

# Chapter 5



## NONISOTHERMAL REACTORS

We have thus far considered only isothermal reactors in which we specified the temperature. However, real reactors are almost always and unavoidably operated nonisothermally. This is because (1) reactions generate or absorb large amounts of heat and (2) reaction rates vary strongly with temperature.

In fact, we usually want to operate exothermic reactions nonisothermally to take advantage of the heat release in the reaction to heat the reactor to a temperature where the rates are higher and reactor volumes can be smaller. However, if the temperature is too high, equilibrium limitations can limit the conversion, as we saw previously for  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  synthesis reactions.

Small lab reactors are frequently thermostatted, either by contact with the surroundings (a small beaker on a bench) or by placing them on a hot plate or in an oven. This is because in a lab reactor the wall area (where heat transfer occurs) is usually large compared to the reactor volume (where reaction heat is generated).

However, the large reactors encountered in industry are usually so large that it is impossible to thermostat the reactor at a fixed temperature that would be independent of the reactions and conversions. Further, it is frequently desired to use the heat release from exothermic reactions to heat the reactor above the feed temperature to attain a higher rate. On the other hand, one of the greatest problems in exothermic reactions is that of overheating if the heat generated is too large.

The temperature dependence of reactions comes from **dependences** in properties such as concentration ( $C_j = P_j/RT$  for ideal gases) but especially because of the temperature dependence of rate coefficients. As noted previously, the rate coefficient usually has the Arrhenius form

$$k(T) = k_0 e^{-E/RT}$$

if we ignore the small temperature dependence in the pre-exponential factor.

One important reason to consider the nonisothermal reactor is because it is the major cause of accidents in chemical plants. Thermal runaway and consequent pressure buildup and release of chemicals is an ever-present danger in any chemical reactor. Engineers must

be intimately acquainted with these characteristics in designing and operating chemical reactors.

Chemical reactors may look similar to other units of chemical processing and sometimes they behave similarly, but the nonisothermal chemical reactor has nonlinearities that never occur in nonreacting systems.

## HEAT GENERATION AND REMOVAL

We first need to develop energy-balance equations for these reactors. Shown in Figure 5-1 is a sketch of a generalized reactor with heat flows indicated. Heat flows into the reactor with the reactants and out with the products. Reaction generates or absorbs heat, depending on whether the reactions are exothermic or endothermic. Any stirring and friction generate heat. Finally, heat is transferred through walls in heat exchange. In a CSTR the temperature in the reactor is equal to the temperature at the exit, but in any other reactor the temperature and conversion are functions of position in the reactor.

A reactor will be isothermal at the feed inlet temperature  $T_0$  if (1) reactions do not generate or absorb significant heat or (2) the reactor is thermostatted by contact with a temperature bath at coolant temperature  $T_0$ . For any other situation we will have to solve the energy-balance equation long with the mass balance to find the temperature in the reactor. We therefore must set up these equations for our mixed and unmixed reactors.

### Thermodynamics of a flow system

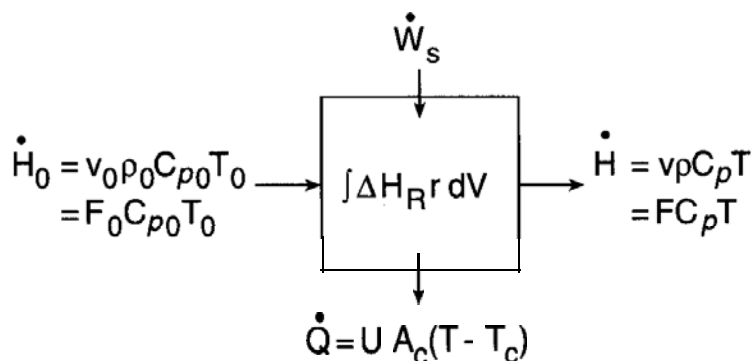
Before we develop the energy balances for our reactors, it is worthwhile to define some quantities from thermodynamics because the energy balances *we* need are *thermal energy balances*. We begin with the First Law of Thermodynamics,

$$dU = dq - dw$$

where  $U$  is the internal energy per mole,  $q$  is the amount of heat *added* to the system per mole, and  $w$  is the work done *by* the system per mole. For a flow system, pressure-volume work is done in flowing a fluid through the system,

$$dw = d(PV) + \mathbf{w}_s$$

where  $\mathbf{w}_s$  is any shaft work that may be done *by* the system. Since the enthalpy is defined through the relation



**Figure 5-1** Energy balance in chemical reactors. The volume shown could be the total reactor volume in a CSTR or a differential volume in a PFTR.

$$d\mathbf{H} = d\mathbf{U} + d(PV)$$

an energy balance on a flow system becomes

$$dH = dq - dw,$$

These are the fundamental thermodynamic equations from which we can develop our energy balances in batch, stirred, and tubular reactors.

In thermodynamics these quantities are usually expressed in *energy per mole* (quantities in bold), while we are interested in the rate of energy change or energy flow in *energy per time*. For these we replace the molar enthalpy  $H$  (cal/mole) of the fluid by the rate of enthalpy flow  $\dot{H}$  in a flow system.

For the energy balance in a flow system we therefore assume that we can make an *enthalpy balance* on the contents of the reactor. We can write the rate of enthalpy generation  $\Delta\dot{H}$  in any flowing or closed system as

$$\begin{aligned}\Delta\dot{H} &= \dot{H}_o - \dot{H} \\ &= \sum_j F_{oj}\mathbf{H}_{oj} - \sum_j F_j\mathbf{H}_j\end{aligned}$$

where the first term on the right is the rate of enthalpy flow into the system and the second is the enthalpy flow out of the system.

## Heat generated by reaction

Our major concern is the heat generated or absorbed by the chemical reactions that occur in the reactor. If  $\mathbf{H}_j$  is the molar enthalpy of a chemical species, then the heat of a chemical reaction is defined as

$$\sum \nu_j \mathbf{H}_j = -\Delta H_R$$

If a reaction is exothermic, then the reaction generates heat, which tends to increase the reactor temperature, while if a reaction is endothermic, the reaction absorbs heat, which tends to cool the reactor.

## Heat removal and addition through reactor walls

Heat can be removed from or added to a reactor through heat exchange across the walls. For an integral reactor we write the rate of heat removal from the reactor  $\dot{Q}$  as

$$\dot{Q} = UA_c(T - T_c)$$

In this equation,  $U$  is the heat transfer coefficient in energy per area  $A$ , per temperature difference (don't confuse this  $U$  with the internal energy  $U$ ), and  $A$ , is the area across which heat exchange occurs between the reactor at temperature  $T$  and coolant at temperature  $T_c$ . We want to define  $\dot{Q}$  as the rate of heat removal as a positive quantity; so  $\dot{Q}$  will be positive if  $T > T_c$ . If  $T < T_c$ , heat flows into the reactor; so the reactor is being heated. We could use  $T_h$  as the heating temperature, but since the cooled reactor is the more interesting situation, we shall use  $T_c$  as the temperature of the fluid, which is exchanging heat with the reactor.

For a differential reactor we write

$$d\dot{Q} = U(T - T_c) dA_c$$

as the heat flow through an element of reactor wall area  $dA_c$  between the reactor at  $T$  and coolant at  $T_c$ .

## Shaft work

Any stirring within the reactor will generate heat, and we call this term  $\dot{W}_s$ . We omit gravity and kinetic energy terms in the energy balance because these are usually very small compared to the other terms in the energy balance in a chemical reactor.

Note **that** we call this term positive when work is done on the system, just as we make  $\dot{Q}$  positive when heat is removed from the reactor. Thus the signs on  $\dot{W}_s$  and  $\dot{Q}$  are opposite to those of  $dq$  and  $dw$ , in the thermodynamic equations. We are always interested in shaft work done by a stirrer on the reactor fluid, and we are usually interested in cooling rather than heating. Therefore, we carry these sign conventions so that we can be sure of the signs of these terms.

## Heat flow with fluid

The other mode of heat interchange with the surroundings in a flow reactor is by inflow and outflow of heat with the fluid entering and leaving the reactor. If the fluid is flowing into the reactor with volumetric flow rate  $v_o$  and has a heat capacity per reactor volume  $\rho C_{p0}$  or **with** total molar flow rate  $F_o$  with a heat capacity per mole  $C_{p0}$  (written in bold), then the rate of enthalpy flow into the reactor is

$$\dot{H} = v_o \rho C_{p0} T_o = F_o C_{p0} T_o$$

and the enthalpy carried out is similarly

$$\dot{H} = v \rho C_p T = F C_p T$$

where the quantities with subscript o represent inflow and without the subscripts those in the outflow. The total molar flow rate  $F$  is the sum of the molar flow rates of all species  $F = \sum F_j$ . The enthalpy per mole of fluid  $H = C_p T$ , so that multiplication of  $H$  by the molar flow  $F$  rate gives  $\dot{H}$ , or  $\dot{H} = FH$ . The reference state of enthalpy where  $H = 0$  is arbitrary, and we always write enthalpy changes; so the above expression is adequate (assuming that  $C_p$  is independent of  $T$ ).

For liquid water and for aqueous solutions we will assume  $C_p = 1 \text{ cal/g K}$ , and, since the density  $\rho$  of water is  $1 \text{ g/cm}^3$ , we have  $\rho C_p = 1 \text{ cal/cm}^3 \text{ K}$  or  $\rho C_p = 1000 \text{ cal/liter K}$ . To estimate the heat capacity of gases, we will usually assume that the molar heat capacity  $C_p$  is  $\frac{7}{2} R \text{ cal/mole K}$ . There are thus three types of heat capacity, the heat capacity per unit mass  $C_p$ , the heat capacity per unit volume  $\rho C_p$ , and the heat capacity per mole  $C_p$ . However, we will use heat capacity per unit volume for much of the next two chapters, and we use the symbol  $\rho C_p$  for most of the equations.

Another approximation we frequently make in simplifying the energy balance is that the molar heat capacity, which might be approximated as

$$C_p(T) = \sum_{j=1}^S y_j C_{pj}(T)$$

is independent of temperature and composition, so that we can assume  $C_{p0} = C_p$  and  $\rho_0 C_{p0} = \rho C_p$ . Thus we continue the approximation that all thermal properties of the fluid in a reactor are constants that are independent of composition and temperature. We can easily modify these to be more accurate, but for most preliminary calculations in chemical reactors, these approximations make the equations much simpler.

In the above expressions we used symbols in bold for thermodynamic quantities per mole to show how these thermodynamic relations are used to develop the energy balance. We will not use them elsewhere except for  $\Delta H_R$ , which is the heat of reaction per mole (but will not be written in bold).

## ENERGY BALANCE IN A CSTR

We first derive the energy balance in a CSTR. For the mass balance in a constant-density reactor we wrote an integral balance on the rate of change of the number of moles  $N_j$  of species  $j$  in the reactor to obtain

$$\frac{dN_j}{dt} = V \frac{dC_j}{dt} = V(C_{j0} - C_j) + V v_j r$$

$$\frac{dN_j}{dt} = V \frac{dC_j}{dt} = V(C_{j0} - C_j) + V \sum_{i=1}^R v_{ij} r_i$$

for single and multiple reactions, respectively. (We follow our custom of ignoring density changes so that  $V$  is a constant and  $C_j$  is an appropriate species density unit.) For the steady-state CSTR we set the time derivatives equal to zero and obtained mass balances on species  $j$  as in the previous chapters

$$C_j - C_{j0} = \tau v_j r$$

$$C_j - C_{j0} = \tau \sum v_{ij} r_i$$

For the corresponding energy balance in a CSTR we write an analogous expression

$$[\text{accumulation of heat}] = [\text{heat flow in}] - [\text{heat flow out}]$$

$$+ [\text{heat generation by reaction}] - [\text{heat removal to surroundings}]$$

The last term is not present in the mass balance (unless the reactor leaks), but heat can be carried in and out not only with flow but also by heat transfer through the walls. An enthalpy balance on the contents of this CSTR gives

$$\frac{dH}{dt} = \rho C_p V \frac{dT}{dt} = v \rho C_p (T_0 - T) + V(-\Delta H_R) r - U A_c (T - T_c) + \dot{W}_s$$

$$\frac{dH}{dt} = \rho C_p V \frac{dT}{dt} = v \rho C_p (T_0 - T) + V \sum_{i=1}^R (-\Delta H_{Ri}) r_i - U A_c (T - T_c) + \dot{W}_s$$

for single and multiple reactions, respectively. Heat transfer occurs across the walls of the reactor with  $A$ , the wall area across which heat transfer occurs (the subscript  $c$  stands for cooling).

Each term in the preceding equations has units of energy/time. Note the signs on each term indicating that heat is removed or added to the reactor. We preserve the minus sign on  $A \dot{H}_R$  because we are more interested in exothermic reactions for which  $A \dot{H}_R < 0$ . The student can recognize each term on the right side from the steady-state enthalpy balance we derived in the previous section from the thermodynamics of a steady-state flow system.

For steady state in the CSTR we set  $d\dot{H}/dt = 0$  and divide each term by  $v\rho C_p$  to yield steady-state energy balance

$$T - T_o = \tau \frac{-\Delta H_R}{\rho C_p} r - \frac{U A_c}{v\rho C_p} (T - T_c)$$

or

$$T - T_o = \tau \sum_{i=1}^R \frac{-\Delta H_{Ri}}{\rho C_p} r_i - \frac{U A_c}{v\rho C_p} (T - T_c)$$

for single and multiple reaction systems, respectively. We have omitted the  $\dot{W}_s$  term from these expressions because, even for very vigorous stirring, this term is usually small compared to the other terms in the energy balance.

## ENERGY BALANCE IN A PFTR

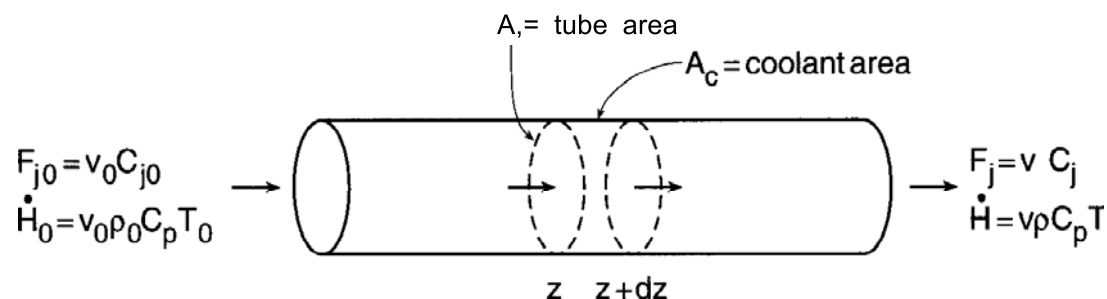
For the PFTR we wrote the mass balance on species  $j$  by writing a shell balance between position  $z$  and  $z + dz$ . After letting  $dz \rightarrow 0$  we obtained the expressions

$$u \frac{dC_j}{dz} = v_j r$$

$$u \frac{dC_j}{dz} = \sum_{i=1}^R v_{ij} r_i$$

for single and multiple reactions, respectively.

