
2

STOICHIOMETRY

This chapter covers a tool used extensively in the analysis of processes involving chemical reactions—stoichiometry. Literally, stoichiometry means measurement of elements. In practice, stoichiometry is an accounting system that provides a framework to describe chemical transformations. Stoichiometry keeps track of the amount of species that are being formed and consumed and enables us to calculate the composition of chemical reactors. This chapter describes a systematic stoichiometric methodology that enables us to handle any reacting system with multiple chemical reactions. Specifically, the methodology indicates how many chemical reactions should be considered to determine all the state quantities of the reactor and the number of design equations necessary to describe the reactor operation. It also indicates what set of chemical reactions is most suitable for the design formulation of chemical reactors. The stoichiometric methodology presented in this chapter is used throughout the text, and therefore a good knowledge of its key definitions and structure is essential.

2.1 FOUR CONTEXTS OF CHEMICAL REACTION

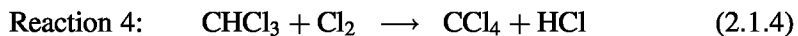
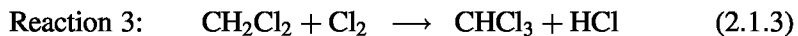
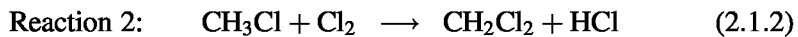
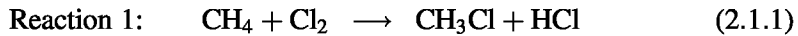
Before we begin the discussion of stoichiometry, it is important to recognize that the term *chemical reaction* is used in four contexts:

- As a chemical formula
- As stoichiometric relation between the species

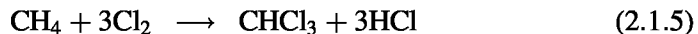
- As a presentation of the pathway of the chemical transformation
- As an elementary reaction

The *chemical formula* is essentially the selection of a framework (or a “basis”) for the calculation of chemical transformations. It is discussed in details in Section 2.2.

A *stoichiometric relation* is merely a representation of the proportion between chemical species. To illustrate, consider the chlorination of methane to produce trichloro methane. When methane and chlorine are contacted in a reactor, the following chemical reactions occur:



To relate the amount of trichloro methane (the desirable product) generated to the reactants (methane and chlorine), we add the first three reactions to obtain the following stoichiometric relation:



Reaction 2.1.5 does not take place, rather it merely provides a relation between the reactants and the desired product. Usually, stoichiometric relations are used to determine the limiting reactant and the yield of the desirable products.

Reaction pathways represent the routes by which the chemical species are formed and consumed. For example, in the methane chlorination above, the four reactions indicate the pathways by which the various species are generated or consumed. In practice, each of these reactions may involve the formation and destruction of intermediates and unstable species (e.g., free radicals). The rates of the reaction pathways should be known in order to determine the rate of formation (or depletion) of the chemical species in the reactor.

An *elementary reaction* is a representation of the interactions between the species on the molecular level. Elementary reactions are used to describe the mechanisms by which species are formed. The term *elementary* is used because each reactant is assumed to be in its most simple form.

2.2 CHEMICAL FORMULAS AND STOICHIOMETRIC COEFFICIENTS

The first step in analyzing any engineering problem is to define the system and select the framework for solving the problem. This step is commonly referred to

as selecting a *basis* for the calculation. A similar step is required when dealing with processes involving chemical reactions. A chemical transformation can be expressed in many forms called chemical formulas, and we have to select one of them as the framework (or basis) for the analysis. To illustrate this point, consider, for example, the reaction between oxygen and carbon monoxide to form carbon dioxide. This chemical transformation can be described by one of many chemical formulas, such as



or, if you wish to do so,



Each chemical formula represents a given amount of mass. For example, Reaction 2.2.1 represents 44 *units* of mass, Reaction 2.2.2 represents 88 *units* of mass, and Reaction 2.2.3 represents 880 *units* of mass. We select one of these chemical formulas and relate all relevant quantities (heat of reaction, rate of reaction, etc.) to it.

