Steady-State Nonisothermal Reactor Design

8

> If you can't stand the heat, get out of the kitchen.
>
> Harry S Truman

Overview. Because most reactions are not carried out isothermally, we now focus our attention on heat effects in chemical reactors. The basic design equations, rate laws, and stoichiometric relationships derived and used in Chapter 4 for isothermal reactor design are still valid for the design of nonisothermal reactors. The major difference lies in the method of evaluating the design equation when temperature varies along the length of a PFR or when heat is removed from a CSTR. In Section 8.1, we show why we need the energy balance and how it will be used to solve reactor design problems. In Section 8.2, we develop the energy balance to a point where it can be applied to different types of reactors and then give the end result relating temperature and conversion or reaction rate for the main types of reactors we have been studying. Section 8.3 shows how the energy balance is easily applied to design adiabatic reactors, while Section 8.4 develops the energy balance on PFRs/PBRs with heat exchange. In Section 8.5, the chemical equilibrium limitation on conversion is treated along with a strategy for staging reactors to overcome this limitation. Sections 8.6 and 8.7 describe the algorithm for a CSTR with heat effects and CSTRs with multiple steady states, respectively. Section 8.8 describes one of the most important topics of the entire text, multiple reactions with heat effects, which is unique to this textbook. We close the chapter in Section 8.9 by considering both axial and radial concentrations and temperature gradients. The *Professional Reference Shelf* R8.4 on the CD-ROM describes a typical nonisothermal industrial reactor and reaction, the SO_2 oxidation, and gives many practical details.

8.1 Rationale

To identify the additional information necessary to design nonisothermal reactors, we consider the following example, in which a highly exothermic rea is carried out adiabatically in a plug-flow reactor.

Example 8–1 What Additional Information Is Required?

Calculate the reactor volume necessary for 70% conversion.

$$A \longrightarrow B$$

The reaction is exothermic and the reactor is operated adiabatically. As a resul temperature will increase with conversion down the length of the reactor.

Solution

1. **Mole Balance (design equation):**

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$ (E8

2. **Rate Law:** $-r_A = kC_A$ (E8

Recalling the Arrhenius equation,

$$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$ (E8·

we know that k is a function of temperature, T.

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

$$F_A = C_A v_0$$
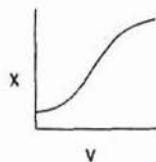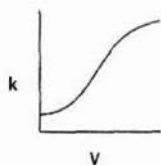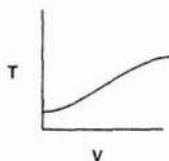
$$F_{A0} = C_{A0} v_0$$

$$C_A = C_{A0}(1 - X)$$ (E8

4. **Combining:**

$$-r_A = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] C_{A0}(1 - X)$$ (E8-

Combining Equations (E8-1.1), (E8-1.2), and (E8-1.4) and canceling the er ing concentration, C_{A0}, yields

$$\frac{dX}{dV} = \frac{k(1 - X)}{v_0}$$ (E8-

Because T varies along the length of the reactor, k will also vary, which · not the case for isothermal plug-flow reactors. Combining Equations (E8- and (E8-1.6) gives us

$$\frac{dX}{dV} = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]\frac{1 - X}{v_0} \tag{E8-1.7}$$

We see that we need another relationship relating X and T or T and V to solve this equation. *The energy balance will provide us with this relationship.*
So we add another step to our algorithm, this step is the energy balance.

5. **Energy Balance:**

In this step, we will find the appropriate energy balance to relate temperature and conversion or reaction rate. For example, if the reaction is adiabatic, we will show the temperature-conversion relationship can be written in a form such as

$$T = T_0 + \frac{-\Delta H_{Rx}}{C_{P_A}} X \tag{E8-1.8}$$

We now have all the equations we need to solve for the conversion and temperature profiles.

8.2 The Energy Balance

8.2.1 First Law of Thermodynamics

We begin with the application of the first law of thermodynamics first to a closed system and then to an open system. A system is any bounded portion of the universe, moving or stationary, which is chosen for the application of the various thermodynamic equations. For a closed system, in which no mass crosses the system boundaries, the change in total energy of the system, $d\hat{E}$, is equal to the heat flow **to** the system, δQ, minus the work done **by** the system **on** the surroundings, δW. For a *closed system*, the energy balance is

$$d\hat{E} = \delta Q - \delta W \tag{8-1}$$

The δ's signify that δQ and δW are not exact differentials of a state function.

The continuous-flow reactors we have been discussing are *open systems* in that mass crosses the system boundary. We shall carry out an energy balance on the open system shown in Figure 8-1. For an open system in which some of the energy exchange is brought about by the flow of mass across the system boundaries, the energy balance for the case of *only one* species entering and leaving becomes

$$
\begin{bmatrix}
\text{Rate of} \\
\text{accumulation} \\
\text{of energy} \\
\textit{within} \text{ the} \\
\text{system}
\end{bmatrix}
=
\begin{bmatrix}
\text{Rate of flow} \\
\text{of heat } \textit{to} \\
\text{the system} \\
\textit{from} \text{ the} \\
\text{surroundings}
\end{bmatrix}
-
\begin{bmatrix}
\text{Rate of work} \\
\textit{done} \text{ by} \\
\text{the system} \\
\text{on the} \\
\text{surroundings}
\end{bmatrix}
+
\begin{bmatrix}
\text{Rate of energy} \\
\text{added to the} \\
\text{system by mass} \\
\text{flow } \textit{into} \text{ the} \\
\text{system}
\end{bmatrix}
-
\begin{bmatrix}
\text{Rate of} \\
\text{energy leaving} \\
\text{system by mass} \\
\text{flow } \textit{out} \text{ of} \\
\text{the system}
\end{bmatrix}
$$

$$\frac{d\hat{E}_{sys}}{dt} \quad = \quad \dot{Q} \quad - \quad \dot{W} \quad + \quad F_{in}E_{in} \quad - \quad F_{out}E_{out}$$

$$\tag{8-2}$$

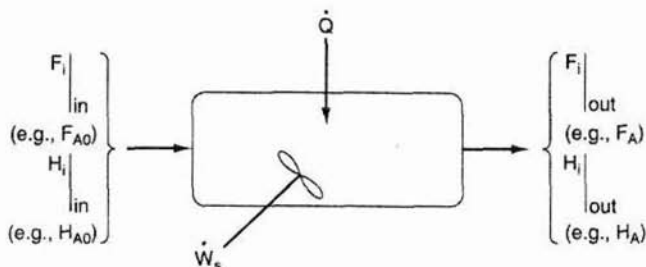Typical units for each term in Equation (8-2) are (Joule/s).