For the energy balance we make a similar differential balance on the enthalpy flow between  $z$  and  $z + dz$  for a tube of length  $L$  and diameter  $D$  as sketched in Figure 5-2. In steady state this energy balance is



**Figure 5-2** Energy balance in a PFTR. A shell balance is made on an element of volume  $dV$  between  $z$  and  $z + dz$ . Species flow  $F_j$  and enthalpy flow in and out of this element of volume are balanced by species and energy generated by reaction.

$$0 = [uA_t\rho C_p T]_z - [uA_t\rho C_p T]_{z+dz} + A_t(-\Delta H_R)r dz - Up_w(T - T_c) dz$$

In this expression  $A_t$  is the cross-sectional area of the tube ( $\pi D^2/4$  for a cylindrical tube); so the volume  $dV$  of this element is  $A_t dz$ . Heat transfer occurs across the external wall of the tube, which has area  $dA_c$  (subscript c stands for coolant), so that

$$dA_c = p_w dz$$

where  $p_w$  is the perimeter length of the wall of the tube ( $\pi D$  for a cylindrical tube). The heat transfer rate in this element is

$$d\dot{Q} = Up_w dz(T - T_c)$$

Next we assume that the fluid density and the tube diameter are the same at  $z$  and  $z + dz$  to obtain

$$0 = A_t u \rho C_p (T_z - T_{z+dz}) + A_t (-\Delta H_R) r dz - Up_w (T - T_c) dz$$

Finally we take the limit as  $dz \rightarrow 0$ ,

$$\lim_{dz \rightarrow 0} (T_z - T_{z+dz}) = -\frac{dT}{dz} dz$$

The energy-balance equation after dividing by  $dz$  is

$$u A_t \rho C_p \frac{dT}{dz} = A_t (-\Delta H_R) r - Up_w (T - T_c)$$

$$u A_t \rho C_p \frac{dT}{dz} = A_t \sum_{i=1}^R (-\Delta H_{Ri}) r_i - Up_w (T - T_c)$$

for single and multiple reactions, respectively. Division by  $A_t \rho C_p$  yields

$$u \frac{dT}{dz} = \frac{-\Delta H_R}{\rho C_p} r - \frac{Up_w}{\rho C_p A_t} (T - T_c)$$

$$u \frac{dT}{dz} = \sum_{i=1}^R \frac{-\Delta H_{Ri}}{\rho C_p} r_i - \frac{Up_w}{\rho C_p A_t} (T - T_c)$$

for single and multiple reactions, respectively.

## Batch reactor

For a single reaction in a nonisothermal batch reactor we can write the species and energy-balance equations

$$V \frac{dC_A}{dt} = -Vr$$

$$V \rho C_p \frac{dT}{dt} = V(-\Delta H_R)r - UA_c(T - T_c)$$

or

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

$$\frac{dT}{dt} = -\frac{\Delta H_R}{\rho C_p} r - \frac{U A_c}{V \rho C_p} (T - T_c)$$

We can also obtain these expressions from the energy-balance equation for the **steady-state** PFTR by simply transforming  $dz/u \rightarrow dt$  with  $A/V$  replacing  $p_w/A_t$ . The solutions of these equations for the batch reactor *are mathematically identical* to those in the PFTR, although the physical interpretations are quite different.

## Assumptions

In deriving these equations we have made many assumptions to keep them simple. We have assumed *constant density* so that we can use concentration as the composition variable. We have also assumed that the parameters in these systems are independent of temperature and composition. Thus parameters such as  $\Delta H_R$ ,  $\rho C_p$ , and  $U$  are considered to be *constants*, even though we know they all depend at least weakly on temperature. To be exact, we would have to find the heat of reaction, heat capacity, and heat transfer coefficient as functions of temperature and composition, and for the **PFTR** insert them within the integrals we must solve for temperature and composition. However, in most situations these variations are small, and the equations written will give good approximations to actual performance.

In this chapter and in Chapter 6 we will usually solve these equations assuming a single first-order irreversible reaction,  $r = k(T)C_A$ . Other orders and multiple reactions could of course be considered, but the equations are much more difficult to solve mathematically, and the solutions are qualitatively the same. We will see that the solutions with these simple kinetics are sufficiently complicated that we do not want to consider more complicated kinetics and energy balances at the same time.

There are many interesting problems in which complex chemistry in nonisothermal reactors interact to produce complex and important behavior. As examples, the autocatalytic reaction,  $A \rightarrow B$ ,  $r = kC_A C_B$ , in a nonisothermal reactor can lead to some quite complicated properties, and polymerization and combustion processes in nonisothermal reactors must be considered very carefully in designing these reactors. These are the subjects of Chapters 10 and 11.

## EQUATIONS TO BE SOLVED

For the nonisothermal reactors we need to solve the mass- and energy-balance equations *simultaneously*.

### CSTR

For a single reaction in a steady-state CSTR the mass-balance equation on reactant  $A$  and temperature  $T$  give the equations

$$C_{A0} - C_A = \tau r(C_A, T)$$

and



$$T - T_0 = \tau \frac{-\Delta H_R}{\rho C_p} r(C_A, T) - \frac{U A_c}{v \rho C_p} (T - T_c)$$

These are two coupled algebraic equations, which must be solved simultaneously to determine the solutions  $C_j(\tau)$  and  $T(t)$ . For multiple reactions the  $R + 1$  equations are easily written down, as are the differential equations for the transient situation. However, for these situations the solutions are considerably more difficult to find. We will in fact consider the solutions of the transient CSTR equations in Chapter 6 to describe phase-plane trajectories and the stability of solutions in the nonisothermal CSTR.

## PFTR

For a single reaction in a steady-state **PFTR** the mass-balance equations on species  $A$  and the temperature are

$$u \frac{dC_A}{dz} = -r(C_A, T)$$

and

$$u \frac{dT}{dz} = \frac{-\Delta H}{\rho C_p} r(C_A, T) - \frac{U p_w}{\rho C_p A_t} (T - T_c)$$

These are first-order ordinary differential equations that have two initial conditions at the inlet to the reactor,

$$C_A = C_{A0} \quad \text{and} \quad T = T_0 \quad \text{at } z = 0$$

We have to solve these two equations simultaneously to find  $C_A(z)$  and  $T(z)$  versus position  $z$  or at the exit  $L$  of the reactor,  $C_A(L)$  and  $T(L)$ .

These are two simultaneous differential equations with two initial conditions for a single reaction. For  $R$  simultaneous reactions we have to solve  $R + 1$  simultaneous differential equations with  $R + 1$  initial equations because there are  $R$  independent mass-balance equations and one temperature equation.

These equations look innocuous, but they are highly nonlinear equations whose solution is almost always obtainable only numerically. The nonlinear terms are in the rate  $r(C_A, T)$ , which contains polynomials in  $C_A$ , and especially the very nonlinear temperature dependence of the rate coefficient  $k(T)$ . For first-order kinetics this is

$$r(C_A, T) = k_0 e^{-E/RT} C_A$$

and it is the factor  $e^{-E/RT}$  that is most nonlinear and creates the most interesting mathematical and physical complexities in the nonisothermal reactor.

We will find that the solutions of the algebraic equations (CSTR) or differential equations (PFTR) can be very complicated. However, we must examine these solutions in some detail because they reveal some of the most important features of chemical reactors.

For a single reaction in the CSTR we solve two algebraic equations

$$F_1(C_A, T) = 0$$

$$F_2(C_A, T) = 0$$

which are generally polynomials in  $C_A$  and exponentials in  $T$ . While algebraic equations are generally simpler to solve than differential equations, these algebraic equations sometimes yield multiple roots, which indicate *multiple steady states* in CSTRs. This will be the subject of the next chapter.

In this chapter we consider mainly the plug-flow reactor. For the PFTR we solve the equations

$$\frac{dC_A}{dz} = F_1(C_A, T)$$

$$\frac{dT}{dz} = F_2(C_A, T)$$

along with the inlet condition

$$C_A = C_{A0}, \quad T = T_0, \quad \text{at } z=0$$

Since  $dC_A/dz$  and  $dT/dz$  are the slopes of the functions  $C_A(z)$  and  $T(z)$ , they must be unique at  $z = 0$  and at all  $z$ . Therefore, in contrast to the CSTR, the PFTR can exhibit only a single steady state.

## HEAT REMOVAL OR ADDITION TO MAINTAIN A REACTOR ISOTHERMAL

One of the first considerations in a reactor is the heat load that is necessary to control the temperature. It was implicit in all the previous chapters on isothermal reactors that the reactor was somehow thermostatted to maintain its temperature at that specified. For this case we did not have to solve the energy-balance equation, but we do need to consider the heat load

$$\dot{Q} = UA_c(T - T_c)$$

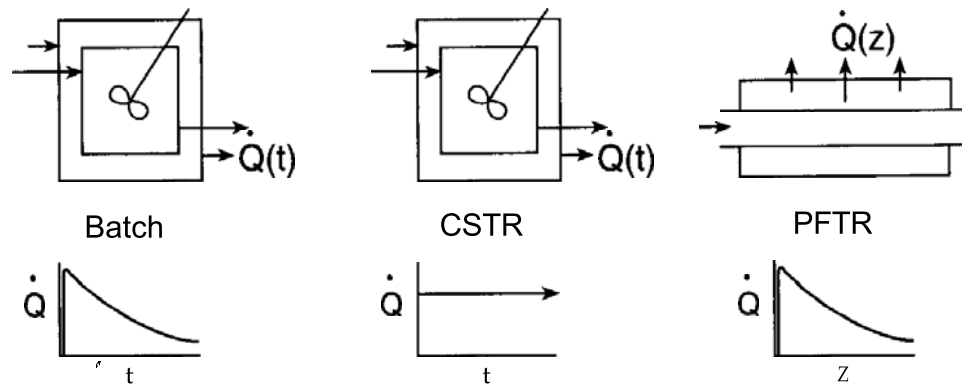
to maintain the reactor temperature at  $T$ .

**Example 5-1** Consider the reaction  $A \rightarrow B$ ,  $r = kC_A$ ,  $k_{300} = 0.05 \text{ min}^{-1}$ ,  $\Delta H_R = -20 \text{ kcal/mole}$  in a 10 liter reactor with  $C_{A0} = 2 \text{ moles/liter}$  and  $T_0 = 300 \text{ K}$ . At what rate must heat be removed to maintain the reactor isothermal at 300 K for (a) a batch reactor at 90% conversion?

This is an isothermal reactor with  $r = 0.05C_A$ . If batch, then

$$C_A = C_{A0}e^{-kt}$$

$$\begin{aligned} \dot{Q}(t) &= V(-\Delta H_R)kC_A(t) \\ &= V(-\Delta H_R)kC_{A0}e^{-kt} \end{aligned}$$



**Figure 53** Plot of reactor configurations and  $\dot{Q}$  necessary to maintain a batch reactor, CSTR, and PFTR isothermal.

$$\begin{aligned}
 &= 10 \times 20 \times 0.05 \times 2 \times e^{-0.05t} \\
 &= 20 e^{-0.05t} \text{ kcal/min}
 \end{aligned}$$

(b) a CSTR at 90% conversion?

In a CSTR

$$\begin{aligned}
 \dot{Q}(\tau) &= V(-\Delta H_R k C_A) \\
 &= 10 \times 20 \times 0.05 \times 0.2 = 2 \text{ kcal/min (constant)}
 \end{aligned}$$

(c) a PFTR at 90% conversion?

In a PFTR the answer is identical to that in a batch reactor except that  $t$  is replaced by  $\tau$ ,

$$\dot{Q}(z) = 20 e^{-0.05z/u} \text{ kcal/min}$$

Note, however, that the significance of heat removal or addition ( $Q$  positive or negative) is quite different with the batch reactor, requiring a heat removal that varies in time, the CSTR requiring a constant heat removal rate, and the PFTR requiring a heat removal rate that varies with position  $z$  in the reactor. These are sketched in Figure 5-3.

If this reaction were endothermic, we would have opposite signs to those shown in the previous example, because we would have to add heat to the reactor to maintain the process isothermal rather than cool it.

Note that the batch reactor requires *programming*  $Q(t)$ , and the PFTR requires either a very high  $UA$ , [to remain at  $T(z)$ ] or programming  $\dot{Q}(z)$ . The CSTR operates with a fixed  $\dot{Q}$  because  $T$  is uniform throughout the reactor for given conditions, and for steady-state operation  $\dot{Q}$  is independent of time. Therefore, the CSTR is usually much simpler to design for stable heat removal. This is another attractive feature of the CSTR: It is much easier to

maintain constant temperature in a CSTR reactor than in a batch or **PFTR** because the heat load required is not a function of either time or position in the reactor. We will see later that the CSTR has even higher heat transfer characteristics when we consider that stirring increases convective heat transfer so that  $U$  is frequently higher in a CSTR.

We still must use a PFTR in many chemical processes, and we must then determine how to program the cooling or heating to attain a temperature profile in the reactor close to that desired. The subject of this chapter is the proper temperature management to attain desired operation of a PFTR. In the next chapter the nonisothermal CSTR will be considered specifically.

## ADIABATIC REACTORS

The mass- and energy-balance equations must be solved numerically in the general situation where heat is transferred to or from walls. There are three terms on the right side of the energy equation, heat flow with reactants and products, reaction heat, and heat transfer through walls. However, the adiabatic reactor is a special case where we need to solve only one equation for a single reaction.

The adiabatic reactor is also an important limiting case of real reactors. As we have noted previously, the isothermal reactor (previous chapters) is a limiting case where the energy equation can be ignored. This situation occurs in practice whenever heat transfer

$$\dot{Q} = UA_c(T - T_c)$$

is so large that the reactor temperature  $T$  is maintained isothermal at  $T = T_c$ .

