculations can be repeated for successive increments until the required conversion is attained.

Runge-Kutta Method The procedure for extending the Runge-Kutta method to any number of independent variables is available.† The working equations for our case of three dependent variables are an extension of those for two dependent variables given in Example 4-7 [Eqs. (4-11) to (4-15)]. With the working equations and a choice of Δz we can solve Eqs. (C), (D), and (E) to obtain (x_1) , $(x_1)_2$, and T for any reactor length. Results up to $z = 20$ ft are given by the solid curves in Figs. 5-5 and 5-6 and in Table 5-5 (nonadiabatic conditions). They are based upon $\Delta z = 1$ ft.

A comparison of the results of the modified Euler and Runge-Kutta methods at $z = 4$ ft is as follows:

	Modified Euler	Runge-Kutta
Reactor length, z , ft	4	4
Comparison per mole feed		
$(x_1)_1$	0.0020	0.0021
$(x_1)_2$	0.0140	0.0142
Temperature, R	893	895

The agreement is good, particularly in view of the larger increment size (4 ft) used for the modified Euler method.

These calculations indicate two trends. First, the rate of reaction 1 is relatively low with respect to reaction 2 at low temperatures but increases

† "Applied Numerical Analysis" by Bruce Carnahan, H. A. Luther, and James O. Wilkes, pp. 376-379; John Wiley & Sons Inc., New York, 1969. This reference includes computer programs for carrying out the calculations for solving a multiple-variable problem.

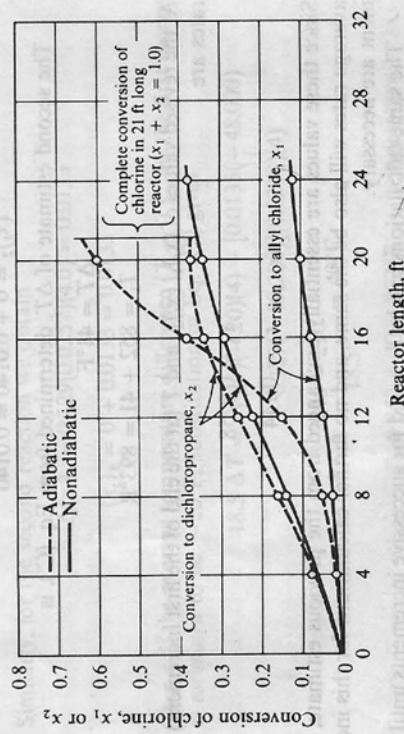


Figure 5-5 Conversion curves for allyl chloride production in a tubular reactor.

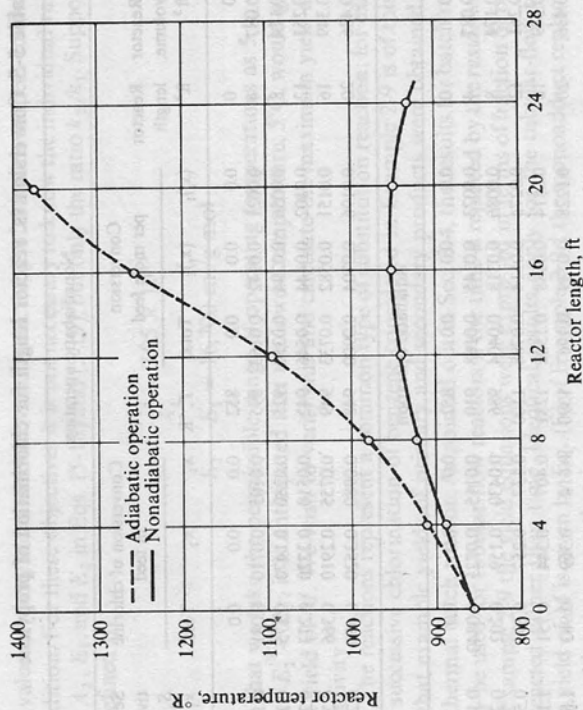


Figure 5-6 Temperature profiles for allyl chloride production in a tubular reactor.

rapidly with temperature, while the rate of reaction 2 is not very sensitive to temperature changes. This is because the activation energy for reaction 1 is greater than that for reaction 2. The second trend is the increase in rate of heat transfer to the surroundings with an increase in reactor length. This effect, which is a consequence of the increase in $(T - T_s)$, offsets the rise in temperature due to the exothermic nature of the reactions, and results ultimately in a decrease in temperature with reactor length. This length is reached when the heat transferred from the reactor tube to the surroundings is greater than the heat evolved from the reactions. Figure 5-6 indicates that this occurs about 18 ft from the entrance to the reactor and is at too low a temperature for the rate of reaction 1 to become large with respect to that of reaction 2. Therefore the conversion to allyl chloride never reaches a high value. Most of the product is dichloropropane, and the selectivity for allyl chloride is always less than unity, as noted in the last column of Table 5-5. A reactor of this type is not well suited for the production of allyl chloride. Adiabatic operation would eliminate the maximum in the temperature and result in higher temperatures, which in turn would favor the production of allyl chloride. The only change in the calculations for such an adiabatic case is that the term $\pi dh_o(T_s - T)$ in Eq. (C) would be zero. For comparison, the temperature and conversion results for such an adiabatic reactor are also shown in Figs. 5-5 and 5-6 and Table 5-5. The selectivity now is greater than unity at high conversions.

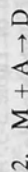
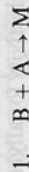
Even adiabatic operation results in the formation of considerable amounts of the undesirable dichloropropane. This occurs in the first part of

Table 5-5 Conversion vs. reactor length for chlorination of propylene

Nonadiabatic operation									
Reactor volume, ft ³	Reactor length, ft ³	Conversion per mole feed		T, °R	Conversion of chlorine in feed		Total	Selectivity $S_p = x_1/x_2$	Total
		(x ₁) ₁	(x ₁) ₂		x ₁	x ₂			
0	0	0.0	0.0	852	0.0	0.0	0.0	0.0	0.0
0.087	4	0.0021	0.0142	895	0.0105	0.0710	0.081	0.15	0.15
0.174	8	0.0056	0.0294	925	0.0280	0.1470	0.175	0.19	0.19
0.261	12	0.0102	0.0444	942	0.0510	0.2220	0.273	0.23	0.23
0.349	16	0.0151	0.0582	949	0.0755	0.2910	0.366	0.26	0.26
0.436	20	0.0196	0.0704	0.0900	0.0980	0.3520	0.450	0.28	0.28
Adiabatic operation									
0	0	0.0	0.0	852	0.0	0.0	0.0	0.0	0.0
0.087	4	0.0023	0.0145	910	0.0115	0.0725	0.0840	0.16	0.16
0.174	8	0.0086	0.0318	986	0.0430	0.159	0.202	0.27	0.27
0.261	12	0.0274	0.0514	1100	0.137	0.257	0.394	0.53	0.53
0.349	16	0.0814	0.0688	1281	0.407	0.344	0.751	1.18	1.18
0.436	20	0.1228	0.0739	1390	0.614	0.369	0.983	1.66	1.66

the reactor, where the temperature of the flowing mixture is low. A tubular-flow reactor is less desirable for this reaction system than a stirred-tank unit. The same reaction system is illustrated in Example 5-3 for a stirred-tank reactor.

Consider next a pair of consecutive reactions where the intermediate component is the desired product. Suppose also that the desired product is produced by the reaction with the lower activation energy. To illustrate the effect of type of reaction on selectivity, assume that the tubular reactor operates isothermally. The two reactions of Example 4-9 starting with isobutylene (B) and acrylonitrile (A) provide an illustration. Suppose now the desired product is the monoamine (M) rather than the diamine (D). The two homogeneous irreversible second-order reactions are



Assume that the density of the system is constant and that the specific reaction rates for the true reactions are

$$k_1 = A_1 e^{-E_1/R_g T} \quad (5-18)$$

$$k_2 = A_2 e^{-E_2/R_g T} \quad (5-19)$$

The problem is to find the constant operating temperature in a tubular-flow reactor for which the yield of M will be a maximum. We would also like to know

the value of the yield and the overall selectivity of M with respect to D at this condition. For these objectives it is not necessary to know the individual values of A_1 , A_2 , E_1 , and E_2 in Eqs. (5-18) and (5-19), but only the ratio k_2/k_1 . Suppose this is defined by

$$\frac{A_2}{A_1} = 7.95 \times 10^{11} \quad (5-20)$$

$$E_2 - E_1 = 16,700 \text{ cal/g mol} \quad (5-21)$$

and that we take the permissible range of operating temperatures as 5 to 45°C.† Since $E_1 < E_2$, it is anticipated that the lowest temperature, 5°C, would give the best yield of M. We wish to verify this and calculate the maximum yield and the selectivity.

The reactions represent a common type of substitution reaction; for example, the successive chlorination of benzene considered in Example 2-9 is of this form. In that example yields of primary and secondary products were obtained for an isothermal batch reactor. As pointed out in Sec. 3-4, the results for batch reactors may be used for tubular-flow reactors if the time is replaced by the residence time. In Example 2-9 the yield equations were expressed in terms of fraction of benzene unreacted rather than time. Identical results apply for the tubular-flow reactor. The yield of M is given by Eq. (F) of Example 2-9,‡ the monoadduct replacing the monochlorobenzene; that is,

$$x_M = \frac{C_M}{C_{B_0}} = \frac{1}{1-\beta} \left[\left(\frac{C_B}{C_{B_0}} \right)^\beta - \frac{C_B}{C_{B_0}} \right] \quad (5-22)$$

where

$$\beta = \frac{k_2}{k_1} = \frac{A_2 e^{-E_2/R_g T}}{A_1 e^{-E_1/R_g T}} = 7.95 \times 10^{11} e^{-16,700/R_g T} \quad (5-23)$$

The yield of monoamine, M, described by Eq. (5-22), has a maximum value at an intermediate value of C_B/C_{B_0} , or at an intermediate value of the conversion $(1 - C_B/C_{B_0})$. We first find this local maximum, and then express it as a function of β . Once this is done, we can find the value of β , and hence the temperature, that gives the overall maximum within the allowable temperature range.

To determine the local maximum, let us set the derivative of x_M with respect to C_B/C_{B_0} (call this z) equal to zero; that is,

$$\frac{dx_M}{dz} = 0 = \frac{1}{1-\beta} [\beta(z)^{\beta-1} - 1]$$

or

$$z = C_B/C_{B_0} = \left(\frac{1}{\beta} \right)^{1/(\beta-1)} \quad (5-24)$$

† Probably the rates are unrealistically high for this temperature range.

‡ Actually, by the equation immediately preceding Eq. (F). The same result is also given by Eq. (2-89), which was developed for consecutive first-order reactions. As shown in Example 2-8, in this case the results are the same for first- or second-order kinetics.