Figure 8-1 Energy balance on a well-mixed open system: schematic.

We will assume the contents of the system volume are well mixed, an assumption that we could relax but that would require a couple pages of text to develop, and the end result would be the same! The unsteady-state energy balance for an open well-mixed system that has n species, each entering and leaving the system at their respective molar flow rates F_i (moles of i per time) and with their respective energy E_i (joules per mole of i), is

The starting point

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W} + \sum_{i=1}^{n} E_i F_i \Big|_{in} - \sum_{i=1}^{n} E_i F_i \Big|_{out} \tag{8-3}$$

We will now discuss each of the terms in Equation (8-3).

8.2.2 Evaluating the Work Term

It is customary to separate the work term, $\dot{W}$, into *flow work* and *other work*, $\dot{W}_s$. The term $\dot{W}_s$, often referred to as the *shaft work*, could be produced from such things as a stirrer in a CSTR or a turbine in a PFR. *Flow work* is work that is necessary to get the mass *into* and *out of* the system. For example, when shear stresses are absent, we write

[Rate of flow work]

Flow work and shaft work

$$\dot{W} = -\sum_{i=1}^{n} F_i P \tilde{V}_i \Big|_{in} + \sum_{i=1}^{n} F_i P \tilde{V}_i \Big|_{out} + \dot{W}_s \tag{8-4}$$

where P is the pressure (Pa) [1 Pa = 1 Newton/m^2 = 1 kg $\cdot$ m/s^2/m^2] and $\tilde{V}_i$ is the specific molar volume of species i (m^3/mol of i).

Let's look at the units of the flow work term, which is

$$F_i \cdot P \cdot \tilde{V}_i$$

where F_i is in mol/s, P is Pa (1 Pa = 1 Newton/m^2), and $\tilde{V}_i$ is m^3/mol.

$$F_i \cdot P \cdot \tilde{V}_i \; [=] \; \frac{mol}{s} \cdot \frac{Newton}{m^2} \cdot \frac{m^3}{mol} = (Newton \cdot m) \cdot \frac{1}{s} = Joules/s = Watts$$

We see that the units for flow work are consistent with the other terms in Equation (8-2), i.e., J/s.

In most instances, the flow work term is combined with those terms in the energy balance that represent the energy exchange by mass flow across the system boundaries. Substituting Equation (8-4) into (8-3) and grouping terms, we have

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_i(E_i + P\tilde{V}_i)\bigg|_{in} - \sum_{i=1}^{n} F_i(E_i + P\tilde{V}_i)\bigg|_{out} \tag{8-5}$$

The energy E_i is the sum of the internal energy (U_i), the kinetic energy $(u_i^2/2)$, the potential energy (gz_i), and any other energies, such as electric or magnetic energy or light:

$$E_i = U_i + \frac{u_i^2}{2} + gz_i + \text{other} \tag{8-6}$$

In almost all chemical reactor situations, the kinetic, potential, and "other" energy terms are negligible in comparison with the enthalpy, heat transfer, and work terms, and hence will be omitted; that is,

$$E_i = U_i \tag{8-7}$$

We recall that the enthalpy, H_i (J/mol), is defined in terms of the internal energy U_i (J/mol), and the product $P\tilde{V}_i$ (1 Pa·m³/mol = 1 J/mol):

Enthalpy

$$H_i = U_i + P\tilde{V}_i \tag{8-8}$$

Typical units of H_i are

$$(H_i) = \frac{J}{\text{mol } i} \text{ or } \frac{Btu}{\text{lb mol } i} \text{ or } \frac{cal}{\text{mol } i}$$

Enthalpy carried into (or out of) the system can be expressed as the sum of the net internal energy carried into (or out of) the system by mass flow plus the flow work:

$$F_i H_i = F_i(U_i + P\tilde{V}_i)$$

Combining Equations (8-5), (8-7), and (8-8), we can now write the energy balance in the form

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_i H_i \bigg|_{in} - \sum_{i=1}^{n} F_i H_i \bigg|_{out}$$

The energy of the system at any instant in time, $\hat{E}_{sys}$, is the sum of the products of the number of moles of each species in the system multiplied by their respective energies. This term will be discussed in more detail when unsteady-state reactor operation is considered in Chapter 9.

We shall let the subscript "0" represent the inlet conditions. Un
scripted variables represent the conditions at the outlet of the chosen sy:
volume.

in

$F_{i0}H_{i0}, \dot{Q}$ $F_iH_i, \dot{W}_s$

out
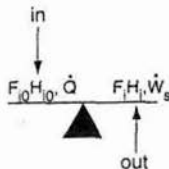
$$\dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_{i0}H_{i0} - \sum_{i=1}^{n} F_i H_i = \frac{d\hat{E}_{sys}}{dt}$$

In Section 8.1, we discussed that in order to solve reaction enginee
problems with heat effects, we needed to relate temperature, conversion,
rate of reaction. The energy balance as given in Equation (8-9) is the most
venient starting point as we proceed to develop this relationship.