We adopt common conventions concerning chemical reactions. Each chemical reaction has an arrow indicating the direction of the chemical transformation and clearly defines the reactants and products of the reaction. Species to the left of the arrow are called *reactants*, and those on the right are called *products*. Reversible reactions are treated as two distinct reactions, one forward and one backward. The arrow also serves as an equality sign for the total *mass* represented by the chemical formula. Thus, each chemical reaction should be balanced; an unbalanced chemical reaction violates the conservation of mass principle.

Once the specific chemical formula is selected, the stoichiometric coefficients of the individual species are defined as follows: For each product species, the stoichiometric coefficient is identical to the coefficient of that species in the chemical formula. For each reactant, the stoichiometric coefficient is the negative value of the coefficient of that species in the chemical reaction. If a species does not participate in the reaction, its stoichiometric coefficient is zero.

Consider the general chemical reaction



The species' stoichiometric coefficients are: $s_A = -a$, $s_B = -b$, $s_C = c$, $s_D = d$, and, for any inert species I , $s_I = 0$. By defining the stoichiometric coefficients in this manner, chemical reactions are expressed as homogeneous algebraic equations. For example, Reaction 2.2.4 is expressed as

$$-aA - bB + cC + dD = 0$$

The advantage of doing so will become clear later when we consider multiple simultaneous chemical reactions.

Each chemical reaction is characterized by the sum of its stoichiometric coefficients,

$$\Delta = \sum_j^J s_j = s_A + s_B + \dots \quad (2.2.5)$$

where J indicates the number of species. The parameter Δ indicates the change in the number of moles per “unit” of the chemical formula selected. For example, for Reaction 2.2.4, $\Delta = (-a) + (-b) + c + d$. As we will see later, this parameter is extremely useful in the design formulation of chemical reactors because it enables us to express the changes in the total number of moles in the reactor.

The following points concerning stoichiometry are worth noting:

1. The stoichiometric coefficient of species j , s_j , is dimensionless, expressed in (moles of j)/(moles of reaction extent), as discussed in Section 2.3.
2. The mathematical condition for a balanced chemical reaction is

$$\sum_j^J s_j(\text{MW}_j) = 0 \quad j = A, B, \dots \quad (2.2.6)$$

where s_j and MW_j are, respectively, the stoichiometric coefficient and the molecular mass of species j .

3. Usually, for convenience, we write chemical equations such that either the largest species' coefficient is one (as in Reaction 2.2.1) or the smallest species' coefficient is the smallest integer (as in Reaction 2.2.2).
4. The numerical values of the species' coefficients of the reaction depend on the specific chemical formula selected. However, the ratio of any two coefficients is the same, regardless of the chemical formula used.

2.3 EXTENT OF A CHEMICAL REACTION

Once the chemical formula is selected, the progress of the chemical reaction can be quantified. It is convenient to express the progress of the chemical reaction in terms of the chemical formula selected. To do so we define a quantity called the reaction extent.

Definition The extent of a chemical reaction is one unit of the chemical formula selected.

The extent represents a certain amount of mass, and its units are mole extent. For example, for Reaction 2.2.1, one extent means that *one mole* of CO reacts with *half a mole* of O₂ to form *one mole* of CO₂ and it represents 44 *units* of mass.

The extent of a chemical reaction is determined from the number of moles of any species, say species j , formed (or depleted) by the reaction

$$X \equiv \frac{\text{Moles of species } j \text{ formed by the reaction}}{\text{Stoichiometric coefficient of species } j} = \frac{n_j - n_{j0}}{s_j} \quad (2.3.1)$$

For example, for Reaction 2.2.4, the extent is calculated by one of the following relations:

$$X = \frac{n_A - n_{A0}}{-a} = \frac{n_B - n_{B0}}{-b} = \frac{n_C - n_{C0}}{c} = \frac{n_D - n_{D0}}{d}$$

The following points concerning the extent of a chemical reaction are worth noting:

1. The extent is a calculated quantity, and in order to obtain it we have to derive relations between the extent and measurable quantities (see Example 2.3). However, when the chemical extent is known, the amount of all species can be readily calculated.
2. The heat of reaction of a chemical reaction is expressed in terms of energy per mole extent.