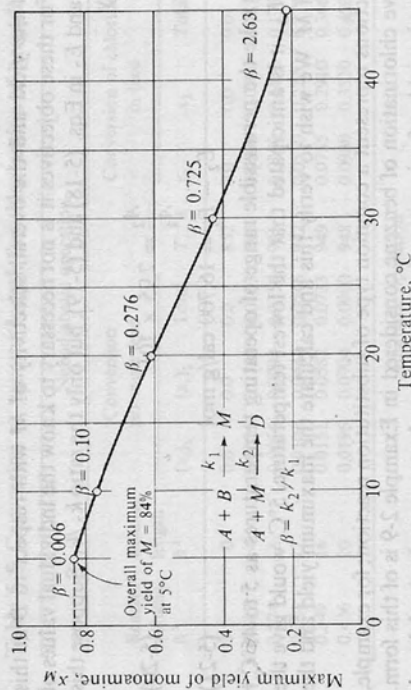


Figure 5-7 Maximum yield of intermediate product (M) for consecutive reactions.

This is the value of C_B/C_{B_0} for the local maximum of x_β . Substituting this value in Eq. (5-22) gives the local maximum in terms of β ,[†]

$$(x_M)_{\max} = \frac{1}{1-\beta} \left[\left(\frac{1}{\beta} \right)^{1/(\beta-1)} \left(\frac{1}{\beta} - 1 \right) \right] = \left(\frac{1}{\beta} \right)^{\beta/(\beta-1)} \quad (5-25)$$

From Eq. (5-23) we can find the value of β for any temperature over the range 5 to 45°C. Substituting these results for β in Eq. (5-25) gives the corresponding local-maximum yields of M . The results are shown in Fig. 5-7, plotted as $(x_M)_{\max}$ vs. temperature. As expected, the overall maximum occurs at 5°C and is about 0.84. The corresponding value of β is 0.06.

The total conversion at maximum yield conditions is, from Eq. (5-24),

$$\begin{aligned} x_i &= 1 - C_B/C_{B_0} = 1 - \left(\frac{1}{\beta} \right)^{1/(\beta-1)} \\ &= 1 - \left(\frac{1}{0.06} \right)^{1/(0.06-1)} = 1 - 0.05 = 0.95 \quad \text{or } 95\% \end{aligned}$$

From the stoichiometry of the reactions, the mass balance for isobutylene is

$$C_B = C_{B_0} - C_M - C_D$$

or

$$\frac{C_B}{C_{B_0}} = 1 - \frac{C_M}{C_{B_0}} - \frac{C_D}{C_{B_0}}$$

$$x_D = \frac{C_D}{C_{B_0}} = 1 - \frac{C_B}{C_{B_0}} - \frac{C_M}{C_{B_0}} = x_i - x_M \quad (5-26)$$

[†] This same result was obtained in Example for 2-8, Eq. (D), for a batch reactor.

Hence

$$x_D = 0.95 - 0.84 = 0.11$$

Of the total conversion of 95%, 84% is to monoamine and 11% to diamine. The overall selectivity of monoamine to diamine is $0.84/0.11 = 7.6$ at the maximum yield of monoamine. The selectivity is not necessarily a maximum at the conditions of maximum yield. If the separation of M from D in the product stream requires an expensive process, it might be more profitable to operate the reactor at a conversion level at which M is less than 84% but the selectivity is higher than 7.6. The selectivity may be evaluated for any total conversion and β from Eqs. (5-22) and (5-26); thus the selectivity is

$$S_o = \frac{x_M}{x_D} = \frac{1/(1-\beta)[(1-x_i)^\beta - (1-x_i)]}{x_i - 1/(1-\beta)[(1-x_i)^\beta - (1-x_i)]} \quad (5-27)$$

Equation (5-27) indicates that S_o decreases sharply with x_i . The relationship is shown for 5°C by the dotted curve in Fig. 5-8. This curve suggests that if a selectivity of 20 is required to reduce separation costs, the reactor should be designed to give a conversion of about 73% at which point the yield of monoamine is only 70%. In this case the maximum yield occurs at a conversion of 95% while the maximum selectivity is at a conversion approaching zero. Figure 5-8 also includes the curves for yield vs. total conversion for several temperatures.

Note that as conditions have been attained for the maximum yield of M , the reactor has become relatively large. At 5°C the reaction rate will be low and the total conversion is approaching 100%. Whether it is advisable to operate at these

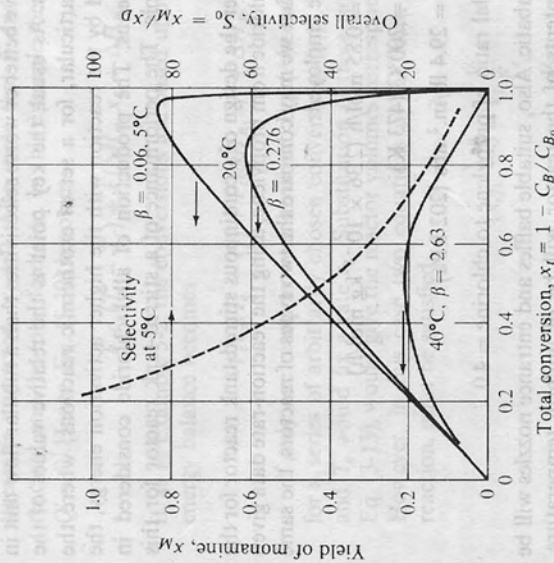


Figure 5-8 Yield of intermediate product (M) vs. total conversion for consecutive reactions.

conditions for maximum conversion depends on the economics of reactor costs, separation costs, and price of the monoamine product.

We can predict qualitatively what effect nonisothermal operations would have on the selectivity. For example, if the reactions were exothermic, it would be preferable to have as much heat transfer as possible in order to operate at low temperatures. Furthermore, a tubular-flow reactor would be preferable to a stirred tank (opposite conclusion from that of Example 5-2) since the latter would favor the production of diamine. This is because the concentration of monoamine would be higher and the temperature is also likely to be higher.

5-4 Continuous Stirred-Tank Reactors

The ideal stirred-tank reactor operates isothermally at a constant rate. However, an energy balance is needed to predict the constant temperature when the heat of reaction is sufficient (or the heat exchange between the surroundings and reactor is insufficient) to cause a difference between feed and reactor temperatures. The proper energy balance is the algebraic relation presented as Eq. (5-4) and the mass balance is Eq. (3-13). Sometimes simultaneous solution of the mass and energy equations is required. For example, if a reactor of known volume is to be used, the calculation of the conversion and the temperature requires a simultaneous trial-and-error solution of Eqs. (3-13) and (5-4), with the rate equation expressing the temperature dependency of r . In contrast, if the objective is the reactor volume needed to obtain a specified conversion, Eq. (5-4) can be solved independently for the reactor-exit temperature T_e . The rate at T_e can be found from the rate equation and used in Eq. (3-13) to obtain the reactor volume. When more than one reaction occurs, a separate mass balance is necessary for each reaction.

A stirred tank may give better or worse selectivities than a tubular-flow unit in multiple-reaction systems. As usual, the key point is the relative values of the activation energies. In particular, for a set of exothermic reactions, where the desired product is formed by the reaction with the higher activation energy, the stirred tank is advantageous. The production of allyl chloride considered in Example 5-2 is an example. The performance of a stirred-tank reactor for this system is discussed next.

Example 5-3 Consider the design of a continuous stirred-tank reactor for the production of allyl chloride from propylene, using the reaction-rate data given in Example 5-2. So that we may compare the two types of reactors, the same feed condition will be employed:

$$F_1 = 0.85 \text{ mol/h } (2.36 \times 10^{-7} \text{ kg mol/h})$$

$$T = 200^\circ\text{C } (473 \text{ K})$$

$$p = 29.4 \text{ lb/in.}^2 \text{ abs } (202 \text{ kPa})$$

$$\text{Molal ratio of propylene to chlorine} = 4.0$$

The operation is adiabatic. Also, suitable baffles and entrance nozzles will be used so that the contents of the reactor will be of uniform temperature, pressure, and composition, even for this gaseous system.

Using the heats of reaction and heat capacities given in Example 5-2, determine the conversion of chlorine to allyl chloride expected for a range of sizes of reactors (i.e., reactor volumes).

SOLUTION The rate of each reaction (allyl chloride and dichloropropane formation) will be a constant and should be evaluated at the temperature and composition of the steam leaving the reactor. The temperature is determined by Eq. (5-4). The enthalpy rates are constant (steady-state operation). They can be written immediately for the feed and effluent streams by applying Equation (5-13) to a stirred-tank reactor. The rate is the same throughout the reactor and F_i and c_p are also constant. Hence, Eq. (5-13) can be integrated between feed and effluent streams to give

$$H_e - H_f = F_1 c_p (T_e - T_f) + \Delta H_R (rV) \quad (5-28)$$

The mass balance, Eq. (3-13) can be used to eliminate the rate from Eq. (5-28) and express the enthalpy change in terms of conversion

$$H_e - H_f = F_1 c_p (T_e - T_f) + F \Delta H_R (x_e - x_f) \quad (5-29)$$

Substituting this expression in Eq. (5-4) yields

$$F_1 c_p (T_e - T_f) + F \Delta H_R (x_e - x_f) = h_0 A_h (T_s - T) \quad (5-30)$$

where the heat transfer rate Q' has been expressed in terms of the temperature difference $(T_s - T)$ as in Eq. (5-14). Equation (5-30) is a general expression for the energy balance in a continuous-flow stirred-tank reactor. If the feed stream is unreacted, $x_f = 0$. Also, note that F and F_1 are the feed rate of reactant and the total feed rate. In this example there are two reactions and $Q' = 0$. Hence, Eq. (5-30) becomes

$$F_1 c_p (T_e - T_f) + F (\Delta H_{R_1} x_1 + \Delta H_{R_2} x_2) = 0$$

If, as in Example 5-2, the conversions are based upon the total feed rate, the energy balance becomes

$$F_1 c_p (T_e - T_f) + F_1 (\Delta H_{R_1} x_{11} + \Delta H_{R_2} x_{12}) = 0 \quad (A)$$

If only one reaction were involved, Eq. (A) could be used to calculate T_e for a series of arbitrarily chosen conversions (x_{11}) . Then each value of (x_{11}) and T_e would fix a rate r_1 . Substitution of these rates in the mass balance, Eq. (3-13), would give the reactor volumes corresponding to the conversions. However, in this case two equations of the form of (3-13), one for each reaction, must be satisfied,

$$(x_1)_1 - 0 = r_1 \frac{V}{F_1} \quad (B)$$

$$(x_1)_2 - 0 = r_2 \frac{V}{F_1} \quad (C)$$

The rate expressions are obtained by substituting T_e for the temperature in Eqs. (F) and (G) of Example 5-2. Thus

$$r_1 = 824,000e^{-1.3,700/T_e} \frac{[0.8 - (x_{r1}) - (x_{r2})][0.2 - (x_{r1}) - (x_{r2})]}{[1 - (x_{r2})]^2} \quad (D)$$

$$r_2 = 46.8e^{-3,460/T_e} \frac{[0.8 - (x_{r1}) - (x_{r2})][0.2 - (x_{r1}) - (x_{r2})]}{[1 - (x_{r2})]^2} \quad (E)$$