The other limit of real reactors is where the heat removal term is not infinite but instead is negligible. We call case where  $\dot{Q} = 0$  the *adiabatic reactor*. For wall cooling,  $A$ , is proportional to  $V^{1/2}$  for a tube and to  $V^{2/3}$  for a spherical reactor. Since heat generation is proportional to  $V$  and cooling is proportional to  $A$ , cooling becomes more difficult to maintain as the reactor becomes larger, and, as noted, large reactors frequently must be operated adiabatically.

Another reason why calculations of the adiabatic reactor is important is for safety. Suppose we have a reactor operating in a stable fashion with cooling. What happens if the cooling is suddenly stopped? The limit of this situation is the adiabatic reactor, and the engineer must always be aware of this mode because it is the worst-case scenario of any exothermic reactor. Note that if  $\Delta H_R > 0$ , we must supply heat to maintain the reactor temperature, and loss of heat will cause the reactor to cool down and the rate will decrease safely.

### Adiabatic CSTR

Here the mass- and energy-balance equations are

$$C_{A0} - C_A = \tau r(C_A, T)$$

$$T - T_0 = \tau \left( \frac{-\Delta H}{\rho C_p} \right) r(C_A, T)$$

We still have the  $r(C_A, T)$  factors in both terms, but note that they are identical in both energy- and mass-balance equations. Therefore,  $r(C_A, T)$  may be eliminated between them by dividing the second equation by the first to yield

$$T - T_0 = \tau \frac{-\Delta H_R}{\rho C_p} r = \left( \frac{-\Delta H_R}{\rho C_p} \right) (C_{A0} - C_A) = \left( \frac{-\Delta H_R}{\rho C_p} \right) C_{A0} X$$

or

$$T - T_0 = - \left( \frac{-\Delta H_R}{\rho C_p} \right) \Delta C_A$$

Note the sign on terms in these equations.  $T$  increases as a reaction proceeds ( $C_A$  decreases) if  $\Delta H_R$  is negative (reaction exothermic), as we know it must be since reaction is then *generating* heat. For an endothermic reaction  $T$  decreases as a reaction proceeds.

To simplify the appearance of these equations, we will find it convenient to define a new variable

$$J = \frac{-\Delta H_R C_{A0}}{\rho C_p}$$

so that the previous equation becomes

$$T - T_0 = JX$$

This has exactly the same significance as the preceding equation, but the constants are grouped in  $J$ , which has the units of temperature and will be positive if the reaction is exothermic.

## Adiabatic PFTR

Here the equations are

$$u \frac{dC_A}{dz} = -r(C_A, T)$$

$$u \frac{dT}{dz} = \left( \frac{-\Delta H_R}{\rho C_p} \right) r(C_A, T)$$

The right-hand sides both contain  $r$ ; so we can divide the first equation by the second to yield

$$\frac{dT}{dC_A} = - \left( \frac{-\Delta H_R}{\rho C_p} \right)$$

The right-hand side is constant (assuming  $\Delta H_R$  and  $\rho C_p$  are independent of  $T$  and composition); so we can integrate this single differential equation between  $T = T_0$  and  $C_A = C_{A0}$  at  $z = 0$  to  $T$  and  $C_A$  at position  $z$ . This gives

$$T - T_0 = \left( \frac{-\Delta H_R}{\rho C_p} \right) (C_{A0} - C_A) = \left( \frac{-\Delta H_R}{\rho C_p} \right) C_{A0} X = JX$$

which is an identical expression as we obtained for the adiabatic CSTR.

We can generalize this for any reactor since we assumed nothing about  $r(C_A, T)$ . The preceding relation is true for any single reaction in any adiabatic reactor, no matter what the kinetics or reactor flow pattern. This simple relation between  $C_A$  or  $X$  versus  $T$  is plotted in Figure 5-4.

**Example 5-2** Find  $C_{A0} - C_A$  versus  $T$  for a reaction with  $\Delta H_R = -20$  kcal/mole,  $\rho C_p = 1000$  cal/liter K,  $T_0 = 300$  K, and  $C_{A0} = 4$  moles/liter in an adiabatic reactor. What is the temperature if the reaction goes to completion?

The previous equation

$$T - T_0 = \left( \frac{-\Delta H_R}{\rho C_p} \right) (C_{A0} - C_A)$$

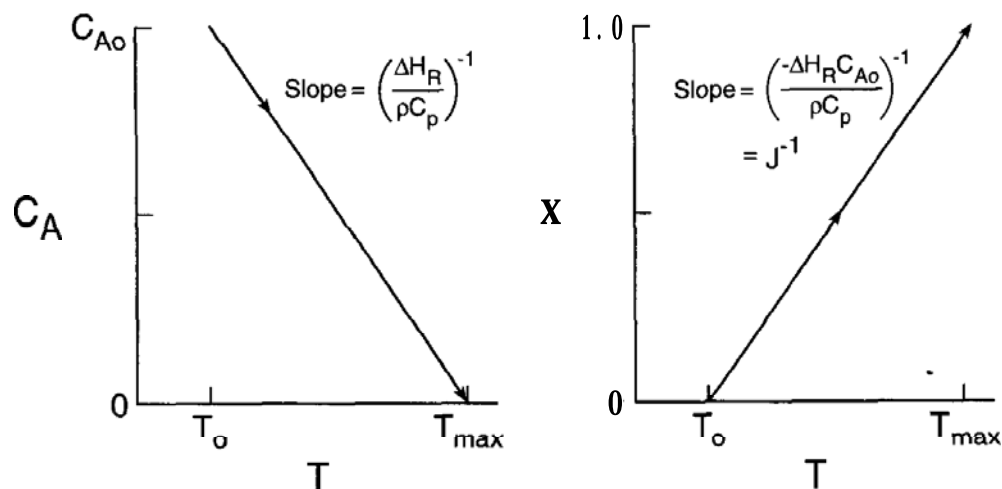
becomes

$$\begin{aligned} T &= 300 + \frac{20000}{1000} (4 - C_A) = 300 + 80 - 20C_A \\ &= 380 - 20C_A \end{aligned}$$

Thus  $T$  is 300 K initially and 380 K if the reaction goes to completion, and this would be true in *any* adiabatic reactor.

This reaction is in aqueous solution. Why might bad things happen if this reactor were operated with  $C_{A0} = 5$  moles/liter?

Throughout this chapter (and throughout this book) we will make the frequently unstated assumption that  $\Delta H_R$  and  $\rho C_p$  are independent of temperature and composition. They are of course dependent on  $T$  because  $C_p$  of each species depends on  $T$ . Each species



**Figure 5-4**  $C_A$  and  $X$  versus  $T$  for an exothermic adiabatic reactor with a single reaction with constant  $-\Delta H_R / \rho C_p$ .

of course has a different heat capacity, but we will unless stated otherwise assume that these can be ignored. The actual value of  $\Delta H_R$  is computed through the relation

$$\Delta H_R = \Delta H_{R, 298} + \int_{298}^T \sum_j \nu_j C_{p,j} dT$$

where  $\Delta H_{R, 298}^\circ$  is the heat of reaction in standard state at 298 K, and  $C_{p,j}$  is usually written as a polynomial in  $T$ . It is frequently a good approximation to assume that  $\Delta H_R = \Delta H_{R, 298}^\circ$ , which is equivalent to having all heat capacities constant. We also assume that the average heat capacity of the fluids is independent of composition, especially when reactants are diluted with solvent. The mathematics becomes more complex if we have to include these factors, although the principles remain the same.

## Multiple reactions

For multiple reactions similar arguments hold. For multiple reactions in the CSTR in which  $A$  is a reactant ( $\nu_A = -1$ ) in all reactions, we can write

$$C_{A0} - C_A = C_{A0} \sum_{i=1}^R X_i = \tau \sum_{i=1}^R r_i$$

$$\rho C_p (T - T_0) = \tau \sum_{i=1}^R (-\Delta H_{Ri}) r_i$$

Therefore, division of the second equation by the first equation yields

$$T - T_0 = \sum_{i=1}^R \frac{-\Delta H_{Ri}}{\rho C_p} C_{A0} X_i$$

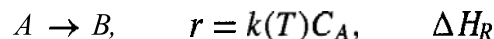
In these expressions we have defined the total conversion of  $A$  as a summation of its conversion in all reactions,

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} = \sum_{i=1}^R X_i$$

Only if  $A$  is a reactant in all reactions ( $\nu_{iA} = -1$ ) can this simple relation be written in terms of  $X_i$ . In the previous chapter we also used conversion to describe a reactant *species* such as  $X_A$ , but this definition of  $X_i$  refers to the conversion of the  $i$ th reaction.

## Solutions

For the adiabatic reactor we have a unique relation between  $T$  and conversion. We can therefore solve for  $T$  and eliminate it from the mass-balance equation. For the CSTR the mass-balance equation for a single first-order irreversible reaction



is

$$C_{A0} - C_A = \tau r(C_A, T) = \tau k(T)C_A$$

We can eliminate  $T$  in  $k(T)$  to obtain

$$C_{A0} - C_A = \tau k_0 C_A \exp \left( -\frac{E}{R[T_0 - (\Delta H_R / \rho C_p)(C_{A0} - C_A)]} \right)$$

This is a *single equation* in  $C_A$  and  $\tau$ . It is not easy to solve explicitly for  $C_A(\tau)$ , but it can easily be solved for  $\tau(C_A)$ ,

$$\tau = \frac{C_{A0} - C_A}{k(T)C_A} = \left[ (C_{A0} - C_A) / C_A k_0 \exp \left( -\frac{E}{R[T_0 - (\Delta H_R / \rho C_p)(C_{A0} - C_A)]} \right) \right]$$

Therefore, this problem can be solved simply by determining values of  $\tau$  versus values of  $C_A$  for specified values of constants.

In the adiabatic PFTR the differential equation is

$$\frac{dC_A}{d\tau} = -C_A k_0 \exp \left( -\frac{E}{R[T_0 - (\Delta H_R / \rho C_p)(C_{A0} - C_A)]} \right)$$

which can be separated and integrated to yield

$$\tau = - \int_{C_{A0}}^{C_A} \frac{dC_A}{k(T)C_A} = - \int_{C_{A0}}^{C_A} dC_A / \left[ C_A k_0 \exp \left( \frac{-E}{R[T_0 - (\Delta H_R / \rho C_p)(C_{A0} - C_A)]} \right) \right]$$

This expression must be solved numerically, but it is a single integral expression, which can be integrated directly rather than two simultaneous differential equations.

**Example 5-3** Plot  $C_A(\tau)$  and  $T(\tau)$  for the reaction  $A \rightarrow B$ ,  $r = k(T) C_A$  in an adiabatic PFTR for  $E = 30$  kcal/mole,  $k_0 = 2.6 \times 10^{20} \text{ min}^{-1}$ ,  $\Delta H_R = -20$  kcal/mole,  $\rho C_p = 1000$  cal/liter K,  $T_0 = 300$  K, and  $C_{A0} = 2$  moles/liter.

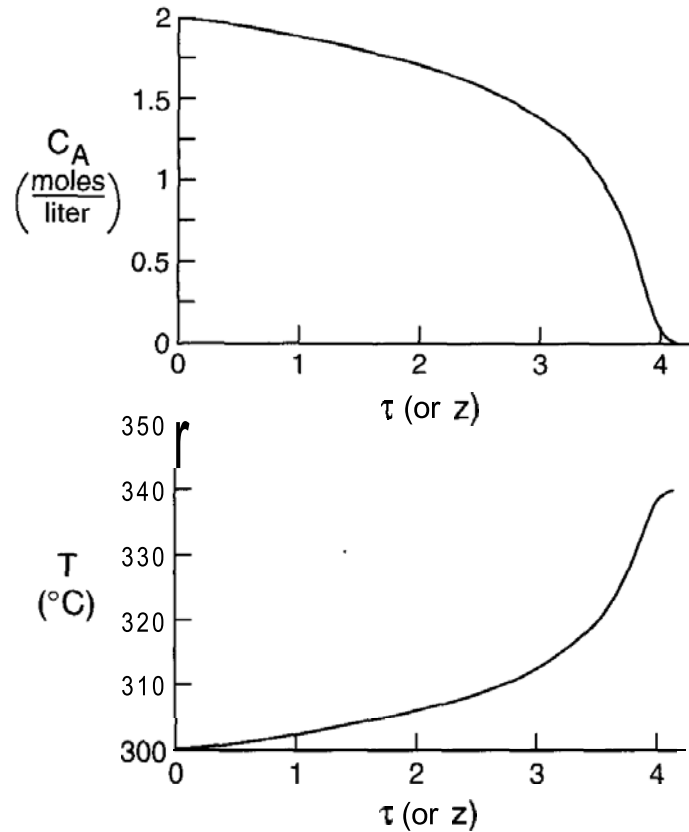
This is the same reaction we used in the previous example, because  $k = 0.05 \text{ min}^{-1}$  at 300 K, but now the temperature varies. The preceding equation becomes

$$\begin{aligned} \tau &= - \int_{C_{A0}}^{C_A} \frac{dC_A}{k(T)C_A} \\ &= - \int_2^{C_A} \frac{dC_A}{C_A \times 2.6 \times 10^{20} \exp\{(-15000)/[300 - 20(2 - C_A)]\}} \end{aligned}$$

We **can** easily integrate this equation numerically to find the solutions for the PFTR. We can also solve the algebraic equation for the CSTR. We will solve this problem numerically using a spreadsheet in the next example, but in Figure 5-5 we just plot the solutions  $X(r)$  and  $T(t)$ .



**Figure 5-5**  $C_A$  and  $T$  versus  $\tau$  or  $z$  in an adiabatic PFTR. The time is in minutes.



It is interesting to compare  $C_A(\tau)$  for the adiabatic reactor with the solution for the reactor maintained isothermal at 300 K. For the isothermal PFTR, the solution is

$$\tau = \frac{1}{k} \ln \frac{C_{A0}}{C_A} = \frac{1}{0.05} \ln \frac{2}{C_A}$$

or

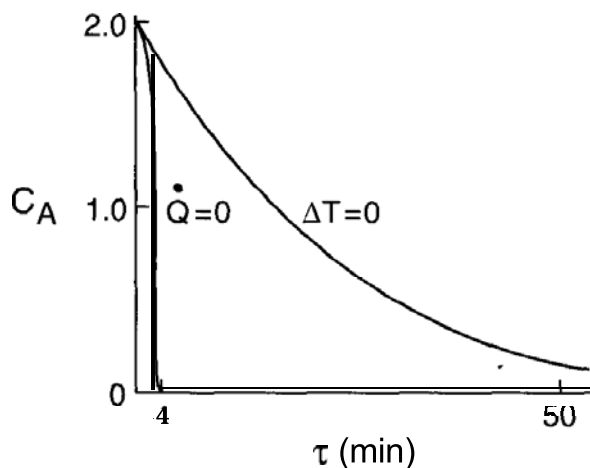
$$C_A(\tau) = 2e^{-0.05\tau}$$

These solutions  $C_A(\tau)$  are plotted in Figure 5-6. Several features of these curves are worth noting. First, the adiabatic reactor requires a much shorter  $\tau$  to attain complete conversion than does the isothermal reactor. Second, the shapes of the curves are quite different, with the isothermal reactor exhibiting the standard exponential decay but the adiabatic reactor exhibiting an *acceleration* in rate as the reaction proceeds because the temperature increases.