8.2.3 Overview of Energy Balances

What is the Plan? In the following pages we manipulate Equation (8-9
order to apply it to each of the reactor types we have been discussing, b
PFR, PBR, and CSTR. The end result of the application of the energy bal
to each type of reactor is shown in Table 8-1. The equations are used in St
of the algorithm discussed in Example E8-1. The equations in Table 8-1 r
temperature to conversion and molar flow rates and to the system param
such as the overall heat-transfer coefficient and area, Ua, and correspor
ambient temperature, T_a, and the heat of reaction, ΔH_{Rx}.
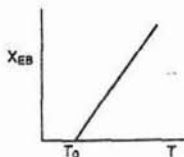
TABLE 8-1.   ENERGY BALANCES OF COMMON REACTORS

1. **Adiabatic** $(\dot{Q} \equiv 0)$ CSTR, PFR, Batch, or PBR. The relationship between conv
   sion, X_{EB}, and temperature for $\dot{W}_s = 0$, constant C_{P_i}, and $\Delta C_P = 0$, is

End results of
manipulating the
energy balance Sec-
tions 8.2.4 to 8.4,
8.6, and 8.8.

$$X_{EB} = \frac{\Sigma \Theta_i C_{P_i}(T - T_0)}{-\Delta H_{Rx}}$$ (T8-1.A

$$T = T_0 + \frac{(-\Delta H_{Rx})X}{\Sigma \Theta_i C_{P_i}}$$ (T8-1.E

For an exothermic reaction $(-\Delta H_{Rx}) > 0$

X_{EB}

T_0 T

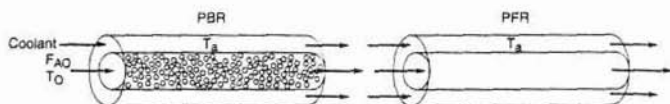2. **CSTR with heat exchanger**, UA $(T_a - T)$, and large coolant flow rate.

$\dot{m}_c$

T_a
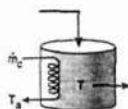
$$X_{EB} = \frac{\left(\dfrac{UA}{F_{A0}}(T - T_a)\right) + \Sigma \Theta_i C_{P_i}(T - T_0)}{-\Delta H_{Rx}}$$ (T8-1

TABLE 8-1.   ENERGY BALANCES OF COMMON REACTORS (CONTINUED)

3. **PFR/PBR with heat exchange**

3A. **PBR in terms of conversion**

$$\frac{dT}{dW} = \frac{\dfrac{Ua}{\rho_B}(T_a - T) + r_A' \, \Delta H_{Rx}(T)}{F_{A0}(\Sigma \, \Theta_i C_{P_i} + \Delta C_P X)} \tag{T8-1.D}$$

3B. **PFR in terms of conversion**

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + r_A \Delta H_{Rx}(T)}{F_{A0}(\Sigma \, \Theta_i C_P + \Delta C_P X)} \tag{T8-1.E}$$

3C. **PBR in terms of molar flow rates**

$$\frac{dT}{dW} = \frac{\dfrac{Ua}{\rho_B}(T_a - T) + r_A' \, \Delta H_{Rx}(T)}{\Sigma \, F_i C_{P_i}} \tag{T8-1.F}$$

3D. **PFR in terms of molar flow rates**

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + r_A \Delta H_{Rx}(T)}{\Sigma \, F_i C_{P_i}} \tag{T8-1.G}$$

4. **Batch**

$$\frac{dT}{dt} = \frac{(-r_A V)(-\Delta H_{Rx}) - UA(T - T_a)}{\Sigma \, N_i C_{P_i}} \tag{T8-1.H}$$

5. **For Semibatch or unsteady CSTR**

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \displaystyle\sum_{i=1}^{n} F_{i0}(C_{P_i}(T - T_{i0}) + [-\Delta H_{Rx}(T)](-r_A V))}{\displaystyle\sum_{i=1}^{n} N_i C_{P_i}} \tag{T8-1.I}$$

6. **For multiple reactions in a PFR**

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + \Sigma r_{ij} \Delta H_{Rxij}}{\Sigma \, F_i C_{P_i}} \tag{T8-1.J}$$

TABLE 8-1.   ENERGY BALANCES OF COMMON REACTORS (CONTINUED)

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7. **For a variable coolant temperature, T_a**

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_{P_c}}$$

(T8-1.K)

These are the equations that we will use to solve reaction engineering problems with heat effects.

– –

[**Nomenclature:** U = overall heat-transfer coefficient, $(J/m^2 \cdot s \cdot K)$; A = CSTR heat-exchange area, (m^2); a = PFR heat-exchange area per volume of reactor, (m^2/m^3); C_{P_i} = mean heat capacity of species i, $(J/mol/K)$; C_{P_c} = the heat capacity of the coolant, $(J/kg/K)$, $\dot{m}_c$ = coolant flow rate, (kg/s); ΔH_{Rx} = heat of reaction, (J/mol);

$\Delta H_{Rx}^\circ = \left(\frac{d}{a} H_D^\circ + \frac{c}{a} H_C^\circ - \frac{b}{a} H_B^\circ - H_A^\circ\right) J/molA$; ΔH_{Rxij} = heat of reaction wrt species

j in reaction i, (J/mol); $\dot{Q}$ = heat added to the reactor, (J/s); and

$\Delta C_P = \left(\frac{d}{a} C_{P_D} + \frac{c}{a} C_{P_C} - \frac{b}{a} C_{P_B} - C_{P_A}\right)$ $(J/molA \cdot K)$. All other symbols are as defined in Chapter 3.]

Examples on How to Use Table 8-1. We now couple the energy balance equations in Table 8-1 with the appropriate reactor mole balance, rate law, stoichiometry algorithm to solve reaction engineering problems with heat effects. For example, recall rate law for a first-order reaction, Equation (E8-1.5) in Example 8-1.

$$-r_A = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] C_{A0}(1 - X)$$

(E8-1.5)

If the reaction is carried out adiabatically, then we use Equation (T8-1.B) for the reaction A $\longrightarrow$ B in Example 8-1 to obtain

Adiabatic

$$T = T_0 + \frac{-\Delta H_{Rx} X}{C_{P_A}}$$

(T8-1.B)

Consequently, we can now obtain $-r_A$ as a function of X alone by first choosing X, then calculating T from Equation (T8-1.B), then calculating k from Equation (E8-1.3), and then finally calculating $(-r_A)$ from Equation (E8-1.5).