Next we derive relationships between the species composition in chemical reactors to the chemical reactions taking place in them. For convenience, we distinguish between two modes of reactor operations: batch operation (batch reactors) and steady continuous operation (flow reactors), shown schematically in Figure 2.1. In batch reactors, reactants are charged into the reactor and, after a certain period of time, the products are discharged from the reactor; hence, the chemical reactions take place over time. In steady-flow reactors, reactants are continuously fed into the reactor, and products are continuously withdrawn from the reactor outlet; hence, the chemical reactions take place over space.

First, consider a batch reactor where n_R simultaneous chemical reactions take place and focus attention on species j . The total number of moles of species j in

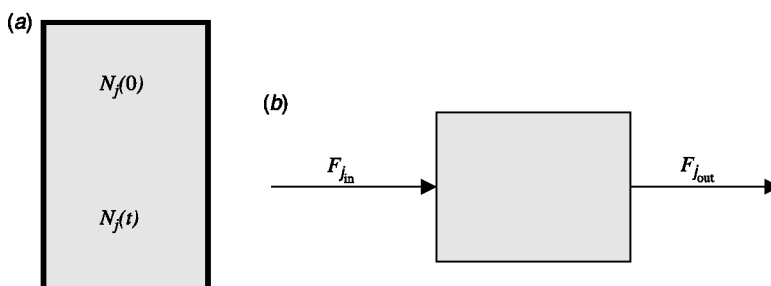


Figure 2.1 Modes of reactor operations: (a) batch reactor and (b) flow reactor.

the reactor at time t , $N_j(t)$, is related to the number of moles of species j formed by each of the individual chemical reactions

$$N_j(t) - N_j(0) = (n_j - n_{j_0})_1 + \cdots + (n_j - n_{j_0})_i + \cdots + (n_j - n_{j_0})_{n_R} \quad (2.3.2)$$

where $(n_j - n_{j_0})_i$ is the number of moles of species j formed by the i th chemical reaction in time t . Note that species j may be formed in some reactions and consumed in others. As will be discussed in Section 2.4, to determine the species composition (and, in general, all other state quantities), only a set of *independent* reactions should be considered, and *not* all the chemical reactions that take place. Hence, using Eq. 2.3.1, Eq. 2.3.2 reduces to

$$N_j(t) = N_j(0) + \sum_m^{n_I} (s_j)_m X_m(t) \quad j = A, B, \dots \quad (2.3.3)$$

where m is an index for independent reactions, $(s_j)_m$ is the stoichiometric coefficient of species j in the m th independent reaction, $X_m(t)$ is the extent of the m th independent reaction at time t , and n_I is the number of independent reactions. Equation 2.3.3 relates the species composition in a batch reactor to the extents of the independent chemical reactions.

To relate the total number of moles in the reactor at time t , $N_{\text{tot}}(t)$ to the extents, we write Eq. 2.2.3 for each species in the reactor and sum the relations, and then collect terms by the individual reaction extents,

$$N_{\text{tot}}(t) = N_{\text{tot}}(0) + \sum_m^{n_I} \Delta_m X_m(t) \quad (2.3.4)$$

where Δ_m is the change in the number of moles per unit extent of the m th independent chemical reaction, defined by Eq. 2.2.5, and $N_{\text{tot}}(0)$ is the total number of moles initially in the reactor.

When a *single* chemical reaction takes place, Eq. 2.3.3 reduces to

$$N_j(t) = N_j(0) + s_j X(t) \quad j = A, B, \dots \quad (2.3.5)$$

Writing Eq. 2.3.5 for any two species, say A and j ,

$$N_j(t) = N_j(0) + \frac{s_j}{s_A} [N_A(t) - N_A(0)] \quad (2.3.6)$$

Equation 2.3.6 provides an algebraic relation between the number of moles of any two species in the reactor at time t without calculating the extent itself. To determine the total number of moles in a batch reactor at time t , $N_{\text{tot}}(t)$, use Eq. 2.3.4,

which reduces to

$$N_{\text{tot}}(t) = N_{\text{tot}}(0) + \Delta X(t) \quad (2.3.7)$$

To determine $N_{\text{tot}}(t)$ without calculating the extent explicitly, take the summation of Eq. 2.3.6 over all species,

$$N_{\text{tot}}(t) = N_{\text{tot}}(0) + \frac{\Delta}{s_A} [N_A(t) - N_A(0)] \quad (2.3.8)$$