Algebraic Eqs. (A) to (E) provide the relations needed to calculate the five unknowns (x_{r1}) , (x_{r2}) , T_e , r_1 , and r_2 at different values of the reactor volume V . One procedure which is not tedious is first to choose a value of T_e . Then, from the ratio of Eqs. (B) and (C), using (D) and (E) for r_1 and r_2 , we obtain the ratio $(x_{r1})/(x_{r2})$. Employing this ratio in Eq. (A) will give separate values for each conversion. Finally, the corresponding reactor volume can be obtained from either Eq. (B) or Eq. (C). This approach will be illustrated by including the numerical calculations for an exit temperature of 1302°R (450°C).

$$\frac{(x_{r1})}{(x_{r2})} = \frac{r_1}{r_2} = \frac{824,000e^{-1.3,700/1,302}}{46.8e^{-3,460/1,302}} = 6.77$$

Using this ratio in Eq. (A) and noting that the heat capacity of the feed $F_r c_p$ was determined in Example 5-2 as 18.5 Btu/(h)(°F), we have

$$18.5(T_r - T_e) + 0.85[6.77(x_{r2})(48,000) + (x_{r2})(79,200)] \\ = 18.5(852 - 1,302) + 343,000(x_{r2}) = 0$$

$$(x_{r2}) = 0.0243$$

$$(x_{r1}) = 6.77(0.0243) = 0.164$$

The reactor volume required for these conversions is, from Eq. (B),

$$0.164 = \frac{V}{0.85} (824,000e^{-1.3,700/1,302}) \\ \times \frac{(0.8 - 0.164 - 0.024)(0.2 - 0.164 - 0.024)}{(1 - 0.0243)^2} \\ V = \frac{0.164(0.85)}{0.167} = 0.83 \text{ ft}^3 \text{ (0.023 m}^3\text{)}$$

The corresponding values of the conversions and volume for other temperatures are summarized in Table 5-6. Comparing the results with those of Example 5-2, we see that the adiabatic stirred-tank reactor gives much higher yields and selectivities for allyl chloride than the tubular-flow type for the same reactor volume. In the tubular-flow equipment considerable dichloropropane is formed in the initial sections of the reactor, where the temperature is relatively low. This is avoided in the adiabatic tank reactor by operation at a constant temperature high enough to favor allyl chloride formation. For example, if the adiabatic tank reactor is operated at 450°C, 82% of the chlorine is converted to allyl chloride and 12% is converted to dichloropropane;

Table 5-6 Conversion vs. reactor volume for adiabatic tank reactor: allyl chloride production

Reactor (or exit) temperature		Conversion per mole feed		Conversion of chlorine in feed		Reactor volume, ft ³	Selectivity $S_o = x_1/x_2$
°R	°C	$(x_1)_1$	$(x_1)_2$	x_1	x_2		
960	260	0.0098	0.0237	0.049	0.119	0.12	0.41
1032	300	0.0282	0.0324	0.14	0.162	0.15	0.86
1122	350	0.0660	0.0341	0.33	0.171	0.18	1.93
1212	400	0.114	0.0298	0.57	0.149	0.24	3.82
1257	425	0.138	0.0273	0.69	0.136	0.34	5.07
1302	450	0.164	0.0243	0.82	0.121	0.83	6.78

the total conversion is 94%. In the adiabatic tubular reactor of Example 5-2 the products contained much greater amounts of dichloropropane for all reactor volumes. These conclusions are summarized in Fig. 5-9, where the fraction of chlorine converted to each product is shown plotted against reactor volume for the tubular and the tank reactors.

In the tubular-flow reactor in Example 5-2 it was necessary to solve simultaneously three differential equations, while for the tank reactor only simultaneous solution of algebraic equations was required.

Examples 5-2 and 5-3 are for a pair of exothermic, parallel reactions where the reaction producing the desired product has the higher activation energy. The results show that for both selectivity and conversion a stirred-tank reactor is preferred over the tubular-flow type.

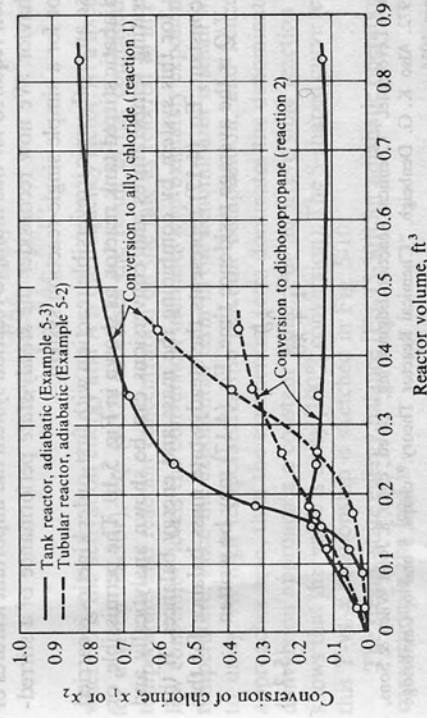


Figure 5-9 Comparison of tubular and tank reactors for allyl chloride production.

The most significant factors in analyzing the selectivity in nonisothermal reactors are the activation energies. Suppose that the activation energy for the reaction producing the desired product is greater than the E values for the other reactions. Then higher temperatures increase the selectivity. For example, for exothermic reactions, adiabatic operations either stirred tank or tubular flow gives a higher selectivity than isothermal operation. If energy is added, the selectivity will be increased above that in the adiabatic reactor for either exothermic or endothermic reactions. Example 5-2 is an illustration for exothermic reactions. The key point is that the temperature should be as high as possible. The same conclusion applies for either parallel or consecutive reactions. The selectivity comparison between stirred tank and tubular flow depends upon activation energies, and, in general, on the kinetics of the reactions and whether they are exothermic or endothermic.

When the desired product is produced by the reaction with the lowest activation energy, selectivity (but not conversion) is favored by lower temperatures. Hence, for endothermic reactions adiabatic operation gives a higher selectivity than an isothermal reactor. For exothermic reactions transfer of energy to the surroundings improves selectivity. Note that if the temperatures become too low, the very low rates may result in unrealistically large reactor volumes. The procedures illustrated in Examples 5-2 and 5-3 are applicable for evaluating selectivity and conversion for any type of reaction system[†] for either stirred-tank or tubular-flow reactors.

5-5 Stable Operating Conditions in Stirred-Tank Reactors[‡]

In Example 5-3 the temperature and conversion leaving the reactor were obtained by simultaneous solution of the mass and energy balances. The results for each temperature in Table 5-6 represented such a solution and corresponded to a different reactor, i.e., a different reactor volume. However, the numerical trial-and-error solution required for this multiple-reaction system hid important features of reactor behavior. We now reconsider the *steady-state* performance of a stirred-tank reactor for a simple single-reaction system.

Suppose an exothermic irreversible reaction with first-order kinetics is carried out in an adiabatic stirred-tank reactor, as shown in Fig. 5-10. The permissible, or stable, operating temperatures and conversions can be shown analytically and graphically for this system by combining the mass and energy balances. If the density is constant, Eq. (4-17) represents the steady-state mass balance for this case. Since $1/Q$ is the average residence time, Eq. (4-17) may be written

$$x = \frac{k\bar{\theta}}{1 + k\bar{\theta}} \quad (5-31)$$

[†] See Octave Levenspiel, "Chemical Reaction Engineering," 2d ed., chap. 8, John Wiley & Sons, New York, 1972. Also K. G. Denbigh, "Chemical Reactor Theory," chaps. 5 and 6, Cambridge University Press, 1956.

[‡] For more complete discussions of this subject see C. van Heerden, *Ind. Eng. Chem.*, **45**, 1242 (1953); K. G. Denbigh, *Chem. Eng. Sci.*, **8**, 125 (1958).

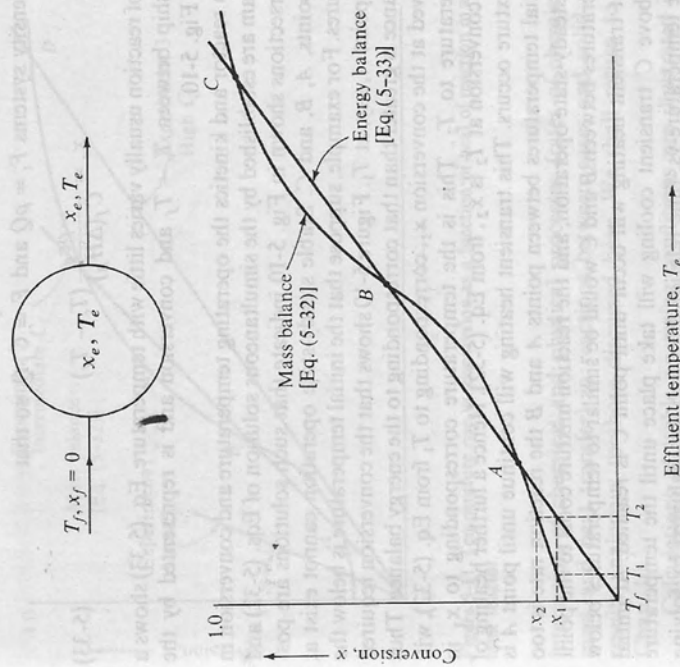


Figure 5-10 Temperature vs. conversion for a first-order irreversible reaction in an adiabatic stirred-tank reactor.

In terms of temperature, this takes the form

$$x = \frac{\bar{\theta} A e^{-E/R_p T_e}}{1 + \bar{\theta} A e^{-E/R_p T_e}} \quad (5-32)$$

where E is the activation energy and A is the frequency factor. At a fixed $\bar{\theta}$ (that is, for a given reactor), Eq. (5-32) expresses the result of the combined effects of temperature and reactant concentration on the rate as referred to in Fig. 5-2. At low conversion levels the conversion increases approximately exponentially with temperature, since the exponential term in the denominator is small with respect to unity. At high temperatures the reactant composition, and hence the rate, approaches zero; then the exponential term dominates the denominator and the conversion approaches a constant value. For an irreversible reaction Eq. (5-32) shows that this value is unity (100% conversion). The S-shaped curve representing this T -vs.- x relationship is sketched in Fig. 5-10.

The steady-state energy balance [Eq. (5-30)] for adiabatic operation and zero conversion in the feed is

$$x_e - 0 = - \frac{F_i c_p (T_e - T_f)}{F(\Delta H_R)}$$

For constant-density systems $F_i = \rho Q$ and $F = C_f Q$, so that

$$x_e = \frac{\rho c_p}{C_f (\Delta H_R)} (T_e - T_f) \quad (5-33)$$

Since the heat of reaction usually varies little with temperature, Eq. (5-33) shows a linear relationship between $T_e - T_f$ and conversion and is represented by the straight line in Fig. 5-10.