Choose $X \rightarrow$ calculate $T \rightarrow$ calculate $k \rightarrow$ calculate $-r_A \rightarrow$ calculate $\dfrac{F_{A0}}{-r_A}$
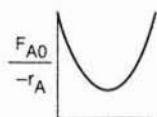
$\dfrac{F_{A0}}{-r_A}$

X
Levenspiel plot

We can use this sequence to prepare a table of $(F_{A0}/-r_A)$ as a function of X. We can then proceed to size PFRs and CSTRs. In the absolute worst case scenario, we could use the techniques in Chapter 2 (e.g., Levenspiel plots or the quadrature formulas in Appendix A).

However, instead of using a Levenspiel plot, we will most likely use Polymath to solve our coupled differential energy and mole balance equations.

If there is cooling along the length of a PFR, we could then apply Equation (T8-1.E) to this reaction to arrive at two coupled differential equations.

Non-adiabatic
PFR

$$\frac{dX}{dV} = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] C_{A0}(1-X)$$

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + r_A \Delta H_{Rx}(T)}{F_{A0} C_{P_A}}$$

which are easily solved using an ODE solver such as Polymath.

Similarly, for the case of the reaction A → B carried out in a CSTR, we could use Polymath or MATLAB to solve two nonlinear equations in X and T. These two equations are combined mole balance

Non-adiabatic
CSTR

$$V = \frac{F_{A0}X}{k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] C_{A0}(1-X)}$$

and the application of Equation (T8-1.C), which is rearranged in the form

$$T = \frac{F_{A0}X(-\Delta H_{Rx}) + UAT_a + F_{A0}C_{P_A}T_0}{UA + C_{P_A}F_{A0}}$$

From these three cases, (1) adiabatic PFR and CSTR, (2) PFR and PBR with heat effects, and (3) CSTR with heat effects, one can see how one couples the energy balances and mole balances. In principle, one could simply use Table 8-1 to apply to different reactors and reaction systems without further discussion. However, understanding the derivation of these equations will greatly facilitate their proper application and evaluation to various reactors and reaction systems. Consequently, the following Sections 8.2, 8.3, 8.4, 8.6, and 8.8 will derive the equations given in Table 8-1.

Why bother?
Here is why!!

Why bother to derive the equations in Table 8-1? Because I have found that students can *apply* these equations *much* more accurately to solve reaction engineering problems with heat effects if they have gone through the derivation to understand the assumptions and manipulations used in arriving at the equations in Table 8.1.

8.2.4 Dissecting the Steady-State Molar Flow Rates to Obtain the Heat of Reaction

To begin our journey, we start with the energy balance equation (8-9) and then proceed to finally arrive at the equations given in Table 8-1 by first dissecting two terms.

1. The molar flow rates, F_i and F_{i0}
2. The molar enthalpies, H_i, $H_{i0}[H_i \equiv H_i(T)$, and $H_{i0} \equiv H_i(T_0)]$

Interactive

Computer Modules
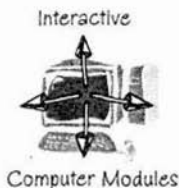
An animated version of what follows for the derivation of the energy ance can be found in the reaction engineering modules "Heat Effects 1" "Heat Effects 2" on the CD-ROM. Here equations move around the sc making substitutions and approximations to arrive at the equations show Table 8-1. Visual learners find these two ICMs a useful resource.

We will now consider flow systems that are operated at steady state. steady-state energy balance is obtained by setting $(d\hat{E}_{sys}/dt)$ equal to zer Equation (8-9) in order to yield

Steady-state energy balance

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_{i0}H_{i0} - \sum_{i=1}^{n} F_iH_i = 0 \qquad (8$$

To carry out the manipulations to write Equation (8-10) in terms of the he reaction, we shall use the generalized reaction

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D \qquad ($$
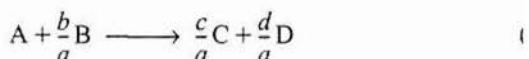
The inlet and outlet summation terms in Equation (8-10) are expanded, res tively, to

In: $\quad \Sigma H_{i0}F_{i0} = H_{A0}F_{A0} + H_{B0}F_{B0} + H_{C0}F_{C0} + H_{D0}F_{D0} + H_{I0}F_{I0} \qquad (8$

and

Out: $\quad \Sigma H_iF_i = H_AF_A + H_BF_B + H_CF_C + H_DF_D + H_IF_I \qquad (8$

We first express the molar flow rates in terms of conversion.

In general, the molar flow rate of species i for the case of no accun tion and a stoichiometric coefficient v_i is

$$F_i = F_{A0}(\Theta_i + v_iX)$$

Specifically, for Reaction (2-2), $A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D$, we have

$$F_A = F_{A0}(1 - X)$$

Steady-state operation

$$F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

$$F_C = F_{A0}\left(\Theta_C + \frac{c}{a}X\right) \qquad \text{where } \Theta_i = \frac{F_{i0}}{F_{A0}}$$

$$F_D = F_{A0}\left(\Theta_D + \frac{d}{a}X\right)$$

$$F_I = \Theta_I F_{A0}$$

We can substitute these symbols for the molar flow rates into Equations (8-11) and (8-12), then subtract Equation (8-12) from (8-11) to give

$$
\sum_{i=1}^{n} H_{i0}F_{i0} - \sum_{i=1}^{n} F_i H_i = F_{A0}[(H_{A0}-H_A)+(H_{B0}-H_B)\Theta_B
$$

$$
+ (H_{C0}-H_C)\Theta_C + (H_{D0}-H_D)\Theta_D + (H_{I0}-H_I)\Theta_I]
$$

$$
- \underbrace{\left(\frac{d}{a}H_D + \frac{c}{a}H_C - \frac{b}{a}H_B - H_A\right)}_{\Delta H_{Rx}} F_{A0}X \tag{8-13}
$$

The term in parentheses that is multiplied by $F_{A0}X$ is called the **heat of reaction** at temperature T and is designated ΔH_{Rx}.