Consider now a *steady-flow* reactor and conduct a species balance over the reactor. At steady state, the molar flow rate of species j at the reactor outlet is equal to the molar flow rate of species j at the reactor inlet plus the rate species j is being generated inside the reactor by the reaction, G_j ,

$$F_{j,\text{out}} = F_{j,\text{in}} + G_j \quad j = A, B, \dots \quad (2.3.9)$$

The generation term, G_j , is discussed in detail in Chapter 4; here, we focus on its relation to the extents of the chemical reactions. The rate species j is being generated by each reaction is expressed in a relation similar to Eq. 2.3.2. Differentiating Eq. 2.3.3 with respect to time, the rate of generation of species j is

$$G_j = \sum_m^{n_I} (s_j)_m \dot{X}_m \quad j = A, B, \dots \quad (2.3.10)$$

where \dot{X}_m is the extent of the m th independent reaction converted per unit time in the reactor. Substituting Eq. 2.3.10 into Eq. 2.3.9,

$$F_{j,\text{out}} = F_{j,\text{in}} + \sum_m^{n_I} (s_j)_m \dot{X}_m \quad j = A, B, \dots \quad (2.3.11)$$

Summing Eq. 2.3.11 over all species, the total molar flow rate at the reactor outlet relates to the extents of the reactions by

$$F_{\text{tot,out}} = F_{\text{tot,in}} + \sum_m^{n_I} \Delta_m \dot{X}_m \quad (2.3.12)$$

where Δ_m is the change in the number of moles per unit extent of the m th independent chemical reaction, defined by Eq. 2.2.5.

For steady-flow reactors with a *single* chemical reaction, Eq. 2.3.11 reduces to

$$F_{j,\text{out}} = F_{j,\text{in}} + s_j \dot{X} \quad j = A, B, \dots \quad (2.3.13)$$

and Eq. 2.3.12 reduces to

$$F_{\text{tot,out}} = F_{\text{tot,in}} + \Delta \dot{X} \quad (2.3.14)$$

We can write Eq. 2.3.11 for any two species, say A and j , to obtain

$$F_{j,\text{out}} = F_{j,\text{in}} + \frac{S_j}{S_A} (F_{A,\text{out}} - F_{A,\text{in}}) \quad j = B, C, \dots \quad (2.3.15)$$

Taking the summation of Eq. 2.3.15 over all species,

$$F_{\text{tot,out}} = F_{\text{tot,in}} + \frac{\Delta}{S_A} (F_{A,\text{out}} - F_{A,\text{in}}) \quad (2.3.16)$$

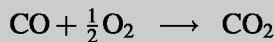
Equations 2.3.15 and 2.3.16 enable us to determine, respectively, the molar flow rate of any species and the total molar flow rate at the reactor outlet in terms of the molar flow rate of any other species without calculating the extent itself.

Example 2.1 A batch reactor contains 4 mol of CO and 1 mol of O₂. Calculate the extent of the reaction and the composition of the reactor when the reaction goes to completion.

- Use Reaction 2.2.1 and determine the species compositions from the extent.
- Use Reaction 2.2.2 and determine the species compositions without calculating the extent.

Solution

- We select the chemical formula



and its stoichiometric coefficients are

$$s_{\text{CO}} = -1 \quad s_{\text{O}_2} = -\frac{1}{2} \quad s_{\text{CO}_2} = 1 \quad \Delta = -\frac{1}{2}$$

The reaction reaches completion when one of the reactants is depleted. Assuming that CO is depleted—hence, $N_{\text{CO}}(t) = 0$, and we write Eq. 2.3.5 to determine the extent of the reaction,

$$X(t) = \frac{N_{\text{CO}}(t) - N_{\text{CO}}(0)}{s_{\text{CO}}} = \frac{0 - 4.0}{-1} = 4 \text{ mol extent}$$