For a given reactor and kinetics the operating temperature and conversion in the effluent stream are established by the simultaneous solution of Eqs. (5-32) and (5-33). The intersections shown in Fig. 5-10 indicate that such solutions are possible at three points, *A*, *B*, and *C*. Stable steady-state operation cannot exist at other temperatures. For example, suppose that the initial temperature is below the temperature at point *A*, say, at T_1 . Figure 5-10 shows that the conversion required by the mass balance is greater than that corresponding to the energy balance. Thus the energy evolved at the conversion x_1 , corresponding to T_1 from Eq. (5-32), will raise the temperature to T_2 . This is the temperature corresponding to x_1 in Eq. (5-33). The conversion at T_2 is x_2 , from Eq. (5-32). Hence a further heating of the reaction mixture occurs. This transient heating will continue until point *A* is reached. At initial temperatures between points *A* and *B* the reaction rate is too small to justify steady-state operation, and the reaction mixture cools to the point *A*. Initial temperatures between *B* and *C* would be similar to temperatures below point *A*, so that transient heating will occur until point *C* is reached. At initial temperatures above *C* transient cooling will take place until the temperature drops to *C*. The temperature-vs.-time relationships may be evaluated by solving the mass and energy balances for non-steady-state operation. This is done in Sec. 5-6.

Point *B* is different from *A* and *C*. After small initial displacements from *B* the system does not return to *B*, whereas disturbances from points *A* and *C* are followed by a return to these stable points.

The relative position of the mass-balance curve and the energy-balance line in Fig. 5-10 depends on the chemical properties (*A*, *E* and ΔH_R) and physical properties (ρ and c_p) of the system and the operating conditions (θ and C_0), according to Eqs. (5-32) and (5-33). These properties and conditions determine whether or not stable operating conditions are possible and how many stable operating points exist. For example, consider a series of experiments in which the only property that changes is C_f . Since θ , *A*, and *E* are constant, the relation between x and T determined by Eq. (5-32) is fixed, as shown by the S-shaped curve in Fig. 5-11. For experiment 1, which has the lowest C_f , the energy-balance line will be steep and will intersect the mass-balance curve at a small value of $T_e - T_f$. This point is the only stable operating condition. The reactor will operate at a low conversion and at a temperature only slightly above the feed temperature. For experiment 2, with an intermediate value of C_f , there will be two stable operating conditions, points *A* and *C* in Fig. 5-11, and a metastable point, *B*. This is the situation described in Fig. 5-7. Experiment 3 is with a large feed concentration; there is just one intersection, and this occurs at nearly complete conversion. As shown in Fig. 5-11, point *D*, the reactor temperature is far above T_f .

Stability behavior in heterogeneous reactions is similar. For example, the

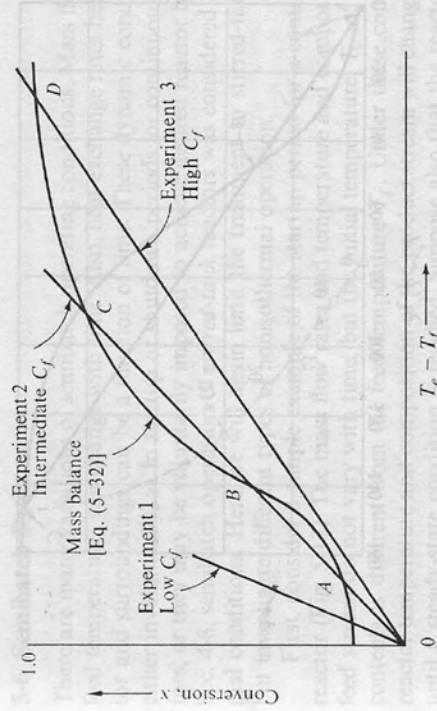


Figure 5-11 Temperature rise vs. conversion as a function of heat of reaction in an adiabatic stirred-tank reactor.

interaction of chemical and physical processes (rates of chemical reaction and mass and heat transfer) in reactions between gases and solid particles causes results analogous to those discussed here. We shall return to this subject in Chap. 10.

Calculations of stable operating conditions are illustrated in the following example.

Example 5-4 A first-order homogeneous (liquid-phase) reaction is carried out in an ideal stirred-tank reactor. The concentration of reactant in the feed is 3.0 kmol/m^3 and the volumetric flow rate is $60 \times 10^{-6} \text{ m}^3/\text{s}$. The density and specific heat of the reaction mixture are constant at 10^3 kg/m^3 and 4.19 kJ/kg K (or 1.0 cal/g K) respectively. The reactor volume is $18 \times 10^{-3} \text{ m}^3$. There is no product in the feed stream and the reactor operates adiabatically. The heat and rate of reaction are

$$\Delta H_R = -2.09 \times 10^8 \text{ J/k mol (or } -50,000 \text{ cal/g mol)}$$

$$r = 4.48 \times 10^6 C \exp\left(-\frac{62,800}{R_g T}\right), \text{ k mol/(m}^3\text{)}(\text{s})$$

where *C* is the reactant concentration in k mol/m^3 ; T is in degrees Kelvin, and $R_g = 8.314 \text{ J/(g mol)(K)}$. The activation energy in these SI units is $62,800 \text{ J/g mol}$. If the feed stream is at 298 K , what are the steady-state conversions and temperatures in the product stream?

SOLUTION Stable operating conditions are given by the simultaneous solution of Eqs. (5-32) and (5-33). Since $A = 4.48 \times 10^6 \text{ s}^{-1}$, the dimensionless quantity θA is

$$\theta A = \frac{18 \times 10^{-3}}{60 \times 10^{-6}} (4.48 \times 10^6) = 1.34 \times 10^9$$

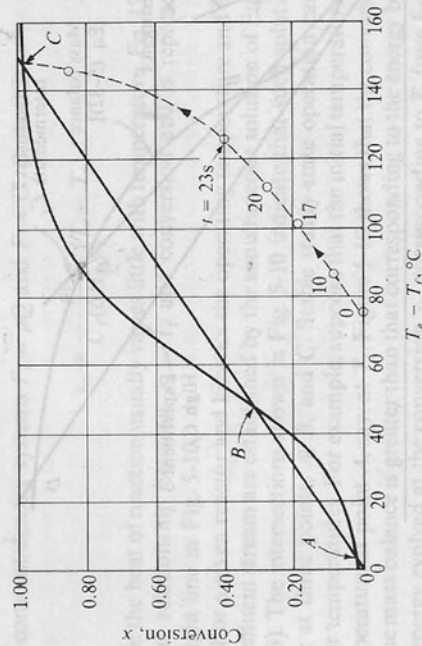


Figure 5-12 Temperature rise vs. conversion.

Then Eq. (5-32) becomes

$$x_e = \frac{1.34 \times 10^9 \exp(-62,800/R_g T)}{1 + 1.34 \times 10^9 \exp(-62,800/R_g T)} \quad (\text{A})$$

This mass-balance relation between x_e and T_e is shown as the S-shaped curve in Fig. 5-12. With the given numerical values, Eq. (5-33) is

$$x_e = \frac{-(10^3)(4.19) \times 10^3}{3.0(-2.09 \times 10^8)} (T_e - T_f) = \frac{1}{150}(T_e - T_f) \quad (\text{B})$$

This energy-balance relation is represented by the straight line in Fig. 5-12.

The intersections of the two curves in Fig. 5-12 give the possible operating temperatures and conversions. The intersections at both ends of the curves are stable operating points and give the results shown in Table 5-7. Point B at $T = 298 + 48 = 346 \text{ K}$ (73°C) represents a metastable point, as described in connection with Fig. 5-10. If the reaction had been started in the usual way by adding feed at 25°C , point A would be the steady-state operating condition at $25 + 3 = 28^\circ\text{C}$ and the conversion would be only 1.5%. To obtain a high conversion the initial temperature would have to be above 73°C (point B). Then the reaction temperature would increase to $25 + 147 = 172^\circ\text{C}$ and the conversion would be 98%. The dynamic behavior of the reactor (dotted curve), showing the temperature-time relation as this steady state is approached, is evaluated in Example 5-5.

Table 5-7

Intersection	$T_e - T_f, ^\circ\text{C}$	T, K	Conversion, %
A	3	301	1.5
C	147	445	98.0

5-6 Semibatch Reactors

There are many variations of semibatch operating conditions. Mass flow rates or feed temperatures can change with time. Also, heat exchange rates between reactor and surroundings can be a function of time. These dynamic conditions arise either involuntarily, as in startup or shutdown periods for continuous-flow reactors, or they may be voluntarily imposed to achieve desired reactor behavior. In Sec. 4-8, semibatch operation of stirred-tank reactors was considered for isothermal conditions. Here we will again limit the treatment to stirred-tank reactors but investigate different types of nonisothermal operation.

First, consider a simple example of the startup period for a continuous-flow reactor (Fig. 5-13). The mass flow rates and temperature and composition of the feed stream do not vary with time, but the initial temperature, T_0 , of the reactor contents is different from the feed temperature T_f . Under these conditions the reactor temperature and composition of the product stream will change with time until a steady-state condition is reached. Suppose also that the reactor operates adiabatically. Then Eq. (5-5) becomes

$$(H'_f - H'_e) dt = dH \quad (5-34)$$

We have already developed expressions for the enthalpy changes. Equation (5-6) for a batch reactor gives the change in enthalpy of the contents of the reactor in time dt . Equation (5-29) is applicable for the difference in enthalpy rates of the feed and effluent streams in a stirred-tank flow reactor. Hence, Equation (5-34) may be written

$$F_t c_p (T_f - T_e) + F \Delta H_R (x_f - x_e) = m_t c_p \frac{dT_e}{dt} + \Delta H_R (rV) \quad (5-35)$$

The term (rV) on the right-hand side is the rate of disappearance of reactant in the vessel. It may be expressed in terms of conversion by using the mass balance for a batch reactor. Suppose the volume of the reaction mixture is constant. Then Eq. (3-8) is applicable so that Eq. (5-35) becomes

$$F_t c_p (T_f - T_e) + F \Delta H_R (x_f - x_e) = m_t c_p \frac{dT_e}{dt} + \Delta H_R V C_0 \frac{dx}{dt} \quad (5-36)$$

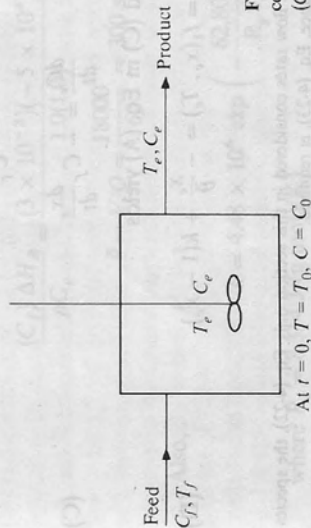


Figure 5-13 Startup period for a continuous-flow, stirred-tank reactor ($C =$ reactant concentration).

where C_0 is the initial reactant concentration in the reactor. Equations (5-35) or (5-36) are suitable forms of the energy balance for this startup problem. One of them, along with the appropriate mass balance developed in Chap. 4 [for example, Eq. (4-22)],[†] and the initial conditions of reactant concentration and temperature, are sufficient to determine how the effluent conversion x_e and temperature T_e vary with time.