<div style="margin-left:0">Heat of reaction at
temperature T</div>

$$
\boxed{\Delta H_{Rx}(T) = \frac{d}{a}H_D(T) + \frac{c}{a}H_C(T) - \frac{b}{a}H_B(T) - H_A(T)} \tag{8-14}
$$

All of the enthalpies (e.g., H_A, H_B) are evaluated at the temperature at the outlet of the system volume, and, consequently, $[\Delta H_{Rx}(T)]$ is the heat of reaction at the specific temperature T. The heat of reaction is always given per mole of the species that is the basis of calculation [i.e., species A (joules per mole of A reacted)].

Substituting Equation (8-14) into (8-13) and reverting to summation notation for the species, Equation (8-13) becomes

$$
\sum_{i=1}^{n} F_{i0}H_{i0} - \sum_{i=1}^{n} F_i H_i = F_{A0} \sum_{i=1}^{n} \Theta_i (H_{i0}-H_i) - \Delta H_{Rx}(T)F_{A0}X \tag{8-15}
$$

Combining Equations (8-10) and (8-15), we can now write the *steady-state* [i.e., $(d\hat{E}_{sys}/dt = 0)$] energy balance in a more usable form:

<div style="margin-left:0">One can use this
form of the steady-
state energy
balance if the
enthalpies are
available.</div>

$$
\boxed{\dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1}^{n} \Theta_i (H_{i0}-H_i) - \Delta H_{Rx}(T)F_{A0}X = 0} \tag{8-16}
$$

If a *phase change* takes place during the course of a reaction, this form of the energy balance [i.e., Equation (8-16)] must be used (e.g., Problem 8-4$_c$).

8.2.5 Dissecting the Enthalpies

We are neglecting any enthalpy changes resulting from mixing so that the partial molal enthalpies are equal to the molal enthalpies of the pure components. The molal enthalpy of species i at a particular temperature and pressure, H_i, is usually expressed in terms of an *enthalpy of formation* of species i at some reference temperature T_R, $H_i^\circ(T_R)$, plus the change in enthalpy ΔH_{Q_i}, that results when the temperature is raised from the reference temperature, T_R, to some temperature T:

$$H_i = H_i^\circ(T_R) + \Delta H_{Qi}$$

For example, if the enthalpy of formation is given at a reference temperature where the species is a solid, then the enthalpy, $H(T)$, of a gas at temperature T is

Calculating the
enthalpy when phase
changes are involved

$$
\begin{bmatrix} \text{Enthalpy of} \\ \text{species} \\ i \text{ in the gas} \\ \text{at } T \end{bmatrix}
=
\begin{bmatrix} \text{Enthalpy of} \\ \text{formation} \\ \text{of species} \\ i \text{ in the solid} \\ \text{phase} \\ \text{at } T_R \end{bmatrix}
+
\begin{bmatrix} \Delta H_Q \text{ in heating} \\ \text{solid from} \\ T_R \text{ to } T_m \end{bmatrix}
+
\begin{bmatrix} \text{Heat of} \\ \text{melting} \\ \text{at } T_m \end{bmatrix}
$$

$$
+
\begin{bmatrix} \Delta H_Q \text{ in heating} \\ \text{liquid from} \\ T_m \text{ to } T_b \end{bmatrix}
+
\begin{bmatrix} \text{Heat of} \\ \text{vaporation} \\ \text{at } T_b \end{bmatrix}
+
\begin{bmatrix} \Delta H_Q \text{ in heating} \\ \text{gas from} \\ T_b \text{ to } T \end{bmatrix}
$$

$$H_i(T) = H_i^\circ(T_R) + \int_{T_R}^{T_m} C_{Ps_i} dT + \Delta H_{mi}(T_m) + \int_{T_m}^{T_b} C_{Pg_i} dT + \Delta H_{vi}(T_b) + \int_{T_b}^{T} C_{Pg_i} dT \quad (8\text{-}17)$$

Here, in addition to the increase in the enthalpies of the solid, liquid, and gas from the temperature increase, one must include the heat of melting at the melting point, $\Delta H_{mi}(T_m)$, and the heat of vaporization at the boiling point, $\Delta H_{vi}(T_b)$. (See Problems P8-4$_C$ and P9-4$_B$.)

The reference temperature at which H_i° is given is usually 25°C. For any substance i that is being heated from T_1 to T_2 in the *absence* of phase change,

No phase change

$$\Delta H_{Qi} = \int_{T_1}^{T_2} C_{P_i} dT \quad (8\text{-}18)$$

Typical units of the heat capacity, C_{P_i}, are

$$(C_{P_i}) = \frac{J}{(\text{mol of } i)(K)} \quad \text{or} \quad \frac{\text{Btu}}{(\text{lb mol of } i)(°R)} \quad \text{or} \quad \frac{\text{cal}}{(\text{mol of } i)(K)}$$

A large number of chemical reactions carried out in industry do not involve phase change. Consequently, we shall further refine our energy balance to apply to *single-phase* chemical reactions. Under these conditions, the enthalpy of species i at temperature T is related to the enthalpy of formation at the reference temperature T_R by

$$H_i = H_i^\circ(T_R) + \int_{T_R}^{T} C_{P_i} dT \quad (8\text{-}19)$$

If phase changes do take place in going from the temperature for which the enthalpy of formation is given and the reaction temperature T, Equation (8-17) must be used instead of Equation (8-19).