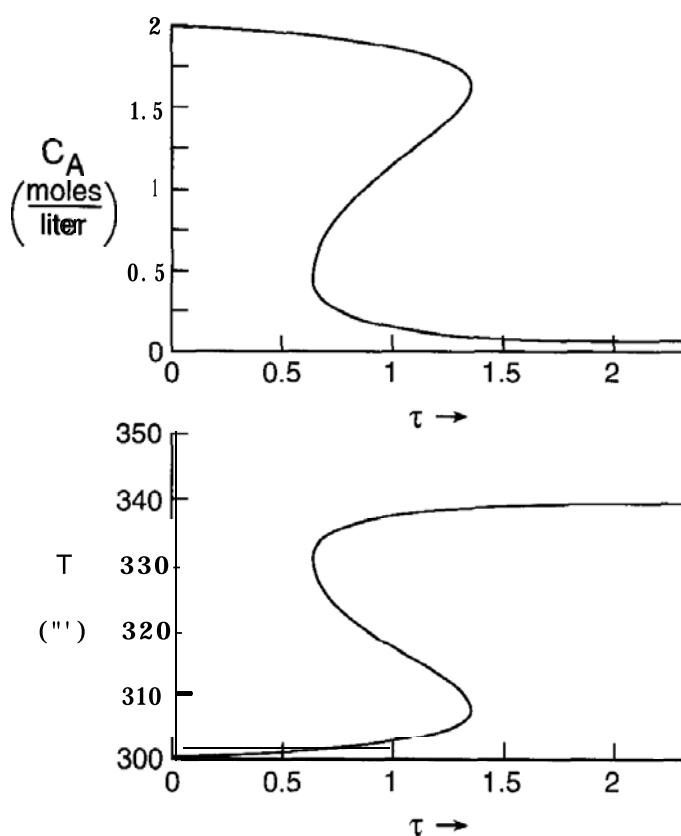
For the adiabatic CSTR we have to solve the equation

$$\begin{aligned} \tau &= \frac{C_{A0} - C_A}{k(T)C_A} = (C_{A0} - C_A) / \left[ k_0 C_A \exp \left( -\frac{E}{R[T_0 - (\Delta H_R / \rho C_p)(C_{A0} - C_A)]} \right) \right] \\ &= \frac{2.0 - C_A}{C_A \times 2.6 \times 10^{20} \exp \left\{ -\frac{15000}{300 - 20(2 - C_A)} \right\}} \end{aligned}$$

This is also plotted in Figure 5-7.



**Figure 5-6**  $C_A$  versus  $\tau$  or  $z$  in an isothermal PFTR maintained at 300 K and in an adiabatic PFTR starting at  $T_0 = 300$  K.



**Figure 5-7**  $C_A$  and  $T$  versus  $\tau$  in an adiabatic CSTR. The unusual shapes of these curves will require considerable examination in this Chapter and in Chapter 6. Residence time is in minutes.

Note several features of these solutions. First the  $C_A(\tau)$  and  $T(\tau)$  solutions have *identical shapes* (but  $T$  increases as  $C_A$  decreases for the exothermic reaction) for the adiabatic reaction in these reactors or in any adiabatic reactor. If we plot  $C_{A0} - C_A$  versus  $T$  from these solutions we obtain Figure 5-8, because, by the previous arguments, this must be a straight line for any single reaction in any reactor as long as parameters do not depend on temperature or composition. Second, note that the CSTR in this example requires a *shorter residence time* for a given conversion than a PFTR. Third, note that the CSTR exhibits *multiple values* of  $C_A$  and  $T$  for a range of  $\tau$ . This situation is physically real and will be the subject of the next chapter.

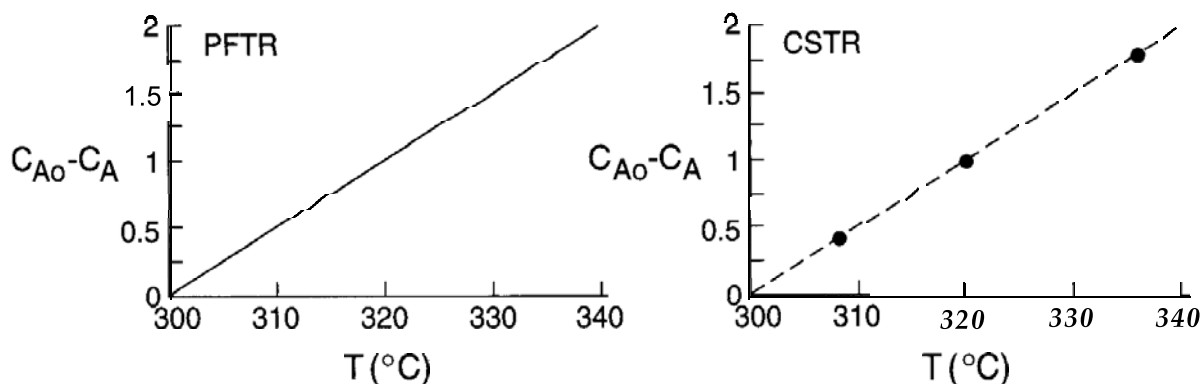


Figure 5-8 Plot of  $C_{A0} - C_A$  versus reactor temperature  $T$  for the adiabatic reactors of Figure 5-7. For the CSTR the points indicate the steady states for  $\tau = 1.0$  min.

While the straight-line graphs of the adiabatic trajectories in the  $X$ - $T$  plane appear similar for CSTR and PFTR (but they are different curves), their significance is quite different. For the PFTR the graphs can be thought of as plots of concentration and temperature versus position in the reactor, while in the CSTR  $\tau = V/v$  is the residence time for a particular set of feed conditions. In the CSTR the solutions  $C_A(\tau)$  and  $T(t)$  are the *locus of solutions* versus residence time. This difference has great significance for the CSTR, and, as we will see, it suggests that sometimes states on these curves are not accessible but are in fact *unstable*.

## Other reactions

We have used the first-order irreversible reaction as an example, but this is easy to generalize for any reaction, irreversible or reversible, with any kinetics. In a PFTR the mass-balance equation for an arbitrary reaction becomes

$$\tau = \int_{C_{A0}}^{C_A} \frac{dC_A}{r(C_A, T)} = \int_{C_{A0}}^{C_A} \frac{dC_A}{r_{ad}(C_A)}$$

where we define  $r_{ad}(C_A)$  as the rate versus  $C_A$  with the temperature varying as the conversion changes.

## The $1/r$ plot

Let us return to the graphical construction we developed in earlier chapters for isothermal reactors, because for nonisothermal reactors  $\tau$  is still the area under curves of plots of  $1/r$  versus  $C_{A0} - C_A$ . For the first-order irreversible reaction in an adiabatic reactor  $1/r_{ad}$  is given by

$$\frac{1}{r_{ad}(C_A)} = \frac{1}{C_A k_0 \exp\{-E/R[T_0 + (-\Delta H/\rho C_p)(C_{A0} - C_A)]\}}$$

**Example 5-4** For the irreversible first-order reaction with parameters in the previous example, calculate  $\tau$  in adiabatic PFTR and CSTR from a table of  $1/r$  versus  $C_A$ .

We compute  $1/r$  versus  $C_{A0} - C_A$  from the equation

$$\frac{1}{r_{ad}(C_A)} = \frac{1}{C_A k_0 \exp\{-E/R[T_0 + (-\Delta H/\rho C_p)(C_{A0} - C_A)]\}}$$

$$= \frac{1}{C_A \times 2.6 \times 10^{20} \exp\{-15000/[300 + 80(2 - C_A)]\}}$$

We can calculate values of  $\tau$  using a simple spreadsheet as shown in Table 5-1. The previous figures of  $C_A$  and  $T$  versus  $\tau$  were obtained from the first and second columns of this spreadsheet for the  $\tau$ s in the last two columns, because from the previous equations, we see that

$$\tau_{PFTR} = \int_{C_{A0}}^{C_A} \frac{dC_A}{kC_A} = \sum \frac{\Delta C_A}{kC_A}$$

$$\tau_{CSTR} = \frac{C_{A0} - C_A}{k(T)C_A}$$

These values of  $1/r$  are plotted versus  $C_{A0} - C_A$  in Figure 5-9. The rectangles have areas indicated in Table 5-1. The sum of these areas is an approximation to the residence time in an adiabatic PFTR because

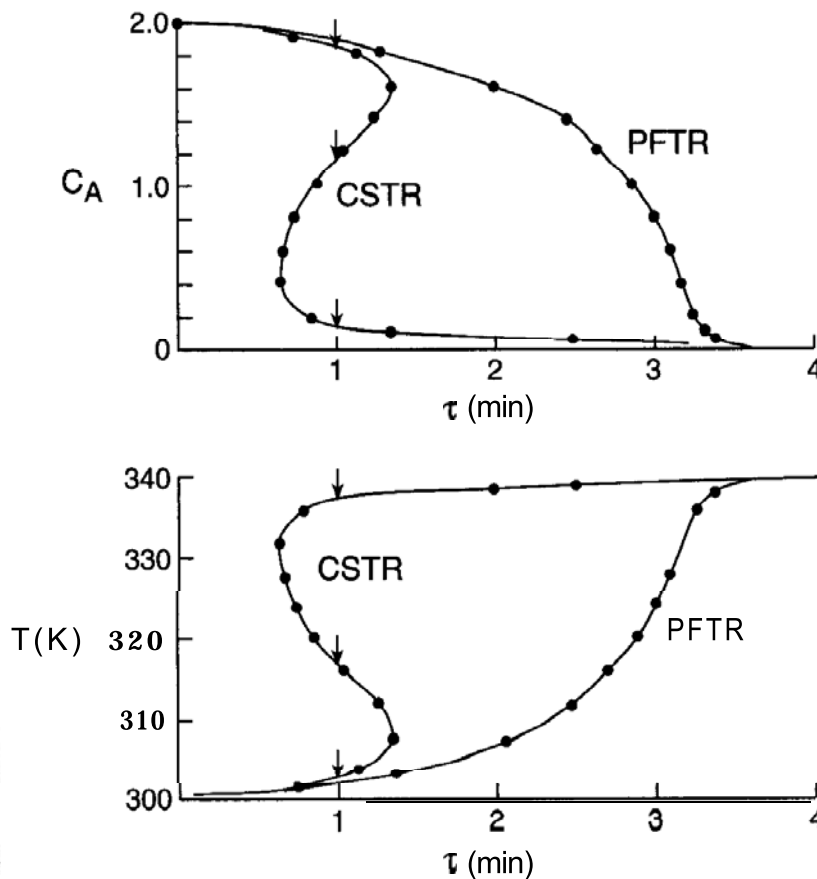
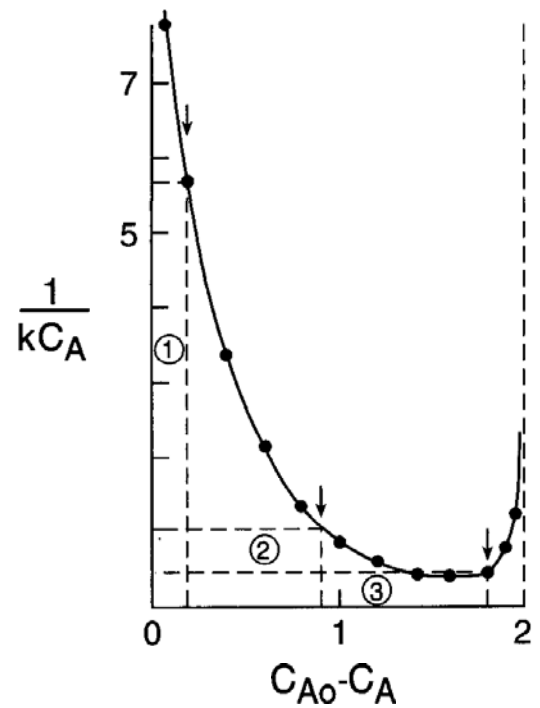
$$\tau_{PFTR} = \int_{C_{A0}}^{C_A} \frac{dC_A}{r_{ad}(C_A)} = \sum \frac{\Delta C_A}{kC_A}$$

The last two columns show  $\tau_{PFTR}$  and  $\tau_{CSTR}$ ; so one can simply read  $C_A(\tau)$  and  $T(t)$  from Table 5-1, and, since this is the same problem worked previously, the previous graphs can be plotted simply from this spreadsheet (see Figure 5-10).

**TABLE 5-1**  
Spreadsheet Solution for Adiabatic PFTR and CSTR

$C_A$	$T$	$k$	$\frac{r}{kC_A}$	$\frac{1/r}{1/kC_A}$	Area $\Delta C_A/kC_A$	$\sum \frac{\tau_{PFTR}}{\Delta C_A/kC_A}$	$\tau_{CSTR}$ $(C_{A0} - C_A)/kC_A$
2.0	300	0.05	0.1	10		—	—
1.8	304	0.097	0.174	5.14	1.15	1.15	1.15
1.6	308	0.184	0.294	3.40	0.680	1.83	1.36
1.4	312	0.343	0.480	2.08	0.416	2.24	1.25
1.2	316	0.630	0.757	1.32	0.264	2.51	1.06
1.0	320	1.14	1.14	0.876	0.175	2.68	0.876
0.8	324	2.04	1.63	0.614	0.123	2.81	0.737
0.6	328	3.58	2.15	0.465	0.093	2.90	0.651
0.4	332	6.21	2.48	0.402	0.080	2.98	0.64
0.2	336	10.6	2.13	0.470	0.094	3.07	0.84
0.0	340	18.0	0	$\infty$	$\infty$	co	co

**Figure 5-9** Plot of  $1/r$  versus  $C_{A0} - C_A$  for the previous example. It is seen that  $r$  increases and then decreases so that  $1/r$  has a strong minimum. The arrows indicate the three possible steady states in a CSTR for  $\tau = 1.0$  min (dashed rectangles).