Ultimately, a steady state is reached at which time the dynamic equations reduce to Eqs. (5-32) and (5-33) of Sec. 5-5. As noted in Sec. 5-5, more than one steady state may be possible.

Example 5-5 shows how Eqs. (5-36) and (4-22) can be used to evaluate the dynamic behavior ultimately leading to the steady-state solutions discussed in Example 5-4.

Example 5-5 Consider the dynamic behavior of the reactor and reaction system of Example 5-4. Initially, the reactor contains 18 liters ($18 \times 10^{-3} \text{ m}^3$) of solution with a reactant concentration of 3.0 mol/liter (3.0 kmol/ m^3). The initial temperature is 373°C. Determine the concentration and temperature of the reactor effluent as a function of time. What is the temperature and conversion in the effluent at steady state? The feed temperature, concentration, and flow rate are the same as in Example 5-4.

SOLUTION Since the density is constant, Q and V are constant. Then the mass balance of reactant [Eq. (4-22)] simplifies to:

$$C_f - C_e - \mathbf{r}(V/Q) = (V/Q) \frac{dC_e}{dt} \quad (\text{A})$$

where \mathbf{r} is the rate of disappearance of reactant. In terms of the average residence time, $\bar{\theta} = V/Q$, and the first-order rate equation, this expression becomes

$$\frac{dC_e}{dt} = \frac{C_f - C_e}{\bar{\theta}} - kC_e \quad (\text{B})$$

where k is a function of temperature. Since the conversion in the feed is zero, the relationship between C_e and x_e is

$$x_e = \frac{C_f - C_e}{C_f} \quad (\text{C})$$

and

$$\frac{dC_e}{dt} = -C_f \frac{dx_e}{dt} \quad (\text{C})$$

Substituting Eqs. (B) and (C) in Eq. (A) yields

$$\frac{dx_e}{dt} = f_1(x_e, T_e) = -\frac{x_e}{\bar{\theta}} + k(1 - x_e) \quad (\text{D})$$

[†] For the case of constant mass flow rates considered in this section only Eq. (4-22), the species mass balance, and not the total balance, Eq. (4-23), is required.

In this example $C_0 = C_f$, so that $C_0 dx$ in Eq. (5-36) is equal to $C_f dx_e$. With this equality, Eq. (5-36), becomes

$$F_i C_p (T_f - T_e) - F(\Delta H_R) x_e = m_i C_p \frac{dT_e}{dt} + \Delta H_R V C_f \frac{dx_e}{dt} \quad (\text{E})$$

For constant density, $F_i = Q\rho$, $F = QC_f$, and $m_i = V\rho$. Therefore, Eq. (E) may be written

$$\frac{dT_e}{dt} = f_2(x_e, T_e) = \frac{T_f - T_e}{\bar{\theta}} - C_f \frac{(\Delta H_R)}{\rho C_p} \left[\frac{x_e}{\bar{\theta}} + \frac{dx_e}{dt} \right] \quad (\text{F})$$

By substituting Eq. (D) for dx_e/dt , Eq. (F) takes the form

$$\frac{dT_e}{dt} = \frac{T_f - T_e}{\bar{\theta}} - \frac{\Delta H_R}{\rho C_p} k C_f (1 - x_e) \quad (\text{G})$$

with initial condition

$$T_e = T_0 \quad \text{and} \quad C_e = C_0 = C_f \quad \text{at} \quad t = 0 \quad (\text{H})$$

Equations (D) and (F) can be solved numerically with (H). If we use the Runge-Kutta method for two dependent variables, x_e and T_e , the working equations for the n th element of time Δt are (following Example 4-7):

$$k_0 = (\Delta t) f_1(x_{e_n}, T_{e_n})$$

$$m_0 = (\Delta t) f_2(x_{e_n}, T_{e_n})$$

etc., for k_1, k_2, k_3 , and m_1, m_2, m_3 , as in Example 4-7. Then

$$x_{e_{n+1}} = x_{e_n} + \frac{1}{6}(k_0 + 2k_1 + 2k_2 + k_3)$$

$$T_{e_{n+1}} = T_{e_n} + \frac{1}{6}(m_0 + 2m_1 + 2m_2 + m_3)$$

The numerical values of the constants are:

$$C_f = 3.0 \times 10^{-3} \text{ g mol/cm}^3 (3.0 \text{ k mol/m}^3)$$

$$T_0 = 373 \text{ K}$$

$$T_f = 298 \text{ K}$$

$$\frac{(C_f) \Delta H_R}{\rho C_p} = \frac{(3 \times 10^{-3})(-5 \times 10^4)}{1.0(1.0)} = -150 \text{ K}$$

$$\bar{\theta} = V/Q = \frac{18000}{60} = 300 \text{ s}$$

Also,

$$k = 4.48 \times 10^6 \exp\left(-\frac{62,800}{R_g T_e}\right) \text{ s}^{-1}$$

where $R_g = 8.314 \text{ J/(g mol)(K)}$.

Using these values and choosing $\Delta t = 10$ s, we have for the first increment, from Eq. (D),

$$k_0 = 10 f_1(x_{e_0}, T_{e_0}) = 10 \left[0 + 4.48 \times 10^6 \exp \left(\frac{-62,800}{R_g(373)} \right) (1 - 0) \right] = 0.071$$

and from Eq. (F)

$$\begin{aligned} m_0 &= 10 f_2(x_{e_0}, T_{e_0}) = 10 \left[\frac{T_f - T_e}{\theta} - \frac{C_f \Delta H}{\rho c_p} \left(\frac{x_e}{\theta} + \frac{dx_e}{dt} \right) \right] \\ &= 10 \left[\frac{298 - 373}{300} + 150(0 + 0.0071) \right] \end{aligned}$$

$$m_0 = 10 \left[\frac{-75}{300} + 1.07 \right] = 8.2 \text{ K}$$

Continuing the calculations to obtain k_1 , k_2 , and k_3 and m_1 , m_2 , and m_3 [using equations analogous to Eqs. (4-12) to (4-15)] yields the following results for the first time increment:

$$x_e = 0 + \frac{1}{6}[0.071 + 2(0.084) + 2(0.088) + 0.112] = 0.088$$

Hence, the conversion at the end of 10 seconds will be 8.8%, and the temperature is

$$T_e = 373 + \frac{1}{6}[8.2 + 2(10.3) + 2(10.8) + 14.4] = 373 + 11 = 386 \text{ K}$$

More accurate calculations, taking $\Delta t = 0.1$ s give $x_e = 0.091$ and $T_e = 384$ K after 10 seconds. Similar calculations for further time increments give the results shown in Fig. 5-12 by the dotted curve. The curve suggests a steady-state conversion corresponding to point C, as found in Example 5-4. These values can be checked by considering the steady-state forms of the mass and energy balances, Eqs. (D) and (F). The time derivatives will be zero so that these two equations reduce to

$$x_e = \frac{k\theta}{1 + k\theta} \quad (1)$$

and

$$x_e = \frac{\rho c_p}{C_f \Delta H_R} (T_f - T_e) \quad (2)$$

These expressions are the same as Eqs. (5-31) and (5-33) developed in Sec. 5-5 for the steady-state solution. Hence, simultaneous solution for T_e and x_e will give 445 K (172°C) and 98% conversion, as found in Example 5-4. The steady-state corresponds to the case where the energy evolved due to the reaction just balances the energy required to heat the feed to the reaction temperature T_e . In this example we started with $T_e = T_0 = 373$ K so that the steady-state temperature 445 K was higher than T_0 . If T_0 had been below, 73 + 273 = 344 K, the steady-state value would have been lower (301 K), as shown in Example 5-4.

As a second illustration of semibatch operation, consider a stirred tank in which one reactant is in the initial charge and the second is continuously fed to the reactor. This arrangement permits flexibility in temperature control. It is useful when the heat of reaction is high and temperatures must be controlled within narrow limits. By reducing the feed rate the temperature change in the reactor can be maintained within any required value. Suppose there is no product stream.

Then Fig. 4-18 describes the reactor and Example 4-15 treated the design calculations for an isothermal case. Here we consider a special case of nonisothermal operation. Equation (5-5) is applicable with $H'_e = 0$. Equation (5-6) gives dH . To evaluate H'_p it is convenient to take, as a reference for enthalpy, zero conversion and the reactor temperature T_c (a variable). Suppose that the conversion in the feed stream is zero. Then H'_f above the reference state is

$$H'_f = F_f c_p (T_f - T_c) \quad (5-37)$$

Substituting these results in Equation (5-5) gives

$$F_f c_p (T_f - T_c) dt + U A_h (T_s - T_c) dt = m_t c_p dT + \Delta H_R (rV) dt \quad (5-38)$$

or

$$F_f c_p (T_f - T_c) + U A_h (T_s - T_c) = m_t c_p \frac{dT}{dt} + \Delta H_R (rV) \quad (5-38)$$

where the heat transferred from the surroundings to the reactor is written in terms of an overall heat transfer coefficient U and the heat transfer area A_h .

When temperature control is critical, the reaction rate is often very fast with respect to the rate of heat transfer. Then the factors that determine the design are the rate of energy exchange with the surroundings, the feed temperature, and the feed rate. Under these circumstances only the energy balance is required. The reaction may be assumed to be at thermodynamic equilibrium, so that the rate equation and mass balance are not required. The rate of reaction in the entire reactor is equal to the rate of addition of reactant in the feed stream. The quantity rV is equal to $C_f Q_f$, and Eq. (5-38) becomes

$$m_t c_p \frac{dT_c}{dt} = F_f c_p (T_f - T_c) + U A_h (T_s - T_c) - \Delta H_R (Q_f C_f) \quad (5-39)$$

Solution of this expression shows how the temperature varies with time for various combinations of feed rate, feed temperature, and heat-exchange rate. The conversion obtained under such conditions is always the equilibrium value corresponding to the temperature at the end of the process. Its application to a practical problem is illustrated in Example 5-6.

Example 5-6 Hexamethylenetetramine (HMT) is to be produced in a semi-batch reactor by adding an aqueous ammonia solution (25 wt % NH_3) at the rate of 2 gal/min ($1.26 \times 10^{-4} \text{ m}^3/\text{s}$) to an initial charge of 238 gal (0.901 m^3) at 25°C of formalin solution containing 42% by weight formaldehyde. The original temperature of the formalin solution is raised to 50°C in order to start the reaction. The temperature of the NH_4OH solution is 25°C. The heat of reaction in the liquid phase may be assumed independent of temperature and

concentration and taken as -960 Btu/lb ($-2.23 \times 10^6 \text{ J/kg}$) of HMT. If the reactor can be operated at a temperature of 100°C , the rate of reaction is very fast in comparison with the rate of heat transfer with the surroundings. Temperatures higher than 100°C are not desirable because of vaporization and increase in pressure.