Now that we know the extent of the chemical reaction, we can calculate the moles of O_2 and CO_2 in the reactor at the end of the operation by Eq. 2.3.5:

$$N_{O_2}(t) = N_{O_2}(0) + s_{O_2}X(t) = 1 + (-0.5)(4) = -1 \text{ mol}$$

$$N_{CO_2}(t) = N_{CO_2}(0) + s_{CO_2}X(t) = 0 + (1)(4) = 4 \text{ mol}$$

Since the number of moles of any species cannot be negative, obtaining such values is an indication that there is an error in the calculation, or that it is based on incorrect information. The error here is, of course, the assumption that the CO is depleted before the oxygen, while actually oxygen is depleted first. Hence, to determine the extent at completion, we write Eq. 2.3.5 for oxygen with $N_{O_2}(t) = 0$,

$$X(t) = \frac{N_{O_2}(t) - N_{O_2}(0)}{s_{O_2}} = \frac{0 - 1.0}{-0.5} = 2 \text{ mol extent}$$

We calculate the moles of CO and CO_2 in the reactor at the end of the operation by Eq. 2.3.5:

$$N_{CO}(t) = N_{CO}(0) + s_{CO}X(t) = 4 + (-1)(2) = 2 \text{ mol}$$

$$N_{CO_2}(t) = N_{CO_2}(0) + s_{CO_2}X(t) = 0 + (1)(2) = 2 \text{ mol}$$

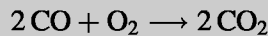
The total number of moles in the reactor at time t is

$$N_{\text{tot}}(t) = N_{O_2}(t) + N_{CO}(t) + N_{CO_2}(t) = 0 + 2 + 2 = 4 \text{ mol}$$

We can also calculate $N_{\text{tot}}(t)$ by Eq. 2.3.7:

$$N_{\text{tot}}(t) = N_{\text{tot}}(0) + \Delta X(t) = 5 + \left(-\frac{1}{2}\right)(2) = 4 \text{ mol}$$

b. In this case, we select the chemical formula



and its stoichiometric coefficients are

$$s_{CO} = -2 \quad s_{O_2} = -1 \quad s_{CO_2} = 2 \quad \Delta = -1$$

Using the given initial composition, $N_{O_2}(0) = 1 \text{ mol}$, and that at completion $N_{O_2}(t) = 0$, we write Eq. 2.3.2 for oxygen with $N_{O_2}(t) = 0$,

$$X(t) = \frac{N_{O_2}(t) - N_{O_2}(0)}{s_{O_2}} = \frac{0 - 1.0}{-1} = 1 \text{ mol extent}$$

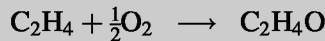
To determine the moles of CO and CO₂ without calculating the extent, Eq. 2.3.6 is used:

$$N_{\text{CO}}(t) = N_{\text{CO}}(0) + \frac{s_{\text{CO}}}{s_{\text{O}_2}} [N_{\text{O}_2}(t) - N_{\text{O}_2}(0)] = 4 + \frac{-2}{-1} (0 - 1) = 2 \text{ mol}$$

$$N_{\text{CO}_2}(t) = N_{\text{CO}_2}(0) + \frac{s_{\text{CO}_2}}{s_{\text{O}_2}} [N_{\text{O}_2}(t) - N_{\text{O}_2}(0)] = 0 + \frac{2}{-1} (0 - 1) = 2 \text{ mol}$$

Note that the final reactor composition does not depend on the specific chemical formula selected. Also, note that the value of the extent in part (b) is half the value of that in part (a).

Example 2.2 Ethylene oxide is produced by catalytic oxidation on a silver catalyst according to the following chemical reaction:



A gaseous stream consisting of 60% C₂H₄, 30% O₂, and 10% N₂ (by mole) is fed at a rate of 40 mol/min into a flow reactor operating at steady state. If the mole fraction of oxygen in the reactor effluent stream is 0.08, calculate the production rate of ethylene oxide.

Solution We select the written chemical reaction as the chemical formula; hence, the stoichiometric coefficients are

$$s_{\text{C}_2\text{H}_4} = -1 \quad s_{\text{O}_2} = -\frac{1}{2} \quad s_{\text{C}_2\text{H}_4\text{O}} = 1 \quad s_{\text{N}_2} = 0 \quad \Delta = -\frac{1}{2}$$

To determine the extent of the chemical reaction, we use the given composition of the oxygen in the exit stream. First, we use Eq. 2.3.13 to express the oxygen molar flow rate at the reactor exit:

$$(F_{\text{O}_2})_{\text{out}} = (F_{\text{O}_2})_{\text{in}} + s_{\text{O}_2} \dot{X} = (0.3)(40) + \left(-\frac{1}{2}\right) \dot{X} \quad (\text{a})$$