The heat capacity at temperature T is frequently expressed as a quadratic function of temperature. that is,

$$C_{P_i} = \alpha_i + \beta_i T + \gamma_i T^2 \tag{8-20}$$

However, while the text will consider only **constant heat capacities**, the PRS R8.3 on the CD-ROM has examples with variable heat capacities.

To calculate the change in enthalpy $(H_i - H_{i0})$ when the reacting fluid is heated without phase change from its entrance temperature, T_{i0}, to a temperature T, we integrate Equation (8-19) for constant C_{Pi} to write

$$H_i - H_{i0} = \left[H_i^\circ(T_R) + \int_{T_R}^{T} C_{P_i}\, dT \right] - \left[H_i^\circ(T_R) + \int_{T_R}^{T_{i0}} C_{P_i}\, dT \right]$$

$$= \int_{T_{i0}}^{T} C_{P_i}\, dT = C_{P_i}[T - T_{i0}] \tag{8-21}$$

Substituting for H_i and H_{i0} in Equation (8-16) yields

Result of dissecting the enthalpies

$$\boxed{\dot{Q} - \dot{W}_s - F_{A0} \sum_{i=1}^{n} \Theta_i C_{P_i}[T - T_{i0}] - \Delta H_{Rx}(T) F_{A0} X = 0} \tag{8-22}$$

8.2.6 Relating $\Delta H_{Rx}(T)$, $\Delta H_{Rx}^\circ(T_R)$, and ΔC_p

The heat of reaction at temperature T is given in terms of the enthalpy of each species at temperature T, that is,

$$\Delta H_{Rx}(T) = \frac{d}{a} H_D(T) + \frac{c}{a} H_C(T) - \frac{b}{a} H_B(T) - H_A(T) \tag{8-14}$$
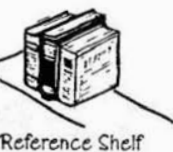
where the enthalpy of each species is given by

$$H_i = H_i^\circ(T_R) + \int_{T_R}^{T} C_{P_i}\, dT = H_i^\circ(T_R) + C_{P_i}(T - T_R) \tag{8-19}$$

If we now substitute for the enthalpy of each species, we have

$+\frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$

$$\boxed{\begin{aligned} \Delta H_{Rx}(T) &= \left[\frac{d}{a} H_D^\circ(T_R) + \frac{c}{a} H_C^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R) \right] \\ &\quad + \left[\frac{d}{a} C_{P_D} + \frac{c}{a} C_{P_C} - \frac{b}{a} C_{P_B} - C_{P_A} \right](T - T_R) \end{aligned}} \tag{8-23}$$

The first set of terms on the right-hand side of Equation (8-23) is the heat of reaction at the reference temperature T_R,

$$\boxed{\Delta H_{Rx}^\circ(T_R) = \frac{d}{a} H_D^\circ(T_R) + \frac{c}{a} H_C^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R)} \tag{8-24}$$

One can look up the heats of formation at T_R, then calculate the heat of reaction at this reference temperature.

The enthalpies of formation of many compounds, $H_i^\circ(T_R)$, are usually ta lated at 25°C and can readily be found in the *Handbook of Chemistry Physics*[1] and similar handbooks. For other substances, the heat of combust (also available in these handbooks) can be used to determine the enthalpy formation. The method of calculation is described in these handbooks. Fr these values of the standard heat of formation, $H_i^\circ(T_R)$, we can calculate heat of reaction at the reference temperature T_R from Equation (8-24).

The second term in brackets on the right-hand side of Equation (8-23 the overall change in the heat capacity per mole of A reacted, ΔC_P,

$$\Delta C_P = \frac{d}{a}C_{P_D} + \frac{c}{a}C_{P_C} - \frac{b}{a}C_{P_B} - C_{P_A} \qquad (8\text{-}$$

Combining Equations (8-25), (8-24), and (8-23) gives us

Heat of reaction at temperature T

$$\Delta H_{Rx}(T) = \Delta H_{Rx}^\circ(T_R) + \Delta C_P(T - T_R) \qquad (8\text{-}$$

Equation (8-26) gives the heat of reaction at any temperature T in ter of the heat of reaction at a reference temperature (usually 298 K) and the Δ term. Techniques for determining the heat of reaction at pressures above atr spheric can be found in Chen.[2] For the reaction of hydrogen and nitrogen 400°C, it was shown that the heat of reaction increased by only 6% as the pr sure was raised from 1 atm to 200 atm!

Example 8–2 Heat of Reaction

Calculate the heat of reaction for the synthesis of ammonia from hydrogen nitrogen at 150°C in kcal/mol of N_2 reacted *and also* in kJ/mol of H_2 reacted.

Solution

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Calculate the heat of reaction at the reference temperature using the heats of for tion of the reacting species obtained from *Perry's Handbook*[3] or the *Handbool Chemistry and Physics*.

$$\Delta H_{Rx}^\circ(T_R) = 2H_{NH_3}^\circ(T_R) - 3H_{H_2}^\circ(T_R) - H_{N_2}^\circ(T_R) \qquad (E8\text{-})$$

Note:

The heats of formation of the elements (H_2, N_2) are **zero** at 25°C.

[1] *CRC Handbook of Chemistry and Physics* (Boca Raton, Fla.: CRC Press, 2003).

[2] N. H. Chen, *Process Reactor Design* (Needham Heights, Mass.: Allyn and Bac 1983), p. 26.

[3] R. Perry, D. W. Green, and D. Green, eds., *Perry's Chemical Engineers' Handbc* 7th ed. (New York: McGraw-Hill, 1999).

$$\Delta H_{Rx}^{\circ}(T_R) = 2H_{NH_3}^{\circ}(T_R) - 3(0) - 0 = 2H_{NH_3}^{\circ}$$

$$= 2(-11,020) \frac{cal}{mol\ N_2}$$

$$= -22,040\ cal/mol\ N_2\ reacted$$

or

$$\Delta H_{R:.}^{\circ}(298\ K) = -22.04\ kcal/mol\ N_2\ reacted$$

$$= -92.22\ kJ/mol\ N_2\ reacted$$

The minus sign indicates the reaction is *exothermic*. If the heat capacities are constant or if the mean heat capacities over the range 25 to 150°C are readily available, the determination of ΔH_{Rx} at 150°C is quite simple.