**Figure 5-10** Residence times in a PFTR and CSTR for adiabatic reactors. The CSTR can require a much smaller  $\tau$  than the PFTR and can exhibit multiple steady states for some  $\tau$  (arrows).

## Euler's method solutions of differential equations

The  $1/r$  solution is in fact just an Euler's method approximation to the integral for the PFTR, in which one approximates the integral as a summation. The calculation is not very accurate because we used a 0.2 moles/liter step size to keep the spreadsheet small, but it illustrates the method and the identity between Euler's method and a spreadsheet solution.

Thus we see that for nonisothermal reactors this  $1/r$  versus  $C_{A0} - C_A$  curve is not always an increasing function of conversion as it was for isothermal reactors even with positive-order kinetics. Since the  $1/r$  curve can have a minimum for the nonisothermal reactor, we confirm the possibility that the CSTR requires a smaller volume than the PFTR for positive-order kinetics. This is true even before the multiple steady-state possibilities are accounted for, which we will discuss in the next chapter. This is evident from our  $1/r$  plot for the PFTR and CSTR and will occur whenever  $r$  has a sufficiently large maximum that the area under the rectangle is less than the area under the curve of  $1/r$  versus  $C_{A0} - C_A$ .

## Reversible reactions

The nonisothermal behavior of reversible reactions is especially interesting because the equilibrium composition is temperature dependent. Recalling our description of reversible reactions, we wrote for the rate expression

$$r = r_f - r_b = k(T) \prod_{j=1}^R C_j^{m_{fj}} - k'(T) \prod_{j=1}^R C_j^{m_{bj}}$$

and we noted that near equilibrium the reaction kinetics become elementary and that the rate coefficients are related to the equilibrium constant by

$$\frac{k(T)}{k'(T)} = \frac{k_0}{k'_0} e^{-(E-E')/RT} \equiv K_{eq}(T) = e^{-\Delta G_0/RT} = K_0 e^{-\Delta H/RT} = \prod C_j^{\nu_j}$$

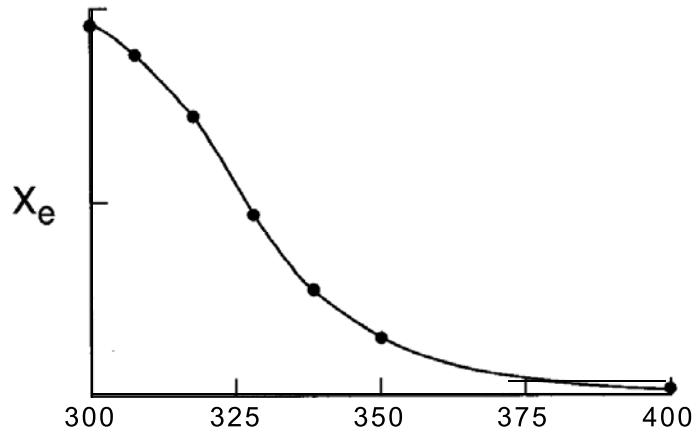
We will find it convenient to use  $X$  rather than  $C_A$  as the composition variable for a single reaction and consider  $C_{Ae}$  and  $X_e$  as the corresponding quantities at equilibrium. For an endothermic reaction  $\Delta H_R > 0$  and  $X_e$  increases with  $T$ , while for an exothermic reaction  $\Delta H_R < 0$  and  $X_e$  decreases with  $T$ .

Since our goal is frequently to attain a high conversion in a reactor, the relation of equilibrium to reactor temperature is obviously important.

**Example 5-5** A chemist obtained the kinetic data in the previous example. [Rumors are circulating that he started out in chemical engineering but failed thermodynamics and never had a course in reaction engineering.] He says that he made a slight mistake and the reaction is not quite irreversible but the equilibrium conversion is actually 0.95 at 300 K. He doesn't think this will be a serious error. Is he correct?

We need to calculate the rate versus temperature and the equilibrium conversion versus temperature. From the requirement that the rate must be consistent with equilibrium, we have

$$\Delta H_R = E - E' = -20 = 30 - 50$$



**Figure 5-11** Equilibrium conversion versus  $T$  for an exothermic reversible reaction in preceding example.

Therefore, since the conversion is given at 300 K, we can determine  $k'_0$  and the complete rate expression,

$$r = 2.6 \times 10^{21} \exp(-30,000/RT) C_{A0}(1 - X) \\ = 3.9 \times 10^{34} \exp(-50,000/RT) C_{A0}X$$

and the equilibrium conversion is given by the expression

$$K_{eq} = 6.7 \times 10^{-14} \exp(+20,000/RT) = \frac{X_e}{1 - X_e}$$

This gives equilibrium conversions in the table:

$T$ (K)	$K_{eq}$	$X_e$
300	19	0.95
310	6.8	0.87
320	2.5	0.71
330	0.97	0.49
340	0.40	0.29
350	0.17	0.15
400	0.005	0.005

These data are plotted in Figure 5-1 1. Thus we have a very serious problem if this reaction is reversible because the adiabatic reactor trajectory intersects the equilibrium curve at a low conversion. For these kinetics, equilibrium limits the process to a very low conversion at high temperatures.

## TRAJECTORIES AND PHASE-PLANE PLOTS

We need to examine the solutions of the reactor mass- and energy-balance equations, starting at  $C_{A0}$ ,  $X = 0$ ,  $T = T_0$  and proceeding (continuously in a PFTR and discontinuously in a CSTR) to  $C_A$ ,  $X$ , and  $T$  at  $\tau$ ,  $z$ , or  $L$ .

For this we will find it convenient to examine **trajectories** of  $C_A(\tau)$  or  $X(r)$  and  $T(t)$  in a **phase plane** of  $X$  versus  $T$ . Thus we do not examine explicitly the time or position dependences but instead examine the trajectory followed as the reaction proceeds.

We need to follow  $r(X, T)$ , and a convenient way to do this is to map out lines of constant  $r$  in the  $X$ - $T$  plane. At equilibrium  $r = 0$  and we have  $X_e(T)$ , which is a curve going from  $X = 0$  at low temperature to  $X_e = 1$  at high temperature for an endothermic reaction and  $X = 1$  at low  $T$  and  $X_e = 0$  at high  $T$  for an exothermic reaction.

We can plot lines of constant  $r$  for any single reaction, but for simplicity we consider  $A \rightarrow B$ ,

$$\begin{aligned} r(X, T) &= k_0 e^{-E/RT} C_A - k'_0 e^{-E'/RT} (C_{A0} - C_A) \\ &= k_0 e^{-E/RT} C_{A0} (1 - X) - k'_0 e^{-E'/RT} C_{A0} X \end{aligned}$$

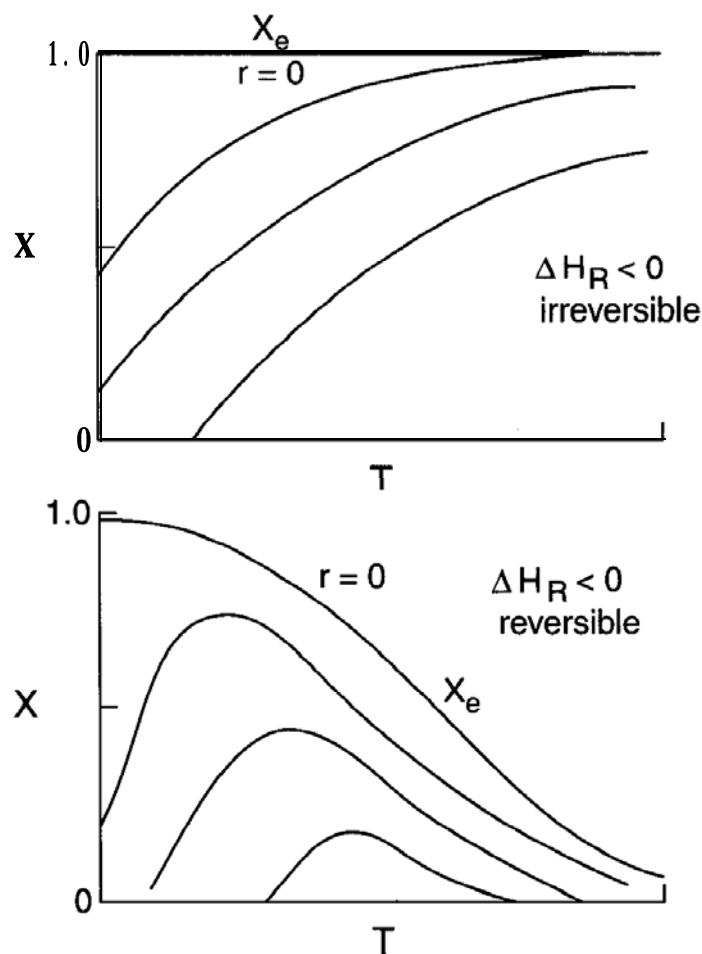
At  $r = 0$  this gives

$$K_{eq}(T) = \frac{[C_B]}{[C_A]} = \frac{X_e}{1 - X_e} = \frac{k_0}{k'_0} e^{-(E-E')/RT} = K_0 e^{-\Delta H/RT}$$

which can easily be plotted.

**Example 5-6** For the example discussed plot lines of constant  $r$  for  $r = 0, 1, 10, 100$  in the  $X(T)$  plane.

We have to solve these equations numerically, and the solutions are shown in Figure 5-12.



**Figure 5-12** Plots of lines of constant rate in the  $X$ - $T$  plane for an exothermic reversible reaction.



## TRAJECTORIES OF WALL-COOLED REACTORS

We next examine trajectories on these graphs. Two of these are simple straight lines: a vertical line at temperature  $T_c$  for the isothermal ( $UA \rightarrow \infty$ ) reactor and a straight line starting at  $T_o$  with slope  $(-C_{Ao}\Delta H/\rho C_p)^{-1}$  for the adiabatic reactor.

### Possible trajectories

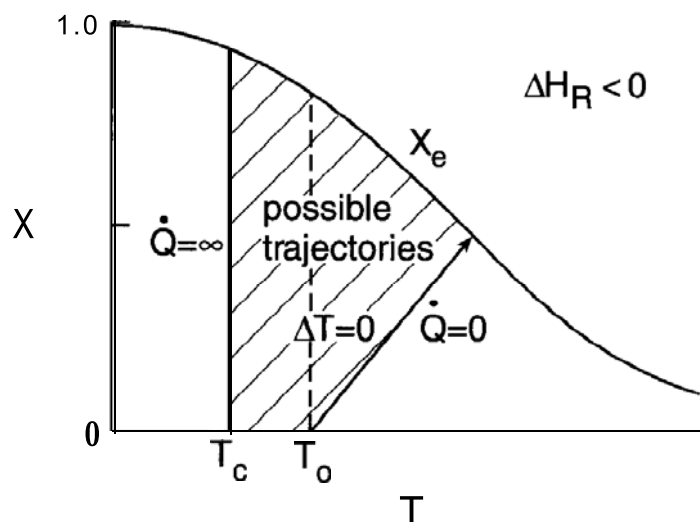
In Figure 5-13 are plotted the possible trajectories for the exothermic reaction. These are the limiting cases of the trajectory in a wall-cooled reactor, and any wall-cooled reactor will have a trajectory between these two straight lines. The trajectory cannot go above the equilibrium curve  $X_e(T)$ . For an adiabatic reactor the curve stops there, and for finite  $UA$ , the curve finishes at  $X_e$  at  $T_c$ .

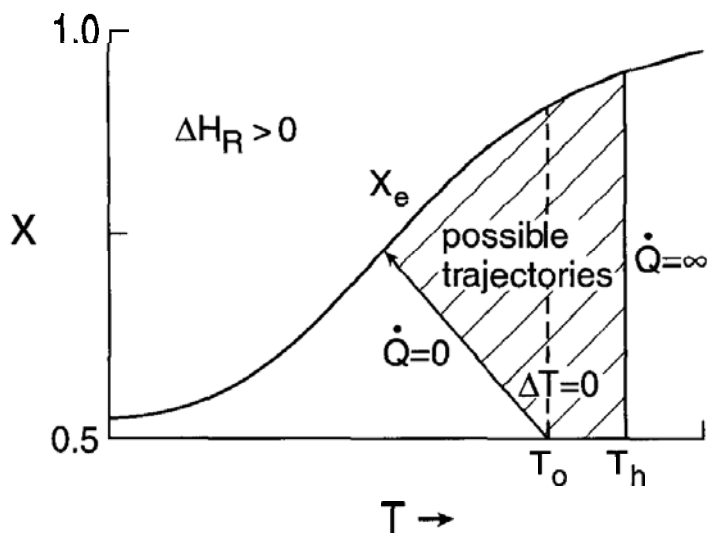
For an endothermic reaction we assume that the reactor is heated rather than cooled so that  $T_c > T_o$ . (We are now usually heating so we should write  $T_h$  rather than  $T_c$ .) Since  $\Delta H_R > 0$ , the slope of the adiabatic curve is also negative, and the equilibrium conversion is the reverse of that for the exothermic reaction. The corresponding regime of possible trajectories for an endothermic reaction is shown in Figure 5-14. This situation is generally uninteresting because we usually want to heat an endothermic reactor as hot as practical because the rate and the equilibrium conversion both increase with temperature (see Figure 5-15).

However, for exothermic reactions we see that we have a tradeoff between high initial rates at high temperature and high equilibrium conversion at low temperature. We therefore seek an optimum where the initial rate is sufficiently high to require a small size and the equilibrium conversion is acceptable. For an exothermic reaction in a tubular reactor there is therefore some optimum program of  $T_o$ ,  $T_c$ , and geometry for a given reactor with given kinetics and feed.