It is proposed to cool the reactor by internal coils through which water is passed. The overall heat-transfer coefficient between the stirred reaction mixture and the cooling water will be $85 \text{ Btu/(h)(ft}^2\text{)(}^\circ\text{F)}$ [$483 \text{ J/(s)(m}^2\text{)(K)}$] or $0.483 \text{ kJ/(s)(m}^2\text{)(K)}$]. The water rate through the coils is such that its temperature varies little, and an average value of 25°C may be used. Given the following data, calculate the length of 1-in.-OD tubing required for the cooling coils.

Density of ammonia solution = 0.91 g/cm^3 ($0.91 \times 10^{-3} \text{ kg/m}^3$)

Density of formalin (42%) at 25°C = 1.10 g/cm^3 ($1.10 \times 10^{-3} \text{ kg/m}^3$)

Specific heat of reaction mixture (assume constant),

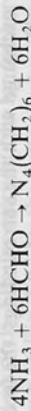
$$c_p = 1.0 \text{ Btu/(lb)(}^\circ\text{F)}$$
 [4.19 kJ/(kg)(K)]

Specific heat of 25 wt% NH_3 solution,

$$c_p = 1.0 \text{ Btu/(lb)(}^\circ\text{F)}$$
 [4.19 kJ/(kg)(K)]

The rate of the reverse reaction is negligible.

SOLUTION: Since the rate is very rapid and the reaction is irreversible, the ammonia in the inlet stream will be completely converted to HMT just as soon as it is added to the reactor according to the reaction



Since 4 moles of ammonia are required for 6 moles of formaldehyde, the total amount of ammonia required to react with all the charge of formalin solution will be

$$(\text{NH}_3)_t = \frac{238(8.33)(1.10)(0.42)}{30} \left(\frac{4}{6} \right) (17) = 346 \text{ lb} \quad (157 \text{ kg})$$

From the ammonia feed rate of 2 gal/min, the total time of reaction will be

$$t_r = \frac{346}{2(8.33)(0.91)(0.25)} = 91.3 \text{ min}$$

The heat-transfer surface is to be sufficient to prevent the temperature from exceeding 100°C . Hence at 100°C , dT/dt in Eq. (5-39) will be zero. At temperatures below 100°C the driving force $T_c - T_s$, will be insufficient to transfer enough energy to the cooling coils to maintain a constant temperature. At the start of the addition of ammonia the last term in Eq. (5-39), which is positive for an exothermic reaction, will be greater than the sum of the first and second terms. Hence, the temperature of the reaction mixture will increase. From a practical standpoint this heating period would be reduced to a minimum by shutting off the flow of cooling water until the temperature reaches 100°C .

To determine the required heat-transfer area, Eq. (5-39) may be used when the temperature is 100°C and $dT_c/dt = 0$. Thus

$$U A_h (T_c - T_s) = -\Delta H_R (Q C_f)_{\text{NH}_3} + F_{t,c} (T_f - T_c)$$

or

$$85 A_h (100 - 25) 1.8 = -\Delta H_R (Q_f C_f)_{\text{NH}_3} + F_{t,c} (1.0)(25 - 100) 1.8 \quad (\text{A})$$

The heat of reaction is $-960 \text{ Btu/(lb of HMT)}$. On the basis of NH_3 , noting that the molecular weight of HMT is 140,

$$\Delta H = -\frac{960(140)}{4} = -33,600 \text{ Btu/(lb mol of NH}_3) \text{ or } -78,000 \text{ kJ/k mol}$$

The total, and NH_3 , feed rates are

$$F_t = 2(60)(8.33)(0.91) = 910 \text{ lb/h} \quad (0.114 \text{ kg/s})$$

$$\begin{aligned} Q_f C_f &= F_t w_f / 17 = 910(0.25) / 17 \\ &= 13.3 \text{ lb mol of NH}_3/\text{h} \quad (0.00168 \text{ k mol/s}) \end{aligned}$$

where w_f is the weight fraction NH_3 in the feed.

Substituting these values in Eq. (A) and solving for the heat transfer area, we obtain

$$\begin{aligned} A_h &= \frac{-(-33,600) 13.3 + 910(1.0)(-75) 1.8}{85(75) 1.8} = 28.3 \text{ ft}^2 \\ A_h &= \frac{-(-78000)(0.00168) + 0.114(4.19)(-75)}{0.483(75)} = 2.62 \text{ m}^2 \end{aligned}$$

In SI units,

If the heat-transfer coefficient of 85 is based on the outside area of the tubes, the length L of 1-in.-OD coil is

$$L = \frac{28.3}{\pi D} = \frac{28.3(12)}{\pi} = 108 \text{ ft}$$

An appropriate size of the reactor can be obtained by noting that the total mass of mixture at the end of the process will be

$$910 \left(\frac{91.3}{60} \right) + 238(8.33)(1.10) = 3,560 \text{ lb}$$

If the density of the HMT solution is 72 lb/ft^3 , the minimum reactor volume is 50 ft^3 . A cylindrical vessel 4 ft in diameter and 6 ft in height would provide 33% excess capacity. If the 1-in. tubing were wound into a 3-ft diameter coil, approximately 12 loops would be needed.

The length of time necessary to raise the reaction temperature from its initial value, 50°C , to 100°C can be obtained by integrating Eq. (5-39). With the water rate shut off $U A_h (T_c - T_s)$ is negligible, and the expression becomes

$$\int_{T_0}^{T_c} \frac{dT_c}{F_{t,c} (T_f - T_c) - \Delta H_R (Q_f C_f)} = \int_0^t \frac{dt}{(m_0 + F_t) k_p}$$

where m_i has been replaced by $m_0 + F_i t$. The initial condition is $m_i = m_0$ and $T_c = T$. If ΔH_R and c_p are constant, this equation may be integrated to yield

$$-\frac{1}{F_i c_p} \ln \frac{-\Delta H_R(Q_f C_f) + F_i c_p(T_f - T_c)}{-\Delta H_R(Q_f C_f) + F_i c_p(T_f - T_0)} = \frac{1}{F_i c_p} \ln \frac{m_0 + F_i t}{m_0} \quad (\text{B})$$

Equation (B) relates the temperature and time during the heating period. We are given that $T_0 = 50^\circ + 253^\circ$ and $T_f = 25^\circ + 273^\circ$. Also

$$\Delta H_R(Q_f C_f) = -33,600(13.3) = -449,000 \text{ Btu/h}$$

$$m_0 = 238(8.33) \cdot 10 = 2180 \text{ lb}$$

Using these values in Eq. (B), the time required for T_c to reach 100°C is

$$-\frac{1}{1(910)} \ln \frac{449,000 + (910)(1)(25 - 100)(1.8)}{449,000 + (910)(1)(25 - 50)(1.8)} = \frac{1}{910(1)} \ln \frac{2,180 + 910t}{2,180}$$

$$\ln(1 + 0.418t) = -\ln \frac{326,000}{408,000}$$

$$1 + 0.418t = 1.25$$

or

$$t = 0.60 \text{ h} \quad \text{or} \quad 36 \text{ min}$$

In summary, the reaction temperature would rise from 50 to 100°C in 36 min after the ammonia feed is started, provided water is not run through the cooling coil. After 36 min the water flow would be started in order to maintain the reactor temperature at 100°C . After a total time of 91 min sufficient ammonia would have been added to convert all the formaldehyde to HMT.

5-7 Optimum Temperature Profiles

In the previous sections we calculated conversion, selectivity, and temperatures for various reactors under conditions where the temperature sequence was fixed. That is, these quantities were determined by the energy and mass balances applicable for *specified* operating conditions. A different problem in nonisothermal reactors is the calculation of the temperature sequence required for optimum reactor performance. For multiple-reaction systems this normally means the temperature sequence needed to give maximum selectivity for the desired product. Some conclusions about such optimum temperatures were given at the end of Sec. 5-4. For single reactions (practically, this corresponds to the situation where side reactions are not significant) the problem is to determine the temperature sequence which minimizes the reactor volume (in a flow reactor) for a given conversion. While we will discuss flow reactors here, the analogous problem in a batch reactor is to minimize the time for a given conversion.

The minimum volume will be achieved if the reaction rate is a maximum at all positions in the reactor [for example, see Eq. (3-18)]. The optimum temperature at any position will be that for which the rate is a maximum at any conversion level. Therefore, the relation $r(T, x)$ is the basic information necessary to determine

optimum temperatures. This relationship is determined by the reaction order (kinetics) and the activation energy.

For an *irreversible* reaction Eq. (2-17) gives for the rate of disappearance of reactant

$$r(T, x) = A(e^{-E/R_f T})^f(x) \quad (5-40)$$

where $f(x)$ is usually a decreasing function of x .[†] Since E is positive, the rate increases with temperature at any composition. Hence the optimum temperature sequence will be the highest temperature that is practical. This conclusion applies for both exothermic and endothermic reactions. Properties of construction materials and the ultimate importance of side reactions can limit the temperature.

For a *reversible* reaction, Eq. (5-40) becomes

$$r(T, x) = A(e^{-E/R_f T})^f(x) - A'(e^{-E'/R_f T})^g(x) \quad (5-41)$$

where E' and $g(x)$ apply for the reverse reaction. The function $g(x)$ is an increasing function of x since the concentrations of products increases with conversion. For an endothermic reaction, $E > E'$ (see Fig. 2-1). Again the rate increases with temperature for any conversion. We conclude that for *reversible, endothermic* reactions, the optimum temperature sequence is also the maximum permissible temperature.

For an *exothermic, reversible* reaction:[‡] E' must be greater than E . Hence, the rate of the reverse reaction increases more rapidly with temperature than that of the forward reaction. Equation (5-41) also shows that the reverse reaction will be slow at low conversions, while the forward reaction rate will be fast. For the rate to be a maximum at any conversion the temperature should be high at low conversions to take advantage of the predominant rate of the forward reaction, and lower at high conversions where the rate of the reverse reaction is high. Hence, for reversible, exothermic reactions the optimum temperature sequence will be continually decreasing temperature. This is illustrated in Fig. 5-14 where the *net* rate from Eq. (5-41) is plotted versus temperature, each curve corresponding to a constant conversion. An optimum temperature program is determined by connecting the maxima in the rate vs. temperature curves in Fig. 5-14, and is shown by the dashed curve.

Suppose the feed stream to a tubular-flow reactor is unconverted ($x = 0$) and its maximum temperature is T_A . The rate at the reactor entrance corresponds to point A in Fig. 5-14. If a conversion x_5 is required, the rate at the reactor outlet would be at point B . The requirement of a maximum in the rate vs. T curves cannot be achieved in the first part of the reactor because the maximum temperature is T_A . Hence, the best that can be done is to operate isothermally at T_A until the conversion at point C is reached, and then follow the dashed line to the required conversion. The optimum temperature path is ACB in Fig. 5-14. If instead of the optimum temperature sequence, the reactor was operated isothermally at the feed temperature, the reaction rate sequence would be that

[†] For example for a first-order reaction, with a feed concentration of reactant $C_{f0}/f(x) = C_f(1 - x)$.