Exothermic reaction

$$C_{P_{H_2}} = 6.992\ cal/mol\ H_2 \cdot K$$

$$C_{P_{N_2}} = 6.984\ cal/mol\ N_2 \cdot K$$

$$C_{P_{NH_3}} = 8.92\ cal/mol\ NH_3 \cdot K$$

$$\Delta C_P = 2C_{P_{NH_3}} - 3C_{P_{H_2}} - C_{P_{N_2}} \qquad (E8-2.2)$$

$$= 2(8.92) - 3(6.992) - 6.984$$

$$= -10.12\ cal/mol\ N_2\ reacted \cdot K$$

$$\Delta H_{Rx}(T) = \Delta H_{Rx}^{\circ}(T_R) + \Delta C_P(T - T_R) \qquad (8-26)$$

$$\Delta H_{Rx}(423\ K) = -22,040 + (-10.12)(423 - 298)$$

$$= -23,310\ cal/mol\ N_2 = -23.31\ kcal/mol\ N_2$$

$$= -23.3\ kcal/mol\ N_2 \times 4.184\ kJ/kcal$$

$$= -97.5\ kJ/mol\ N_2$$

(Recall: 1 kcal = 4.184 kJ)

The heat of reaction based on the moles of H_2 reacted is

$$\Delta H_{Rx}(423\ K) = \frac{1\ mol\ N_2}{3\ mol\ H_2}\left(-97.53\ \frac{kJ}{mol\ N_2}\right)$$

$$= -32.51\ \frac{kJ}{mol\ H_2}\ at\ 423\ K$$

Now that we see that we can calculate the heat of reaction at any temperature, let's substitute Equation (8-22) in terms of $\Delta H_R(T_R)$ and ΔC_P [i.e., Equation (8-26)]. The steady-state energy balance is now

Energy balance in terms of mean or constant heat capacities

$$\boxed{\dot{Q} - \dot{W}_s - F_{A0}\sum_{i=1}^{n}\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H_{Rx}^{\circ}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0}\qquad (8-27)$$

From here on, for the sake of brevity we will let

$$\Sigma = \sum_{i=1}^{n}$$

unless otherwise specified.

In most systems, the work term, $\dot{W}_s$, can be neglected (note the exception in the California Registration Exam Problem P8-5$_B$ at the end of this chapter) and the energy balance becomes

$$\dot{Q} - F_{A0}\Sigma\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H_{Rx}^{\circ}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0 \quad (8\text{-}28)$$

In almost all of the systems we will study, the reactants will be entering the system at the same temperature; therefore, $T_{i0} = T_0$.

We can use Equation (8-28) to relate temperature and conversion and then proceed to evaluate the algorithm described in Example 8-1. However, unless the reaction is carried out adiabatically, Equation (8-28) is still difficult to evaluate because in nonadiabatic reactors, the heat added to or removed from the system varies along the length of the reactor. This problem does not occur in adiabatic reactors, which are frequently found in industry. Therefore, the adiabatic tubular reactor will be analyzed first.

8.3 Adiabatic Operation

Reactions in industry are frequently carried out adiabatically with heating or cooling provided either upstream or downstream. Consequently, analyzing and sizing adiabatic reactors is an important task.

8.3.1 Adiabatic Energy Balance

In the previous section, we derived Equation (8-28), which relates conversion to temperature and the heat added to the reactor, $\dot{Q}$. Let's stop a minute and consider a system with the special set of conditions of no work, $\dot{W}_s = 0$, adiabatic operation $\dot{Q} = 0$, and then rearrange (8-27) into the form

For adiabatic operation, Example 8.1 can now be solved!

$$X = \frac{\Sigma\,\Theta_i C_{P_i}(T - T_{i0})}{-[\Delta H_{Rx}^{\circ}(T_R) + \Delta C_P(T - T_R)]} \quad (8\text{-}29)$$

In many instances, the $\Delta C_P(T - T_R)$ term in the denominator of Equation (8-29) is negligible with respect to the ΔH_{Rx}° term, so that a plot of X vs. T will usually be linear, as shown in Figure 8-2. To remind us that the conversion in

this plot was obtained from the energy balance rather than the mole balance, it is given the subscript EB (i.e., X_{EB}) in Figure 8-2. Equation (8-29) applies to a CSTR, PFR, PBR, and also to a batch (as will be shown in Chapter 9). For $\dot{Q} = 0$ and $\dot{W}_s = 0$, Equation (8-29) gives us the explicit relationship between X and T needed to be used in conjunction with the mole balance to solve reaction engineering problems as discussed in Section 8.1.
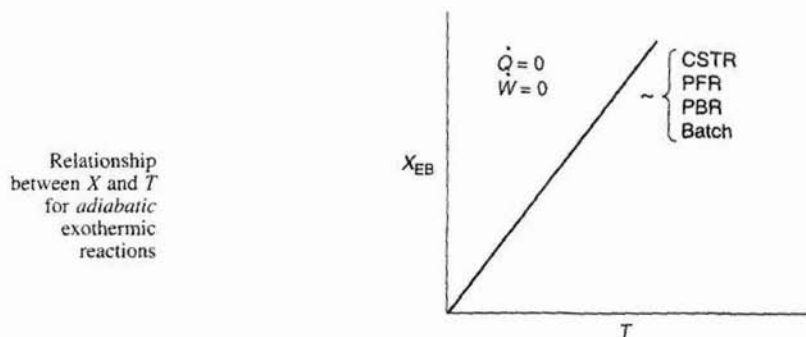
Relationship
between X and T
for *adiabatic*
exothermic
reactions

Figure 8-2   Adiabatic temperature–conversion relationship.