Next, we use Eq. 2.3.14 to express the total molar flow rate of the effluent stream:

$$(F_{\text{tot}})_{\text{out}} = (F_{\text{tot}})_{\text{in}} + \Delta \dot{X} = 40 + \left(-\frac{1}{2}\right) \dot{X} \quad (\text{b})$$

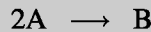
Thus, the oxygen mole fraction in the exit stream is

$$(y_{\text{O}_2})_{\text{out}} = \frac{(F_{\text{O}_2})_{\text{out}}}{(F_{\text{tot}})_{\text{out}}} = \frac{(0.3)(40) + \left(-\frac{1}{2}\right) \dot{X}}{40 + \left(-\frac{1}{2}\right) \dot{X}} = 0.08 \quad (\text{c})$$

Solving (c), $\dot{X} = 19.13$ mol/min. Now that the value of \dot{X} is known, Eq. 2.3.13 is used to calculate the production rate of ethylene oxide:

$$(F_{C_2H_4O})_{out} = (F_{C_2H_4O})_{in} + s_{C_2H_4O} \dot{X} = 0 + (1)(19.13) = 19.13 \text{ mol/min}$$

Example 2.3 An aqueous solution with a concentration of 0.8 mol/L of reactant A is fed into a flow reactor at a rate of 150 L/min. The following chemical reaction takes place in the reactor:



Conductivity cells are used to determine the compositions of the inlet and outlet streams. The conductivity reading at the inlet is 140 units and at the outlet is 90 units. If the conductivity is proportional to the sum of the concentrations of A and B, determine:

- The extent of the reaction
- The production rate of B

Solution This example illustrates how the reaction extent can be determined from a measurable quantity. The stoichiometric coefficients are

$$s_A = -2 \quad s_B = 1 \quad \Delta = -1$$

- To determine the extent, we have to derive a relationship between the extent and the conductivity. Since the conductivity is proportional to $(C_A + C_B)$, we can write

$$\frac{\lambda_{out}}{\lambda_{in}} = \frac{C_{A_{out}} + C_{B_{out}}}{C_{A_{in}} + C_{B_{in}}} = \frac{90}{140} \quad (a)$$

The species concentrations are related to the molar flow rates and the volumetric flow rates by

$$C_A = \frac{F_A}{v} \quad C_B = \frac{F_B}{v} \quad (b)$$

For liquid-phase reactions, the density is constant. Using Eq. 2.3.12 and noting that $C_{B_{in}} = 0$, the molar flow rates of species A and B at the reactor outlet are

$$F_{A_{out}} = F_{A_{in}} + s_A \dot{X} = vC_{A_{in}} + s_A \dot{X} = 120 - 2\dot{X} \quad (c)$$

$$F_{B_{out}} = F_{B_{in}} + s_B \dot{X} = vC_{B_{in}} + s_B \dot{X} = \dot{X} \quad (d)$$

Substituting (c) and (d) into (b) and the latter into (a)

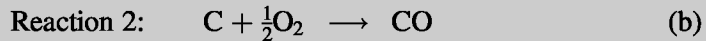
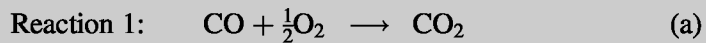
$$\frac{\lambda_{\text{out}}}{\lambda_{\text{in}}} = \frac{F_{A_{\text{in}}} - \dot{X}}{F_{A_{\text{in}}}} = \frac{120 - \dot{X}}{120} = \frac{90}{140} \quad (\text{e})$$

or

$$\dot{X} = 120 \left(1 - \frac{90}{140} \right) = 42.86 \text{ mol/min} \quad (\text{f})$$

b. Using (d), the production rate of product *B* is 42.86 mol/min.