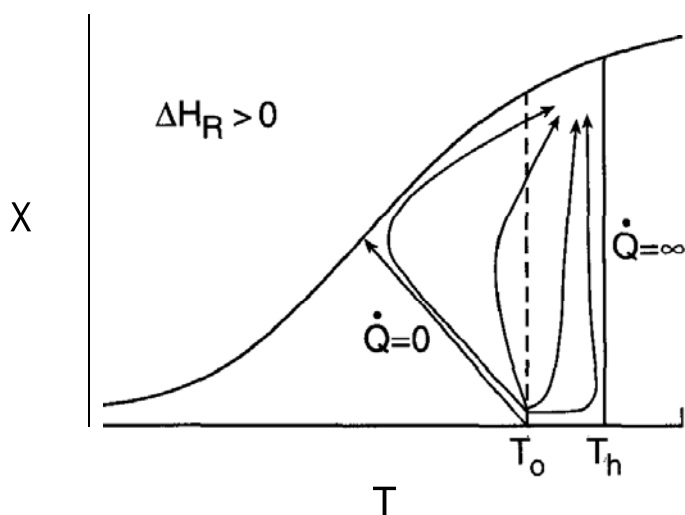
These arguments do not hold in a CSTR because the conversion and temperature jump discontinuously from  $X = 0$ ,  $T = T_o$  to  $X$ ,  $T$  in the reactor and at the exit. Trajectories are continuous curves for the PFTR but are only single points for the CSTR. We will examine this in more detail in the next chapter.

Figure 5-13 Possible region of trajectories for exothermic reversible reactions, starting at feed temperature  $T_o$  with cooling from the wall at temperature  $T_c$ . Trajectories must be in the shaded region between the adiabatic and isothermal curves and below the equilibrium curve.





**Figure 5-14** Possible region of trajectories for endothermic and for reversible reactions, starting at feed temperature  $T_0$  with heating from the wall at temperature  $T_h$ . Trajectories must be in the shaded region between the adiabatic and isothermal curves and below the equilibrium curve.



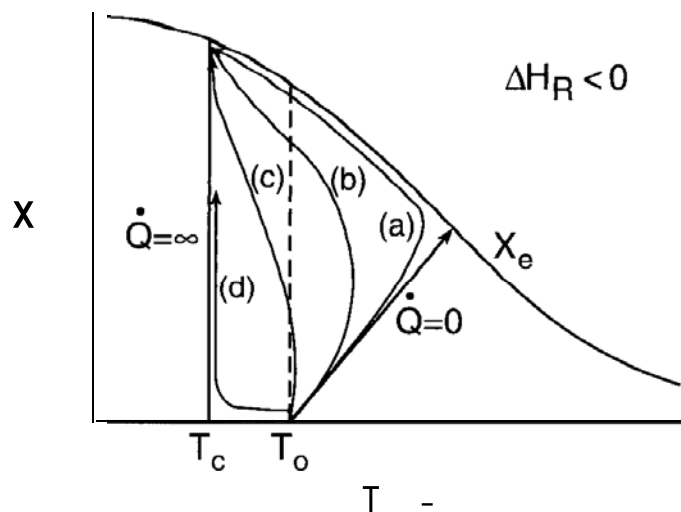
**Figure 5-15** Possible trajectories for different amounts of wall heating for an endothermic reversible reaction, starting at feed temperature  $T_0$  with heating from the wall at temperature  $T_h$ .

Finally we sketch the possible trajectories that might be followed in an exothermic reaction in a cooled reactor. The trajectory starts at the feed condition of  $C_A = C_{A0}$ ,  $X = 0$ ,  $T = T_0$ , and when  $\tau$  goes to infinity, the trajectory will end up at  $T_c$  at the equilibrium composition  $X_e$ . Sketched in Figure 5-16 are three trajectories.

We distinguish between four types of trajectories of these curves:

- Nearly adiabatic. If  $UA$  is small, then the reaction first follows the adiabatic trajectory up to  $X_e$  at the adiabatic temperature, and then it moves along the equilibrium curve out to  $T_c$ . This is not efficient because the rate will be very small near  $X_e$ .
- Optimal trajectory. If we choose  $UA$ , **optimally**, we initially trace the adiabatic curve (maximum  $T$  and therefore maximum rate) out to where the rate is a maximum. Then the temperature falls as conversion increases to finally wind up at  $X_e$  and  $T_c$ .
- Moderate cooling. Here the cooling is enough that the temperature does not increase strongly but rises nearly isothermally until the rate slows enough that the temperature cools back to  $T_c$  as  $X$  approaches 1.

**Figure 5-16** Possible trajectories for an exothermic reversible reaction, starting at feed temperature  $T_0$  with cooling from the wall at temperature  $T_c$ .



- (d) Strong cooling.
- (e) Nearly isothermal. If  $UA_c$  is large, then the reactants immediately cool down to  $T_c$  and the reaction proceeds up to  $X_e$  at temperature  $T_c$ . This curve gives a high conversion, but the rate should be slow because the temperature in the reactor is low.

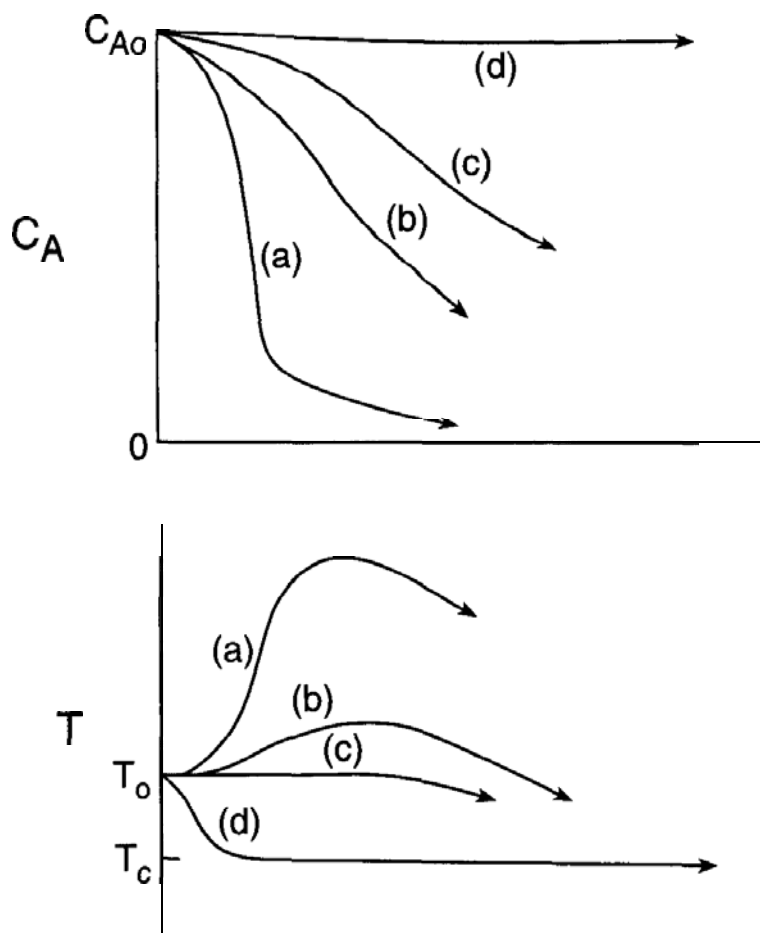
In designing a wall-cooled tubular reactor, we want to operate such that the trajectory stays near the maximum rate for all temperatures. Thus for an exothermic reversible reaction the temperature should increase initially while the conversion is low and decrease as the conversion increases to stay away from the equilibrium constraint. One can easily program a computer to compute conversion and  $T$  versus  $\tau$  to attain a desired conversion for minimum  $\tau$  in a PFTR. These curves are shown in Figure 5-17 for the three situations.

Another way of visualizing the optimal trajectory for the exothermic reversible reaction is to consider isothermal reaction rates at increasing temperatures. At  $T_1$  the equilibrium conversion is high but the rate is low, at  $T_2$  the rate is higher but the equilibrium conversion is lower, at  $T_3$  the rate has increased further and the equilibrium conversion is even lower, and at a high temperature  $T_4$  the initial rate is very high but the equilibrium conversion is very low.

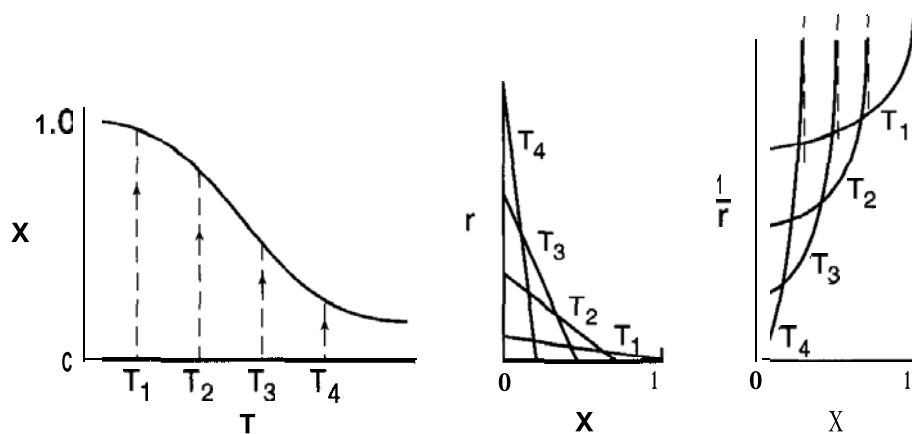
These four isothermal trajectories are shown in Figure 5-18, along with plots of  $r$  versus  $X$  and plots of  $l/r$  versus  $X$ . It is seen that the minimum residence time in such a reactor is one in which the temperature decreases to maintain the lowest  $l/r$  as the conversion increases from 0 to 1.

## EXOTHERMIC VERSUS ENDOTHERMIC REACTIONS

It is interesting to note that the exothermic reversible reaction  $A \rightleftharpoons B$  is *identical* to the same endothermic reversible reaction  $B \rightleftharpoons A$ . This can be seen by plotting  $X$  versus  $T$  and noting that the  $r = 0$  equilibrium line separates these two reactions. In the reaction  $A \rightleftharpoons B$  the rate in the upper portion where  $r < 0$  is exactly the reaction  $B \rightleftharpoons A$ . We defined all rates as *positive* quantities, but if we write the reaction as its reverse, both  $r$  and  $\Delta H_R$  reverse signs. This is plotted in Figure 5-19.



**Figure 5-17** Plots of  $C_A$  and  $T$  versus  $\bar{t}$  for an exothermic reversible reaction for situations sketched in the previous figure.



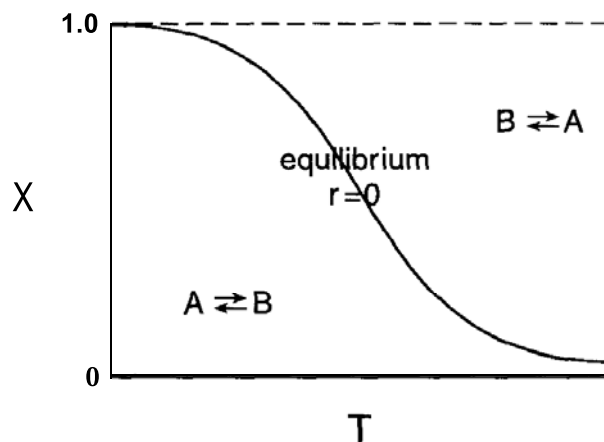
**Figure 5-18** Illustration of isothermal trajectories for an exothermic reversible reaction. At the lowest temperature the rate is low but the equilibrium conversion is high, while at the highest temperature the initial rate is high but the equilibrium conversion is low. From the  $1/r$  versus  $X$  plot at these temperatures, it is evident that  $T$  should decrease as  $X$  increases to require a minimum residence time.

## OTHER TUBULAR REACTOR CONFIGURATIONS

### Multiple reactors with interstage cooling

It is sometimes possible to overcome the problem of low  $X_e$  with adiabatic operation by using several adiabatic reactors with cooling between reactors. Thus one runs the first reactor

**Figure 5-19** Plot of  $X$  versus  $T$  for an exothermic reversible reaction  $A \rightleftharpoons B$ . The upper portion of this curve where  $r < 0$  can be regarded as the endothermic reversible reaction  $B \rightleftharpoons A$  if the sign of  $r$  is reversed or if  $X$  is replaced by  $1 - X$ .



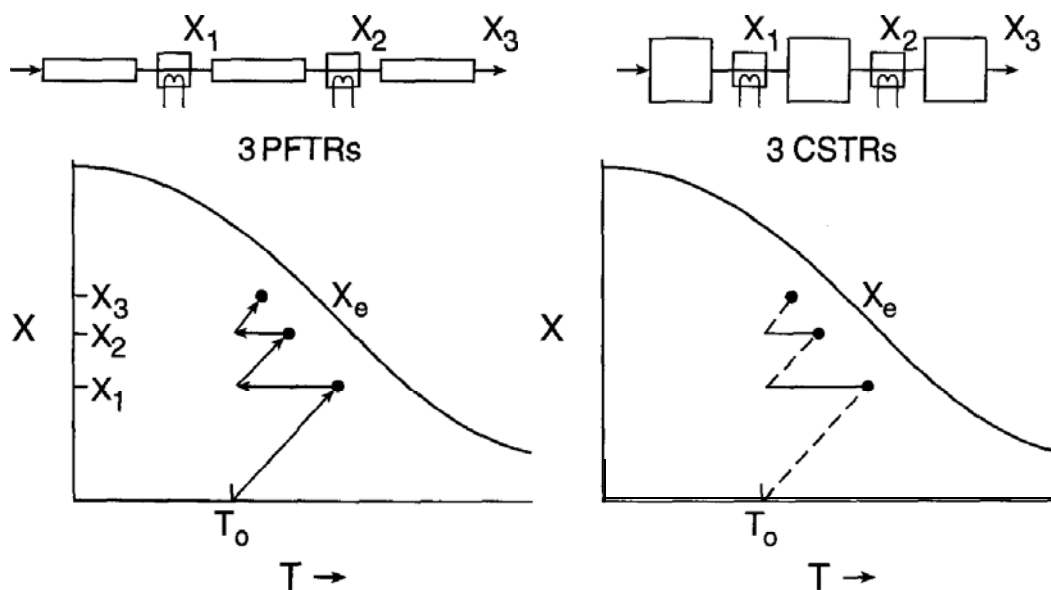
up to near the maximum rate, then cools and runs the second reactor up to near the maximum at that temperature, and continues through successive reactors and heat exchangers until a satisfactory conversion is attained.

The reactor configurations and possible trajectories for three adiabatic reactors with interstage cooling are shown in Figure 5-20.