8.3.2 Adiabatic Tubular Reactor

We can rearrange Equation (8-29) to solve for temperature as a function of conversion; that is

Energy balance for
adiabatic operation
of PFR

$$T = \frac{X[-\Delta H_{Rx}(T_R)] + \Sigma\Theta_i C_{P_i}T_0 + X\Delta C_P T_R}{\Sigma\Theta_i C_{P_i} + X\Delta C_P} \qquad (8\text{-}30)$$

This equation will be coupled with the differential mole balance

$$F_{A0}\frac{dX}{dV} = -r_A(X,T)$$

to obtain the temperature, conversion, and concentration profiles along the length of the reactor. One way of analyzing this combination is to use Equation (8-30) to construct a table of T as a function of X. Once we have T as a function of X, we can obtain $k(T)$ as a function of X and hence $-r_A$ as a function of X alone. We could then use the procedures detailed in Chapter 2 to size the

different types of reactors; however, software packages such as Polymath a
MATLAB can be used to solve the coupled energy balance and mole balan
differential equations more easily.

The algorithm for solving PFRs and PBRs operated adiabatically
shown in Table 8-2.

TABLE 8-2A.   ADIABATIC PFR/PBR ALGORITHM

The elementary reversible gas-phase reaction

$$A \rightleftharpoons B$$

is carried out in a PFR in which pressure drop is neglected and pure A enters the reactor.

Mole Balance:
$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \tag{T8-2.1}$$

Rate Law:
$$-r_A = k\left(C_A - \frac{C_B}{K_C}\right) \tag{T8-2.2}$$

with
$$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] \tag{T8-2.3}$$

$$K_C = K(T_2) \exp\left[\frac{\Delta H_{Rx}^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right] \tag{T8-2.4}$$

Stoichiometry: Gas, $\varepsilon = 0$, $P = P_0$

$$C_A = C_{A0}(1 - X)\frac{T_0}{T} \tag{T8-2.5}$$

$$C_B = C_{A0}X\frac{T_0}{T} \tag{T8-2.6}$$

Combine:
$$-r_A = kC_{A0}\left[(1 - X) - \frac{X}{K_C}\right]\frac{T_0}{T} \tag{T8-2.7}$$

Energy Balance:
To relate temperature and conversion, we apply the energy balance to an adia-
batic PFR. If all species enter at the same temperature, $T_{i0} = T_0$.
Solving Equation (8-29), with $\dot{Q} = 0$, $\dot{W}_s = 0$, to obtain T as a function of
conversion yields

$$T = \frac{X[-\Delta H_{Rx}^\circ(T_R)] + \Sigma\,\Theta_i C_{P_i} T_0 + X\,\Delta C_P T_R}{\Sigma\,\Theta_i C_{P_i} + X\,\Delta C_P} \tag{T8-2.8}$$

If pure A enters and **iff** $\Delta C_P = 0$, then

$$T = T_0 + \frac{X[-\Delta H_{Rx}^\circ(T_R)]}{C_{P_A}} \tag{T8-2.9}$$

Equations (T8-2.1) through (T8-2.9) can easily be solved using either Simp-
son's rule or an ODE solver.

TABLE 8-2B.   SOLUTION PROCEDURES FOR ADIABATIC PFR/PBR REACTOR

The numerical technique is presented to provide insight to how the variables (k, K_c, etc.) change as we move down the reactor from $V = 0$ and $X = 0$ to V_f and X_f.

A. Numerical Technique

Integrating the PFR mole balance,

$$V = \int_0^{X_3} \frac{F_{A0}}{-r_A} dX \qquad (T8\text{-}2.10)$$

1. Set $X = 0$.
2. Calculate T using Equation (T8-2.9).
3. Calculate k using Equation (T8-2.3).
4. Calculate K_C using Equation (T8-2.4).
5. Calculate T_0/T (gas phase).
6. Calculate $-r_A$ using Equation (T8-2.7).
7. Calculate $(F_{A0}/-r_A)$.
8. If X is less than the X_3 specified, increment X (i.e., $X_{i+1} = X_i + \Delta X$) and go to Step 2.
9. Prepare table of X vs. $(F_{A0}/-r_A)$.
10. Use numerical integration formulas given in Appendix A, for example,

Use evaluation techniques discussed in Chapter 2.

$$V = \int_0^{X_3} \frac{F_{A0}}{-r_A} dX = \frac{3}{8} h \left[\frac{F_{A0}}{-r_A(X=0)} + 3\frac{F_{A0}}{-r_A(X_1)} + 3\frac{F_{A0}}{-r_A(X_2)} + \frac{F_{A0}}{-r_A(X_3)} \right]$$

$$(T8\text{-}2.11)$$

with $h = \dfrac{X_3}{3}$

B. Ordinary Differential Equation (ODE) Solver

1. $$\frac{dX}{dV} = \frac{kC_{A0}}{F_{A0}} \left[(1-X) - \frac{X}{K_C} \right] \frac{T_0}{T} \qquad (T8\text{-}2.12)$$

Almost always we will use an ODE solver.

2. $$k = k_1(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \qquad (T8\text{-}2.13)$$

3. $$K_C = K_{C2}(T_2) \exp \left[\frac{\Delta H_{Rx}}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right] \qquad (T8\text{-}2.14)$$

4. $$T = T_0 + \frac{X[-\Delta H_{Rx}(T_R)]}{C_{P_A}} \qquad (T8\text{-}2.15)$$

5. Enter parameter values k_1, E, R, K_{C2}, $\Delta H_{Rx}(T_R)$, C_{P_A}, C_{A0}, T_0, T_1, T_2.
6. Enter in intial values $X = 0$, $V = 0$ and final value reactor volume, $V = V_f$.