[‡] The discussion about exothermic, reversible reactions follows that given by K. G. Denbigh in "Chemical Reactor Theory," Cambridge University Press, 1965.

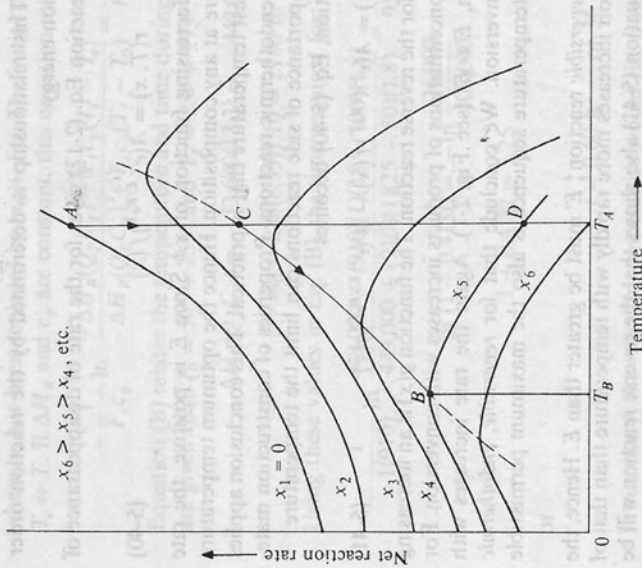
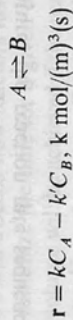


Figure 5-14 Optimum temperature sequence for an exothermic reversible reaction.

corresponding to the vertical line ACD . Such rates would be lower than those for the optimum sequence at every conversion, except from $x = 0$ to x at point C . Hence, the reactor volume would be greater.†

A stirred-tank reactor operates at constant temperature and conversion. If the required conversion is x_5 , the optimum condition, that is, the maximum rate, would require operation at a temperature T_B . Since the rate is less at point B than at point A , the volume of the stirred-tank reactor would be greater than that for the plug-flow type. These conclusions are demonstrated in Example 5-7.

Example 5-7 There are many industrially important reactions that are of the exothermic, reversible type: the oxidation of SO_2 , hydration of ethylene to produce ethyl alcohol, and ammonia and methanol syntheses. These reactions all require a catalyst, and the kinetics of catalytic reactions is not discussed until Chap. 9. However, we can illustrate the optimum temperature problem by considering a first-order, gaseous, reversible reaction of the form



† The question of optimum temperatures in various types of reactors has been studied extensively; for example R. Aris, "The Optimal Design of Chemical Reactors," Academic Press, New York, 1961.

where

$$k = A \exp\left(-\frac{E}{R_g T}\right) = 0.02 \exp\left(-\frac{29,300}{R_g T}\right), (\text{s})^{-1}$$

$$k' = A' \exp\left(-\frac{E'}{R_g T}\right) = 0.33 \exp\left(-\frac{46,000}{R_g T}\right), (\text{s})^{-1}$$

If the equilibrium constant K is equal to k/k' (see Sec. 2-7)

$$K = \frac{k}{k'} = 0.061 \exp\left(-\frac{E-E'}{R_g T}\right) = 0.061 \left(\exp \frac{16,700}{R_g T}\right)$$

At 873 K, $K = 0.61$, while at 473 K, $K = 4.3$. For a maximum permissible feed temperature of 873 K and a feed rate F_A ($k \text{ mol/s}$) of reactant at a feed concentration C_{A_f} , what is the optimum temperature profile in a plug-flow reactor? A conversion of 60% is required and the feed concentration of A is C_{A_f} and $C_{B_f} = 0$. What would be the required reactor volume? If the reactor operated isothermally at 873 K, what is the V/F_A required for 60% conversion? To simplify the calculations, neglect the effect of temperature on the concentration (i.e., assume constant density).

SOLUTION We first express the rate in terms of the conversion (of A) by noting that

$$x = \frac{C_{A_f} - C_A}{C_{A_f}} = \frac{C_B}{C_{A_f}}$$

Hence,

$$r = C_{A_f} \left[A(1-x) \exp\left(-\frac{E}{R_g T}\right) - A'x \exp\left(-\frac{E'}{R_g T}\right) \right] \quad (\text{A})$$

If Eq. (A) is differentiated with respect to T (at constant conversion) and the derivative set equal to zero, the following requirement for maximum rate is obtained:

$$\frac{x}{(1-x)} = \frac{EA}{E'A'} \exp\left[-\frac{(E-E')}{R_g T}\right] \quad (\text{B})$$

or

$$T, K = \frac{(E'-E)/R_g}{\ln\left(\frac{A'E x}{AE(1-x)}\right)} = \frac{2010}{\ln\left(\frac{20.2 x}{1-x}\right)} \quad (\text{C})$$

Solving this equation for T for various values of x gives the results shown in the first two columns of Table 5-8. The optimum temperature exceeds the limit of 873 K until the conversions reaches 0.33. Hence, the temperature sequence will be an isothermal path at 873 K up to 33% conversion, followed by the decreasing temperatures in Table 5-8 until $x = 0.60$.

Table 5-8 Optimum temperature sequence for Example 5-7

Conversion x	Temperature $^{\circ}\text{C}$	Max rate, r/C_{A_f} , (s) $^{-1}$	Rate at 873 K r/C_{A_f} , (s) $^{-1}$
0		3.52×10^{-4}	3.52×10^{-4}
0.1	2250	2.59×10^{-4}	2.59×10^{-4}
0.2	979	1.82×10^{-4}	1.82×10^{-4}
0.3	664	0.73×10^{-4}	0.73×10^{-4}
0.33	600	0.45×10^{-4}	0.45×10^{-4}
0.38	0	0
0.4	505	0.23×10^{-4}	
0.5	399	0.18×10^{-4}	
0.6	319	0.037×10^{-4}	

The reaction volume is given by Eq. (3-18). For $x = 0$ to 0.33, the rate is obtained from Eq. (A) by substituting $T = 873$ K:

$$r = C_{A_f} \left[0.02 \exp \left(-\frac{29,300}{R_g(873)} \right) (1-x) - 0.33 \exp \left(-\frac{46,000}{R_g T} \right) (x) \right] \quad (\text{D})$$

$$r = C_{A_f} [3.52 \times 10^{-4} (1-x) - 5.78 \times 10^{-4} x] \quad (\text{E})$$

For $x \geq 0.33$ the corresponding x and T given in the first two columns of Table 5-8 are used in Eq. (D) to calculate r . All of these rates are given in the third column of the table. Then V/F_A may be obtained by integrating Eq. (3-18) graphically, by plotting $1/r$ vs. x_A according to the equation

$$\frac{V}{F_A} = \int_0^{0.6} \frac{dx_A}{r} \quad (\text{F})$$

The results give V/F_A equal to $0.23 \times 10^4/C_{A_f}$ for $x = 0$ to 0.33, and $2.35 \times 10^4/C_{A_f}$ for $x = 0.33$ to 0.6. The total value is

$$\frac{V}{F_A} = 2.58 \times 10^4/C_{A_f}, \text{ m}^3/(\text{k mol/s})$$

For an isothermal reactor operating at 873 K, Eq. (F) would be applicable with rate values determined at 873 K from Eq. (E). These rates are tabulated in the fourth column of Table 5-8 and indicate a zero value by the time the conversion has reached 0.38. In other words, at 873 K the equilibrium conversion is 38%. Regardless of the reactor volume, it is not possible to achieve the required 60% conversion. This situation would correspond to a conversion x_6 in Fig. 5-14. A higher conversion could be reached by operating isothermally at a lower temperature than 873 K. However, the required V/F_A for 60% conversion would always be greater than $2.58 \times 10^4/C_{A_f}$.

A continuous change in temperature as indicated in Example 5-7 is not practical. However, the optimum can be approached by operating different parts of the reactor at different temperature levels (i.e., discontinuous temperature changes).

One way of accomplishing this is to divide the reactor into sections with intercoolers between sections (see Fig. 1-7f). An important aspect of the optimum calculations is that one then knows the *minimum* reactor volume for a given set of conditions. Such a result can be useful for comparison with actual behavior.

PROBLEMS

5-1 The liquid-phase hydrolysis of dilute aqueous acetic anhydride solutions is second order and irreversible, as indicated by the reaction



A batch reactor for carrying out the hydrolysis is charged with 200 liters of anhydride solution at 15°C and a concentration of 2.16×10^{-4} g mol/cm 3 . The specific heat and density of the reaction mixture are essentially constant and equal to 0.9 cal/(g)($^{\circ}\text{C}$) and 1.05 g/cm 3 , respectively. The heat of reaction may be assumed constant at $-50,000$ cal/g mol. The rate has been investigated over a range of temperatures, of which the following results are typical:

$t, ^{\circ}\text{C}$	10	15	25	40
$r, \text{g mol}/(\text{cm}^3)(\text{min})$	0.0567C	0.0806C	0.1580C	0.380C

where C is acetic anhydride concentration, in gram moles per cubic centimeter. (a) Explain why the rate expression can be written as shown in the table even though the reaction is second order. (b) If the reactor is cooled so that operation is isothermal at 15°C , what time would be required to obtain a conversion of 70% of the anhydride? (c) Determine an analytical expression for the rate of reaction in terms of temperature and concentration. (d) What time is required for a conversion of 70% if the reactor is operated adiabatically?

5-2 A reactor for the production of drying oils by the decomposition of acetylated castor oil is to be designed for a conversion of 70%. The initial charge will be 500 lb and the initial temperature 340°C , as in Example 5-1. In fact, all the conditions of Example 5-1 apply, except instead of adiabatic operation, heat will be supplied electrically with a cal-rod unit in the form of a 1-in.-OD coil immersed in the reaction mixture. The power input and the stirring in the reactor will be such that the surface temperature of the heater is maintained constant at 700 K. The heat-transfer coefficient may be taken equal to 60 Btu/(h)(ft 2)($^{\circ}\text{F}$). What length of heater will be required if the conversion of 70% is to be obtained in 20 min?

5-3 The thermal (noncatalytic) decomposition of acetaldehyde,



is studied in an ideal tubular-flow reactor at a constant total pressure of P_0 atm. Suppose pure acetaldehyde vapor enters the reactor at T_0 K and a steady rate of F g/s. The heat of reaction specific heat of the reaction mixture can be assumed constant and equal to ΔH cal/g mol and c_p cal/(g mol)($^{\circ}\text{C}$). The rate of reaction is given by the second-order equation

$$r = A(e^{-E/R_g T})^2 P_A^2 \quad \text{g mol}/(\text{s})(\text{cm}^3) \quad (\text{A})$$

where E is the activation energy, in calories per gram mole, and P_A is the partial pressure of acetaldehyde, in atmospheres. If the reactor operates adiabatically, express the rate of reaction in terms of the conversion as the sole variable.