There are several examples of exothermic reversible reactors where interstage cooling is practiced. One is methanol synthesis from syngas



As discussed in Chapter 3, this reaction is reversible at  $250^\circ\text{C}$ , where the commercial reactors are operated, and it is common practice to use interstage cooling and cold feed injection to attain high conversion and extract reaction heat. Another important reaction is the water-gas shift, used to prepare industrial  $\text{H}_2$  from syngas,

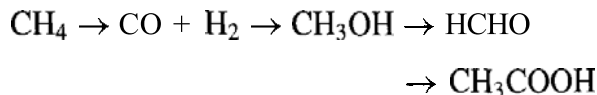


**Figure 5-20** Trajectories in the  $X$  versus  $T$  plane for three reactors in series with interstage cooling.



This process is typically run with two reactors, one at  $\sim 800^\circ\text{C}$ , where the rate of the reaction is high, and the second at  $\sim 250^\circ\text{C}$ , where the equilibrium conversion is higher.

We have discussed these reactions previously in connection with equilibrium limitations on reactions, and we will discuss them again in Chapter 7, because both use catalysts. These reactions are very important in petrochemicals, because they are used to prepare industrial  $\text{H}_2$  and CO as well as methanol, formaldehyde, and acetic acid. As noted previously, these processes can be written as

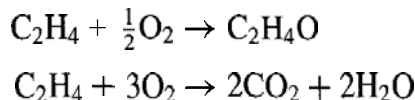


All steps except the first are exothermic, all reactions except HCHO synthesis are reversible, and all involve essentially one reaction. Energy management and equilibrium considerations are crucial in the design of these processes.

## Jacketed PFTR

The cooled TR is frequently operated with a cooling jacket surrounding the reactor in a tube-and-shell configuration. This looks simply like a tube-in-shell heat exchanger, typically with catalyst in the tube to catalyze the reaction.

A major example of this reactor is ethylene oxidation to ethylene oxide (EO)

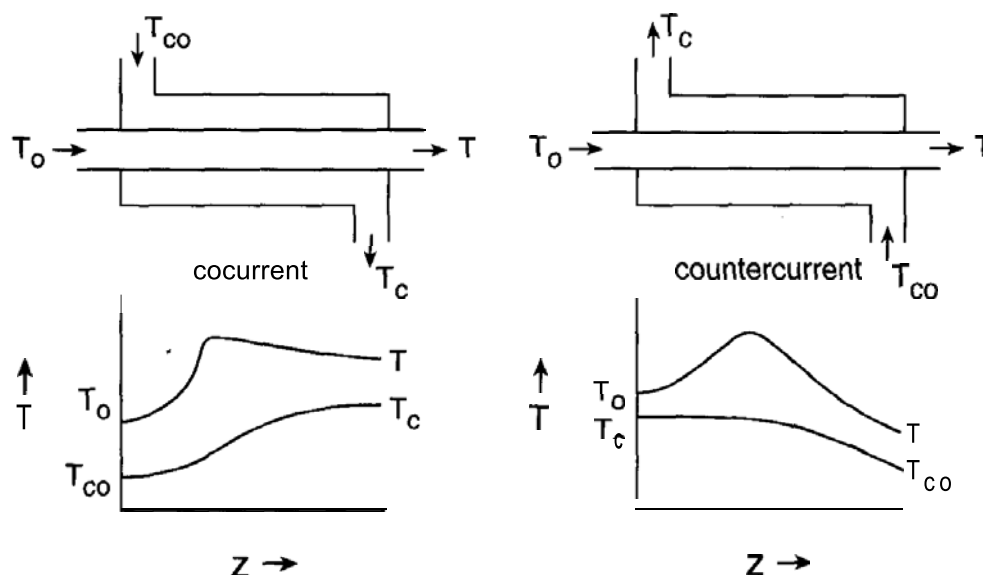


As noted in Chapter 2, the heat release in the second reaction is much greater, so that much more heat is released if the selectivity to EO decreases. For world-scale ethylene oxide plants the reaction is run in a reactor consisting of several thousand 1-in-diameter tubes -20 ft long in a tube-and-shell heat exchanger. Heat transfer is accomplished using boiling recirculating hydrocarbon on the shell side to absorb the reaction heat. This heat transfer method assures that the temperature of the tubes is constant at the boiling point of the fluid.

If the coolant flow rate is sufficiently high in a jacketed reactor or if boiling liquid is used as the heat transfer fluid, then  $T_c$  is constant, as we have assumed implicitly in the previous discussion.

However, with finite flow rate in the jacket, the coolant may heat up, and we must now distinguish between cocurrent and countercurrent flows. While it is true that countercurrent operation gives better heat transfer for an ordinary exchanger, this is not usually desired for a tubular reactor. Heat is generated mostly near the reactor entrance, and the maximum amount of cooling is needed there. In countercurrent flow, the coolant has been heated before it reaches this region, while in cocurrent operation, the coolant is the coldest exactly where the heat load is greatest. Thus cocurrent operation reduces the hot spot, which can plague cooled tubular reactors with exothermic reactions.

Illustrated in Figure 5-21 are possible temperatures of reactor and coolant versus position  $z$  for cocurrent and countercurrent operation.



**Figure 5-21** Temperature profiles for **cocurrent** and **countercurrent** cooled PFTR with feed temperature  $T_0$  and coolant feed temperature  $T_{co}$ .

A major goal in wall cooling is to spread out the hot zone and prevent very high peak temperatures. High peak temperatures cause poor reaction selectivity, cause carbon formation, deactivate catalysts, and cause corrosion problems in the reactor walls. **Cocurrent** flows spread out the hot zone and cause lower peak temperatures, but many additional design features must be considered in designing jacketed reactors.

Temperature profiles in jacketed reactors can be examined rather simply by writing the energy balance on the coolant and on the reactor. In analogy with the energy-balance equation in the **PFTR**

$$u \frac{dT}{dz} = \frac{-A H}{\rho C_p} r(C_A, T) - \frac{U p_w}{\rho C_p A_t} (T - T_c)$$

we assume that the coolant also obeys plug flow; so the energy balance on the coolant becomes

$$u_c \frac{dT_c}{dz} = + \frac{U p_w}{\rho C_{pc} A_t} (T - T_c)$$

We have of course omitted any heat generation by reaction in the coolant, and we have defined the corresponding quantities for the coolant with the subscript c. Note also that we have reversed the sign of the heat-removal term because whatever heat is transferred from the reactor must be transferred into the coolant.

The student should recognize these problems with the jacketed reactor as similar to those encountered in analysis of heat exchangers. The only difference in chemical reactors is that now we have considerable heat generation by chemical reaction on one side of the heat exchanger. The equipment used for these reactors in fact looks very similar to heat exchangers, but pressures, temperatures, and catalysts must be chosen very carefully, and materials of construction are frequently more difficult to deal with in the reactive environment.

## Feed cooling

A final mode of heat transfer in tubular reactors is the feed-cooled reactor, where the hot products from the reactor are cooled by the feed before it enters the reactor. As shown in Figure S-22, the cold feed in the jacket is preheated by the reaction in the inner tube or a heat exchanger is used for this purpose before the reactor. Temperature profiles for feed cooling are shown in Figure 5-22.

One interesting characteristic of this type of reactor is that the maximum temperature of the products can be above the adiabatic temperature predicted for reactant temperatures before heat exchange. Heat is retained in the reactor by preheating the feed, and temperatures in some situations can be many hundreds of degrees above adiabatic. This can be useful in combustors for pollution abatement where dilute hydrocarbons need to be heated to high temperatures to cause ignition and attain high conversion with short residence times.

## THE TEMPERATURE PROFILE IN A PACKED BED

Thus far we have only considered the PFTR with gradients in the axial direction. The heat transfer to the wall at temperature  $T_c$  was handled through a heat transfer coefficient  $U$ . The complete equations are

$$\frac{\partial C_j}{\partial t} + \mathbf{u} \cdot \nabla C_j = D_j \nabla^2 C_j + v_j r$$

$$\rho C_p \left( \frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T \right) = k_T \nabla^2 T + (-\Delta H_R) r$$

where  $\mathbf{u}$  is the velocity vector,  $\nabla C_j$  and  $\nabla T$  are the gradients of concentration and temperature, respectively, and  $k_T$  is the effective thermal conductivity in the reactor. If we retain the plug-flow approximation, then these gradients are in the  $z$  direction only and we lump heat transfer in the radial direction through an overall heat transfer coefficient  $h$ . However, heat transfer from the walls must occur by temperature gradients in the radial direction  $R$ , and these show up in the term

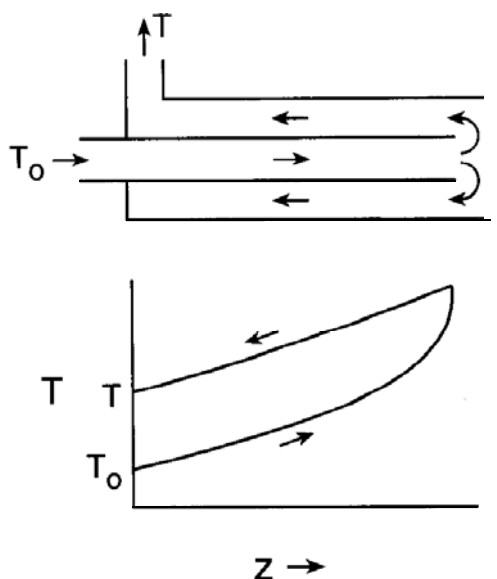


Figure 5-22 Temperature profiles in a wall-cooled reactor with countercurrent feed cooling.



$$\nabla^2 T = \frac{\partial^2 T}{\partial z^2} + \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial T}{\partial R} \right)$$

If we assume that the reactor is in steady state and that in the  $z$  direction the reactor is still in plug flow, then the equations for a first-order irreversible reaction become

$$u \frac{\partial C_A}{\partial z} = -k C_A(z, R)$$

$$\rho C_p u \frac{\partial T}{\partial z} = k_T \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial T}{\partial R} \right) + (-\Delta H_R) k C_A$$

We need to solve these equations with inlet conditions

$$C_A = C_{A0}$$

$$T = T_0$$

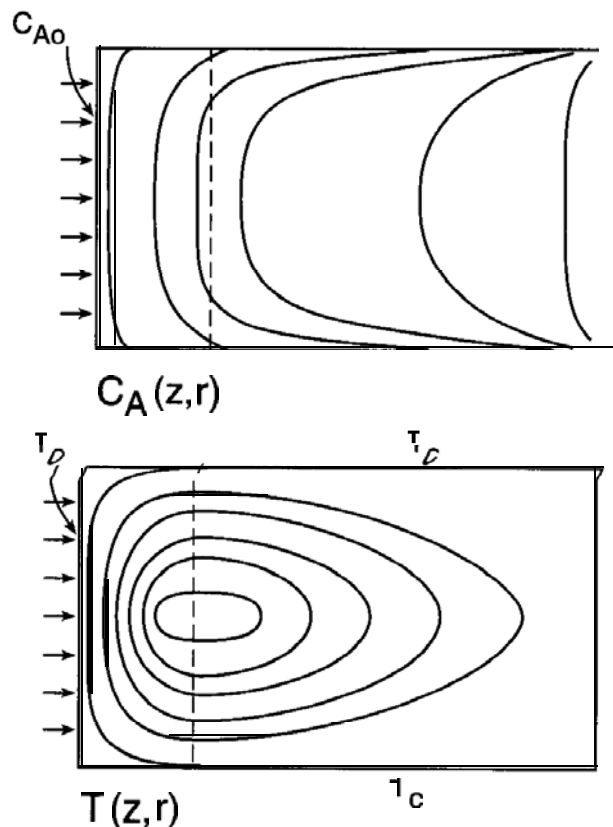
at  $z = 0$  as before. However, now we need to add two boundary conditions on temperature in the radial direction,

$$T = T_w, \quad R = \pm R_0/2$$

$$\frac{\partial T}{\partial R} = 0, \quad R = 0$$

as well as additional boundary conditions on  $C_A$ . For a tubular reactor we can solve these equations numerically to yield  $C_A(z, R)$  and  $T(z, R)$ . These solutions are plotted in Figure 5-23.

Figure 5-23 Plots of reactant and temperature profiles versus axial position  $z$  and radial position  $r$  in a wall-cooled tubular reactor. The reactor can exhibit a hot spot near the center where the rate is high and cooling is least.



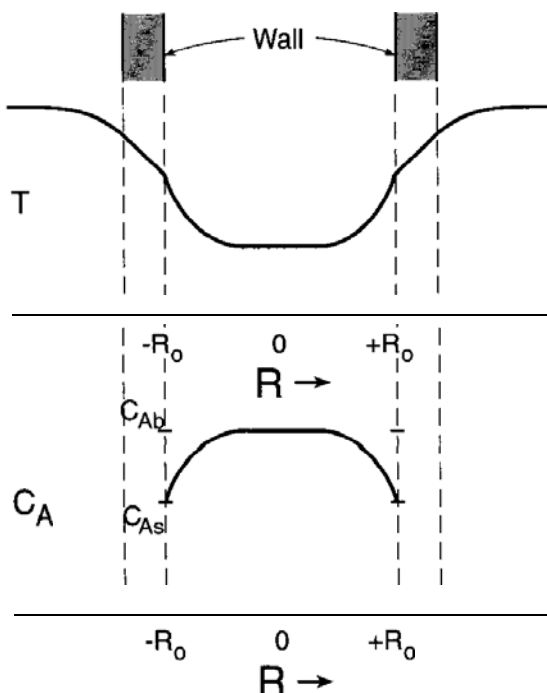
The notable feature of the wall-cooled tubular reactor is that there can exist a hot *spot* near the center of the reactor and near the entrance. We saw this for the lumped model, which allowed only for variations in the  $z$  direction, but when radial variations are allowed, the effect can become even more severe as both temperature and concentration vary radially.

If we examine the temperature and concentration profile in the radial direction for the plot in Figure 5-23, we obtain graphs approximately as those in Figure 5-24.

We used the wall temperature  $T_w$  in the boundary condition, and this may be different from the coolant temperature  $T_c$ . There may be temperature variations across the wall as well as through the coolant. These are described through the overall heat transfer coefficient  $U$ , but in practice all these effects must be considered for a detailed description of the wall-cooled tubular reactor.