5-4 A tubular-flow reactor is to be designed for the production of butadiene from butene by the gas phase reaction:



The composition of the feed is 10 moles of steam per mole of butene and no butadiene or hydrogen. The reactor operates at 2 atmospheres pressure with an inlet (feed) temperature of 1200°F. The reaction rate follows a first-order, irreversible equation for which the rate constant k as a function of temperature is:

T, K	922 (1200°F)	900	877	855	832
k	11.0	4.90	2.04	0.85	0.32

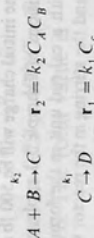
($k = \text{g mol butene reacted}/(\text{h})(\text{liter}/\text{atm})$.)

The heat of reaction may be taken as constant and equal to $\Delta H_R = 26,360 \text{ cal/g mol}$. Similarly the specific heat of the feed stream may be regarded as constant and equal to $0.5 \text{ Btu/lb}^\circ\text{R}$.

- What would be the volume required for a conversion (of butenes) of 20% if the reactor were operated isothermally at 1200°F with a butene-plus-steam feed rate of 22 lb mol/h?
- It is desired to determine the conversion as a function of reactor volume (ft^3) for adiabatic operation if the feed rate is 2.0 lb mol of butene per hour and 20 lb mol of steam per hour. Demonstrate your ability to solve this type of problem by calculating the reactor volume for conversions (of butenes) of 10 and 20%. What changes in operating conditions could be employed to reduce the volume required for a given conversion?

5-5) Reconsider the pilot plant discussed in Example 5-2 for the production of allyl chloride. It has been proposed to reduce the extent of the side reaction to dichloropropane by preheating the feed to 300°C. To obtain a more uniform axial temperature profile, inert nitrogen will be added to the feed to give a composition corresponding to 5 moles of N_2 , 4 moles of C_3H_6 , and 1 mole of Cl_2 . The total feed rate will be 0.85 lb mol/h. If all other conditions are also the same, calculate the temperature and conversion profiles for a tube length of 20 ft. Comment on this method of operation in comparison with that in Example 5-2 with respect to selectivity and production rate of allyl chloride.

5-6 Consider the irreversible constant-density reaction sequence



The rate constants are

$$k_2 = A_2 e^{-E_2/R_2 T}$$

$$k_1 = A_1 e^{-E_1/R_1 T}$$

Component C is the desired product. The feed contains no C or D , and $C_A = C_{A_0}$, $C_B = C_{B_0}$. (a) If an isothermal tubular-flow reactor is employed, develop equations for calculating the conversion of A for which the yield of C is a maximum and for the constant temperature at which the reactor should operate to give the highest value of the maximum yield of C . (b) Develop equations for predicting the conversion of A for which the selectivity of C with respect to D is a maximum.

5-7 Repeat Prob. 5-6 for a stirred-tank reactor.

5-8 The vapor-phase decomposition of phosphine, which is irreversible and first order, follows the reaction



Pure phosphine is fed to a tubular-flow reactor, operating at 1 atm and adiabatically with a feed temperature of 953 K. The reaction is endothermic, $\Delta H_R = 23,900 \text{ J/mol}$ of phosphine at 25°C. The

molar heat capacities ($J/(\text{mol})(K)$) are

$$\text{P}_4(g) \quad C_p = 25.1 + 0.00407T$$

$$\text{PH}_3(g) \quad C_p = 28.0 + 0.0277T$$

$$\text{H}_2(g) \quad C_p = 30.1$$

The rate constant $k, (\text{s})^{-1}$, is the following function of temperature:

$$\ln k = -27.94 + 2 \ln T - 43,672$$

What volume to molar feed rate ratio (V/F) would be required to obtain a conversion of 10% in one pass through the reactor? What would be the conversion for the same V/F if the reactor operated isothermally at 953 K?

5-9 The gas-phase cracking of light hydrocarbons is a thermal (noncatalytic) process that requires a high temperature. Since the reactions are endothermic, energy must be supplied to maintain a high temperature. This can be accomplished, in part, by adding steam to the feed, but in addition it is desirable to add heat from the surroundings. This is done commercially by constructing the reactor of rows of tubes installed in a furnace (pipe still).

A laboratory study of such a cracking process indicates that the required conversion is obtained with a tube of length L_L , diameter d_L , for a hydrocarbon feed rate F_L and an average temperature difference $(T_w - T_L)$. T_w is the tube-wall temperature and T is the bulk temperature of the reaction mixture.

It is necessary to scale-up the laboratory reactor to pilot-plant size. An exact scale-up would require that the dimensionless axial and radial temperature profiles in the laboratory and pilot-plant tubes be the same. As an approximation, assume that it is sufficient for the dimensionless energy balances as written in Chap. 5 to be the same.

If the same conversion is to be obtained in the pilot-plant as in the laboratory reactor, what relations between reactor diameter and length and feed rate are required? Base the scale-up on the mass and energy balances. Do not consider pressure drop in the scale-up and neglect the effect of pressure on the rate of reaction.

5-10 Reconsider Example 5-3 for the case where the feed composition is $\text{N}_2 = 50 \text{ mole } \%, \text{C}_3\text{H}_6 = 40 \text{ mole } \%, \text{Cl}_2 = 10 \text{ mole } \%$. The feed temperature will be 300°C, with all other conditions the same as in Example 5-3. Determine conversions and temperatures for reactor volumes up to 0.5 ft^3 .

5-11 A first-order irreversible (liquid-phase) reaction is carried out in a stirred-tank flow reactor. The density is 1.2 g/cm^3 and the specific heat is $0.9 \text{ cal/(g)(}^\circ\text{C)}$. The volumetric flow rate is $200 \text{ cm}^3/\text{s}$ and the reactor volume is 10 liters. The rate constant is

$$k = 1.8 \times 10^5 e^{-12,000/R_2 T} \quad \text{s}^{-1}$$

where T is in degrees Kelvin. If the heat of reaction is $\Delta H_R = -46,000 \text{ cal/g mole}$ and the feed temperature is 20°C, what are the possible temperatures and conversions for stable, adiabatic operation at a feed concentration of 4.0 g mol/liter?

5-12 The reaction between sodium thiosulfate and hydrogen peroxide in dilute aqueous solution is irreversible and second order in thiosulfate.† The rate constant is the following function of temperature:

$$k = 6.85 \times 10^{14} \exp\left(-\frac{18300}{R_2 T}\right), \text{ cm}^3/\text{mole}(\text{s})$$

Reaction stoichiometry indicates that 2 moles of H_2O_2 react with one mole of $\text{Na}_2\text{S}_2\text{O}_3$. The heat of reaction at 25°C is $\Delta H_R = -131,000 \text{ cal/g mole}$.

† Kearns, D. L. and Manning, F. S., *AIChE J.*, **15**, 660 (1969).

Kearns and Manning experimental studies in a stirred-tank reactor included the following conditions:

$$\text{Reactor volume} = 2790 \text{ cm}^3$$

$$\text{Feed temperature} = 25^\circ\text{C}$$

$$\text{Feed rate} = 14.2 \text{ cm}^3/\text{s}$$

Consider adiabatic operation and feed concentrations of 2.04×10^{-3} g mol/cm³ and 4.08×10^{-4} g mol/cm³ of thiosulfate and hydrogen peroxide, respectively. What would be the conversion and temperature in the reactor effluent?

5-13 The exhaust gas from an internal combustion engine contains some unburned fuel and carbon monoxide. Combustion can be continued if an afterburner is placed in the exhaust line. Suppose such an afterburner operates as an adiabatic, stirred-tank reactor with an average residence time of 9 seconds. Consider only the further oxidation of CO and assume that, in excess air, the oxidation is first order and irreversible with the following rate constant:

$$k(\text{s}^{-1}) = 1.5 \times 10^{10} \exp\left(-\frac{272}{R_g T}\right)$$

$$E = 272 \text{ kJ/mol}$$

If the combustion gases (consider the properties to be those of air) enter at 1073 K, what are the steady-state values of the temperature and CO conversion in the effluent from the afterburner?

5-14 It is desired to evaluate the dynamic behavior of the reaction and reactor system of Example 5-4 at a different initial condition than that for Example 5-5. Suppose initially that the reactor contains 18×10^{-3} m³ of solution with a reactant concentration of 3.0 k mol/m^3 at a temperature of 308 K. Determine curves of effluent temperature and conversion vs. time. Also calculate the steady-state temperature and conversion.

5-15 As noted in Sec. 5-7, for exothermic, reversible reactions increasing the temperature reduces the maximum (equilibrium) conversion but increases the forward rate. To obtain the maximum conversion a high temperature is needed at low conversions (where the reverse reaction is unimportant) and a lower temperature at higher conversions.

Consider a reversible first-order reaction $A \rightleftharpoons B$ for which, at 298 K,

$$\Delta F_{298}^\circ = -2500 \text{ cal/g mol}$$

$$\Delta H_{298}^\circ = -20,000 \text{ cal/g mol}$$

The reaction mixture is an ideal liquid solution (constant density) at all temperatures. (a) Assuming that ΔH° is constant, plot a curve of the equilibrium conversion vs. temperature from 0 to 100°C. (b) If the forward-rate constant is

$$k = 5 \times 10^8 e^{-12,500/R_g T} \text{ min}^{-1}$$

determine the conversion in the effluent from an isothermal tubular-flow reactor for which the volumetric feed rate is 100 liters/min and the volume is 1500 liters. Calculate the conversion for a series of temperatures from 0 to 100°C and plot the results on the figure prepared for part (a). (c) Suppose that the maximum permissible temperature is 100°C and the concentration of A in the feed stream is 2 g mol/liter (the feed contains no B). Determine the maximum conversion obtainable in the reactor of part (b) if the temperature can be varied along the length of the reactor. First prepare curves (similar to Fig. 5-14) of net rate vs. temperature at constant conversion for several conversion levels. Then plot the optimum temperature profile, first as temperature vs. conversion and then as temperature vs. V/Q .

5-16 Consider the same reaction system, rate equation, feed rate, and composition as in Prob. 5-15. The reaction is to be carried out in two stirred-tank reactors, each with a volume of 750 liters. What

should be the temperature (within the range 0 to 100°C) in each reactor in order to obtain the maximum conversion in the effluent from the second reactor? The graphical method for multiple-stirred-tank reactors (described in Sec. 4-6) may be helpful.

5-17 The HMT reactor described in Example 5-6 is to be redesigned so that the reaction temperature rises from 50 to 100°C as uniformly as possible as the ammonia solution is added. To accomplish this the rate of addition of ammonia must be varied. The cooling water will flow through the coils throughout the run. Determine the feed rate as a function of time, and the time required to add all the ammonia, to meet these operating requirements. All other conditions are the same as in Example 5-6.