### PROBLEMS

- 5.1 Find  $\dot{Q}(t)$  or  $\dot{Q}(z)$  necessary to maintain a 5 liter batch reactor or PFTR isothermal reactor at 300 K for the reaction  $A \rightarrow B$ ,  $r = kC_A$  in aqueous solution with  $k = 2.0 \text{ min}^{-1}$ ,  $C_{A0} = 2$  mole/liter,  $\Delta H_R = -30 \text{ kcal/mole}$ . What is the average rate of heat removal for 95% conversion?
- 5.2 Calculate  $C_A(\tau)$  and  $T(\tau)$  if the above reaction is run in an adiabatic PFTR to 90% conversion if the reaction activation energy is 6000 cal/mole.
- 5.3 Under what conditions would you have to worry about boiling in the reaction of the previous problem? How might one design a reactor to process 5 molar feed to eliminate boiling?
- 5.4 What is the ratio of volumes required for adiabatic and isothermal operation for this reaction?
- 5.5 Compare  $T(z)$  and  $T_c(z)$  trajectories of a wall-cooled PFTR with **cocurrent** and countercurrent flows. Which configuration is more likely to produce more problems with a hot spot in the reactor?



**Figure 5-24** Plots of  $C_A$  and  $T$  versus radial position  $R$  for a wall-cooled reactor. The temperature is highest and the conversion is lowest near the centerline.

- 5.6 The maximum reactor temperature is much more sensitive to feed temperature for feed-cooled tubular reactors than for tubular reactors with a separate cooling stream. Why?
- 5.7 A tubular reactor in which the feed is heated by product in a countercurrent adiabatic configuration can attain a maximum temperature much hotter than the adiabatic temperature (and in fact it can be infinite). Sketch  $T(z)$  to show why this is so.
- 5.8 [Computer] Plot  $C_A(\tau)$  and  $T(\tau)$  for the reaction  $A \rightarrow B$ ,  $r = k(T)C_A$  in an adiabatic PFTR for  $E = 30$  kcal/mole,  $k_0 = 2.6 \times 10^{20} \text{ min}^{-1}$ ,  $A H_R = -20$  kcal/mole,  $\rho C_p = 1000$  cal/liter K,  $T_0 = 300$  K, and  $C_{A0} = 2$  moles/liter. [This is the example in the text.] Repeat these calculations for  $C_{A0} = 0.1, 0.5, 1.0, 2.0, 4.0$ , and  $10.0$ . Wherever possible, plot  $C_A(\tau)$  and  $T(\tau)$  on the same graphs to display the differences with initial concentration.
- 5.9 [Computer] Plot  $C_A(\tau)$  and  $T(\tau)$  for the reaction  $A + B \rightarrow C$ ,  $r = k(T)C_A^2$  in an adiabatic PFTR for  $E = 30$  kcal/mole,  $k_0 = 2.6 \times 10^{20} \text{ liter/mole min}$ ,  $A H_R = -20$  kcal/mole,  $\rho C_p = 1000$  cal/liter K,  $T_0 = 300$  K, and  $C_{A0} = C_{B0} = 2$  moles/liter. [This is the example in the text but with second-order kinetics.] Repeat these calculations for  $C_{A0} = C_{B0} = 0.1, 0.5, 1.0, 2.0, 4.0$ , and  $10.0$ . Wherever possible, plot  $C_A(\tau)$  and  $T(\tau)$  on the same graphs to display the differences with initial concentration.
- 5.10 [Computer] Plot  $C_A(\tau)$  and  $T(\tau)$  for the reaction  $A \rightarrow B$ ,  $r = k(T)C_A$  in an adiabatic PFTR for  $E = 30$  kcal/mole,  $k_0 = 2.6 \times 10^{20} \text{ min}^{-1}$ ,  $A H_R = -20$  kcal/mole,  $\rho C_p = 1000$  cal/liter K,  $T_0 = 300$  K, and  $C_{A0} = 2$  moles/liter. [This is the example in the text.] Repeat these calculations for  $T_0 = 280, 290, 300, 310, 320, 330, 340$ , and  $350$  K. Plot  $C_A(\tau)$  and  $T(\tau)$  on the same graphs to display the differences with initial  $T_0$ .
- 5.11 The reaction  $A \rightarrow B$ ,  $r = kC_A$  is carried out in an adiabatic CSTR with  $C_{A0} = 2.0$  moles/liter and  $T_0 = 300$  K. It is found that 50% conversion is obtained with  $\tau = 4$  min, and the reactor temperature is 350 K.
- Find  $k$  at 350 K.
  - The reaction is in water with  $\rho C_p = 10^3$  cal/liter K. Find the heat of the reaction.
- 5.12 [Computer] Sketch lines of  $r(X, T)$  on an  $X$  versus  $T$  plot for  $A \rightarrow B$  assuming the reaction is (a) irreversible, (b) reversible and endothermic, and (c) reversible and exothermic.
- 5.13 Show that  $r(X, T)$  for  $A \rightarrow B$ ,  $r = k_f C_A - k_b C_B$  has a maximum  $(\partial X / \partial T)_r = 0$  if the reaction is exothermic but not if endothermic.
- 5.14 [Computer] Plot  $C_A(\tau)$  and  $T(\tau)$  in a wall-cooled tubular reactor for the liquid-phase reaction  $A \rightarrow B$ ,  $k(T) = 1000 \exp(-3000/T) \text{ min}^{-1}$ ,  $A H_R / \rho C_p = 17$  K liter/mole,  $C_{A0} = 1$  mole/liter. The heat transfer coefficient is  $5 \text{ min}^{-1}$ . Consider a feed temperature of 300 K and different wall temperatures in 50 K increments starting with 250 K.
- 5.15 (a) Sketch  $r$  versus  $C_{A0} - C_A$  for a reversible exothermic reaction if the reactor is operated isothermally at a range of temperatures where the equilibrium conversions go from high to low.
- From  $1/r$  plots show how several isothermal PFTRs in series could achieve a higher conversion with a smaller total volume than a single isothermal PFTR.
  - Why is this generally not an economical reactor design?

- 5.16 Sketch  $r$  and  $1/r$  versus  $C_{A0} - C_A$  for a reversible exothermic reaction for fixed  $T_0$  and a fairly low  $T_c$  if the reactor
- is adiabatic,
  - is isothermal at  $T_0$ , or
  - quickly cools to  $T_c$ .
- 5.17 Sketch some possible  $r$  and  $1/r$  versus  $C_{A0} - C_A$  curves for an irreversible exothermic reaction for nonisothermal operation. Show that a CSTR becomes even more attractive for nonisothermal operation.
- 5.18 The reaction



is to be run in aqueous solution at atmospheric pressure.

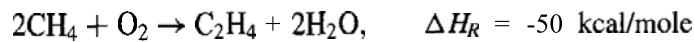
- If the reactor is adiabatic and  $T_0 = 300$  K, what is the highest  $C_{A0}$  for the reactor not to boil?
  - It is found that  $k$  at 300 K is  $0.2 \text{ min}^{-1}$  and the activation energy is 30,000 cal/mole. Calculate  $X(\tau)$  in an adiabatic PFTR and in an adiabatic CSTR for  $C_{A0} = 2$  moles/liter.
- 5.19 In the preceding reaction it is found that the equilibrium constant is 0.99 at 300 K.
- What is the maximum conversion attainable in an adiabatic reactor?
  - Calculate  $X(t)$  in an adiabatic PFTR and in an adiabatic CSTR for  $C_{A0} = 2$  moles/liter.
- 5.20 The reaction



is to be run in aqueous solution in an adiabatic CSTR with  $T_0 = 300$  K,  $C_{A0} = 2$  moles/liter,  $k = 2.0 \text{ min}^{-1}$  at 300 K, and  $E = 30,000 \text{ cal/mole}$ . Calculate and plot  $X(t)$ ,  $T(t)$ , and  $X(T)$ , for initial temperatures varying in 10 K increments starting at 280 K for initial conversions of  $X = 0$  and 1. Do calculations for  $\tau =$

- 0.3 min,
  - 1.5 min,
  - 3.0 min.
- 5.21 Consider methanol synthesis from CO and  $H_2$  with a stoichiometric feed at pressures of 10, 30, and 100 atm.
- If the reactor goes to equilibrium, what conversions will be obtained at 250, 300, and 350°C at each of these pressures?
  - If the reactor operates adiabatically, what  $T_0$  will give these conversions? Assume  $C_p = \frac{7}{2} R$ .
  - How many stages are necessary to give 90% conversion in adiabatic reactors with interstage cooling to 25°C at each of these pressures?
  - Repeat with interstage methanol separation.
  - What are the final temperatures expected to compress these gases isentropically to these pressures starting at 1 atm and 25°C? Assume  $C_p = \frac{7}{2} R$ .
  - Assuming that electricity costs \$0.02/kwh, what is the cost per pound of compression for each pressure?

- 5.22 Construct a table of the reactors needed to synthesize methanol from natural gas and water. Include reactions,  $\Delta H_R$ , reactor type, heat management method, and catalyst.
- 5.23 Plywood contains approximately 30% binder, which is a urea-formaldehyde polymer. Indicate the reactions and steps in its synthesis from natural gas and water (and trees). Approximately how many SCF of natural gas go into a 4x 8 sheet of **3/4-in.** plywood?
- 5.24 Consider an autocatalytic reaction  $A \rightarrow B$ ,  $r = k(T)C_A C_B$ , in an adiabatic **PFTR**. This reaction has both chemical autocatalysis, which can produce a lag in the rate as the concentration of product **B** builds up, and also thermal autocatalysis, in which the rate accelerates at the temperature increases. Solve these equations for the example in the text but replacing the kinetics by the above expression to show how the temperature and  $C_A$  vary with  $\tau$ .
- 5.25 The oxidative coupling of methane to ethylene



occurs in an adiabatic tube wall reactor. The feed is 90%  $\text{CH}_4$  in  $\text{O}_2$  at atmospheric pressure at 300 K. In excess  $\text{CH}_4$  the reaction can be regarded as  $\text{O}_2 \rightarrow \text{products}$  with a rate first order in  $P_{\text{O}_2}$ , and the change in moles may be ignored. [Do these arguments make sense?] Assume that the heat capacity of the gases is  $\frac{7}{2}R$ .

- Find the adiabatic temperature if the reaction goes to completion assuming the wall has negligible thermal conductivity. [Answer:  $\approx 800^\circ\text{C}$ .]
- Find the reactor wall temperature versus oxygen conversion  $X$ .
- It is found that 90%  $\text{O}_2$  conversion occurs in a reactor with a very large wall thermal conductivity such that the wall is isothermal at the exit temperature. For a velocity of 1 m/s, a tube diameter of 0.5 mm, and a length of 1 cm, find the surface reaction rate coefficient in molecules/cm<sup>2</sup>·sec atm at this temperature. Assume that the gases are incompressible (not a very good assumption).
- Assuming instead that the wall thermal conductivity is zero, show that the conversion versus position  $z$  is given by the expression

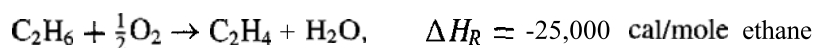
$$z(X) = u \int_0^X dX / \left[ (1 - X)k_0 \exp \left( \frac{-E}{R[T_0 + (-\Delta H_R/NC_p)X]} \right) \right]$$

- The reactive sticking coefficient of  $\text{O}_2$  has an activation energy of 20 kcal/mole. Estimate  $k_0$ .
  - Find  $L$  for 90% conversion of  $\text{O}_2$ .
- 5.26 Suppose your apartment has a 50 gallon hot water heater and your shower uses 10 gallons per minute. The water in the tank initially is at 120°F and the supply water is at 60°F. The heater has an **on-off** control and requires 1 h to heat 60°F water to 120°F.
- Describe the temperature of your shower versus time assuming a mixed tank, ignoring the effect of the heater.
  - What is the wattage of the heater?
  - Describe  $T(t)$  assuming that the heater is on continuously.
  - This design is clearly unsatisfactory, and manufacturers configure hot water tanks to minimize mixing. How can this be done fairly simply? What is  $T(t)$  for this system?

- (e) Expensive water heaters provide hot water continuously on demand. Sketch the reactor diagram and control system that will accomplish this with no storage reservoir. What heater wattage is required to maintain your shower at  $120^{\circ}\text{F}$ ?

5.27 Derive the mass-balance equation on species  $A$  and the energy-balance equation for a batch reactor of volume  $V$  with rate  $r(C_A, T)$  with wall coolant area  $A$ , and heat transfer coefficient  $U$ .

5.28 [Computer] We have a catalyst that causes the oxidative dehydrogenation of ethane to ethylene



The process produces only ethylene in a reaction that goes to completion with a feed of 5 mole %  $\text{C}_2\text{H}_6$  in air in an adiabatic CSTR operated at a pressure of 2 atm with  $\tau = 10$  min. We find that the reaction rate is given approximately by the expression

$$r = k_0 \exp(-E/RT) C_{\text{C}_2\text{H}_6}$$

with  $k_0 = 1.4 \times 10^8$  mole/liter min and  $E = 30,000$  cal/mole. Assume constant density and that the heat capacity is  $\frac{7}{2}R$  at all temperatures and compositions. Calculate  $C_{\text{C}_2\text{H}_6}$  and  $T$  versus  $\tau$  in steady state in a CSTR and in a PFTR using a spreadsheet to solve the equations as discussed in the example in the text. Assume  $C_{\text{C}_2\text{H}_6} = P_{\text{C}_2\text{H}_6,0}(1 - X)/RT_0$ .

5.29 We have a catalyst that causes the oxidative dehydrogenation of ethane to ethylene



The process produces only ethylene in a reaction that goes to completion with a feed of 5 mole %  $\text{C}_2\text{H}_6$  in air in a CSTR operated at a pressure of 2 atm.

- If the reaction goes to completion, how many moles are produced for each mole fed into the reactor?
- Find an approximate expression for the temperature versus conversion in an adiabatic reactor with  $T_0 = 350^{\circ}\text{C}$ . Assume constant density and that the heat capacity is  $\frac{7}{2}R$  at all temperatures and compositions. [Answer:  $T = 500^{\circ}\text{C}$  at completion.]
- What is the relationship between the space time and the residence time if the reaction goes to completion?
- We find that the reaction rate is given approximately by the expression

$$r = k_0 \exp(-E/RT) C_{\text{C}_2\text{H}_6}$$

with  $k_0 = 1.4 \times 10^8$  mole/liter min and  $E = 30,000$  cal/mole. Plot  $X(T)$  for  $\tau = 1, 3, 10, 30$ , and 100 min. [This problem can be worked with a calculator and graphed by hand or on a spreadsheet with graphics].

- From this graph determine the conversion and reactor temperature for these residence times. What startup procedure would you use to attain the upper steady state for  $\tau \approx 10$  min?
- From these curves plot (by hand is OK)  $X$  versus  $\tau$ .

5.30 Solve (or at least set up) the preceding problem exactly, taking account of the density change caused by mole number changes in the reaction and to the temperature variations.