Example 2.4 The following two simultaneous chemical reactions take place in a batch reactor:



Initially, the reactor contains 4 mol of CO, 4 mol of O₂, and 2 mol of C. At the end of the operation, the reactor contains 2 mol of CO and 2 mol of O₂. Determine:

- The composition of the reactor at the end of the operation
- The portion of O₂ that reacts in each reaction

Solution Since each chemical reaction has a species that does not participate in the other, the two reactions are independent. The stoichiometric coefficients of the species in the respective reactions are

$$(s_{\text{CO}})_1 = -1 \quad (s_{\text{O}_2})_1 = -\frac{1}{2} \quad (s_{\text{CO}_2})_1 = 1 \quad (s_{\text{C}})_1 = 0 \quad \Delta_1 = -\frac{1}{2}$$

$$(s_{\text{CO}})_2 = 1 \quad (s_{\text{O}_2})_2 = -\frac{1}{2} \quad (s_{\text{CO}_2})_2 = 0 \quad (s_{\text{C}})_2 = -1 \quad \Delta_2 = -\frac{1}{2}$$

- To determine the extents of the chemical reactions, we first write Eq. 2.3.3 for CO:

$$N_{\text{CO}}(t) = N_{\text{CO}}(0) + (s_{\text{CO}})_1 X_1(t) + (s_{\text{CO}})_2 X_2(t) = 2 \text{ mol}$$

Substituting the numerical values for the stoichiometric coefficients and the initial composition, we obtain

$$-X_1(t) + X_2(t) = -2 \quad (\text{c})$$

Next we write Eq. 2.3.3 for O_2 :

$$N_{O_2}(t) = N_{O_2}(0) + (s_{O_2})_1 X_1(t) + (s_{O_2})_2 X_2(t) = 2 \text{ mol}$$

and obtain

$$X_1(t) + X_2(t) = 4 \quad (d)$$

Solving (c) and (d), $X_1(t) = 3 \text{ mol}$ and $X_2(t) = 1 \text{ mol}$. Now that the extents of the two chemical reactions are known, we can calculate the amount of C and CO in the reactor. Using Eq. 2.3.3,

$$N_C(t) = N_C(0) + (s_C)_1 X_1(t) + (s_C)_2 X_2(t) = 1 \text{ mol}$$

$$N_{CO_2}(t) = N_{CO_2}(0) + (s_{CO_2})_1 X_1(t) + (s_{CO_2})_2 X_2(t) = 3 \text{ mol}$$

The total number of moles at time t is

$$N_{\text{tot}}(t) = N_{CO}(t) + N_{O_2}(t) + N_C(t) + N_{CO_2}(t) = 8 \text{ mol}$$

It can be calculated also by using Eq. 2.3.4,

$$N_{\text{tot}}(t) = 10.0 + \left(-\frac{1}{2}\right)(3.0) + \left(-\frac{1}{2}\right)(1.0) = 8.0 \text{ mol}$$

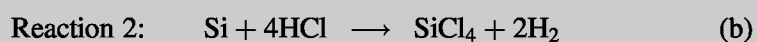
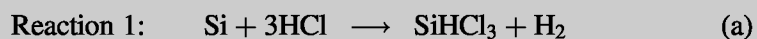
- b. To determine the number of moles of oxygen reacted by each chemical reaction we use Eq. 2.3.1:

$$(n_{O_2} - n_{O_2,0})_1 = (s_{O_2})_1 X_1(t) = \left(-\frac{1}{2}\right)(3.0) = -1.5 \text{ mol}$$

$$(n_{O_2} - n_{O_2,0})_2 = (s_{O_2})_2 X_2(t) = \left(-\frac{1}{2}\right)(1.0) = -0.5 \text{ mol}$$

The minus sign indicates that oxygen is being consumed in the chemical reactions. Thus, 75% of the oxygen is consumed by Reaction 1 and 25% by Reaction 2.

Example 2.5 Wafers for integrated circuits are made of pure silicon that is produced by reacting raw silicon with HCl to form silicon trichloride, $SiHCl_3$. The silicon trichloride is reduced later with hydrogen to provide pure silicon. At the reactor operating conditions, silicon tetrachloride, $SiCl_4$, is also formed. Molten raw silicon is fed into a flow reactor at a rate of 80 lbmol/h, and gaseous HCl is fed in proportion of 4 mol HCl per mole silicon. The reactor operates at 1250°C and the following reactions take place:



If all the silicon is consumed, and the effluent stream contains 40% H_2 (by mole), determine:

- The production rate of $SiHCl_3$
- The amount of HCl reacted

Solution Since each chemical reaction has a species that does not appear in the other, the two reactions are independent, and their stoichiometric coefficients are

$$(s_{Si})_1 = -1 \quad (s_{HCl})_1 = -3 \quad (s_{SiHCl_3})_1 = 1 \quad (s_{SiCl_4})_1 = 0 \quad (s_{H_2})_1 = 1 \quad \Delta_1 = -2$$

$$(s_{Si})_2 = -1 \quad (s_{HCl})_2 = -4 \quad (s_{SiHCl_3})_2 = 0 \quad (s_{SiCl_4})_2 = 1 \quad (s_{H_2})_2 = 2 \quad \Delta_2 = -2$$

- We select the inlet stream as a basis for the calculation; thus, $(F_{Si})_{in} = 80$ lbmol/h and $(F_{HCl})_{in} = 320$ lbmol/h, and $(F_{tot})_{in} = 400$ lbmol/h. Using Eq. 2.3.11, the production rate of $SiHCl_3$ is

$$(F_{SiHCl_3})_{out} = 0 + (s_{SiHCl_3})_1 \dot{X}_1 + (s_{SiHCl_3})_2 \dot{X}_2 = \dot{X}_1 \quad (c)$$

To obtain the extents of the reactions, we first use the fact that all the silicon is consumed in the reactor; hence, $(F_{Si})_{out} = 0$. Using Eq. 2.3.11,

$$(F_{Si})_{out} = 80 + (-1)\dot{X}_1 + (-1)\dot{X}_2$$

or

$$\dot{X}_1 + \dot{X}_2 = 80 \text{ lbmol/h} \quad (d)$$

Next we use the given composition of H_2 in the outlet stream:

$$(y_{H_2})_{out} = \frac{(F_{H_2})_{out}}{(F_{tot})_{out}} = 0.4 \quad (e)$$

Using Eq. 2.3.11,

$$(F_{H_2})_{out} = 0 + \dot{X}_1 + 2\dot{X}_2 \quad (f)$$

and using Eq. 2.3.12,

$$(F_{tot})_{out} = 400 - 2\dot{X}_1 - 2\dot{X}_2 \quad (g)$$

Substituting (f) and (g) into (e),

$$(1.8)\dot{X}_1 + (2.8)\dot{X}_2 = 160 \text{ lbmol/min} \quad (h)$$

Solving (h) and (d), $\dot{X}_1 = 64$ lbmol/h, $\dot{X}_2 = 16$ lbmol/h, and from (c), the production rate of $SiHCl_3$ is $(F_{SiHCl_3})_{out} = 64$ lbmol/h.

b. Using Eq. 2.3.11, the flow rate of HCl at the reactor exit is

$$(F_{\text{HCl}})_{\text{out}} = 320 + (-3)(64) + (-4)(16) = 64 \text{ lbmol/h} \quad (\text{i})$$

The amount of HCl reacted in the reactor is

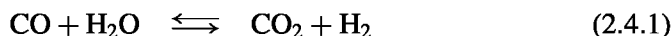
$$(F_{\text{HCl}})_{\text{in}} - (F_{\text{HCl}})_{\text{out}} = 320 - 64 = 256 \text{ lbmol/h} \quad (\text{j})$$

2.4 INDEPENDENT AND DEPENDENT CHEMICAL REACTIONS

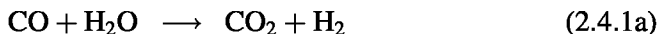
In the preceding section we noted that when multiple chemical reactions take place, only a set of independent chemical reactions should be considered to determine the species composition. As indicated, the summations in Eq. 2.3.3 and Eq. 2.3.11 are taken over a set of *independent* chemical reactions and not over *all* the reactions that take place. This point deserves a closer examination.

The concept of independent reactions, or, more accurately, independent stoichiometric relations, is an important concept in stoichiometry and reactor analysis. The number of independent reactions indicates the smallest number of stoichiometric relations needed to describe the chemical transformations that take place and to determine all the *state* quantities of a chemical reactor (species composition, temperature, enthalpy, etc.). As will be seen later, the number of independent reactions also indicates the smallest number of design equations needed to describe the reactor operation. Since state quantities are independent of the path, we can select different sets of independent reactions to determine the change from one state to another. Below, we discuss the roles of independent and dependent reactions in describing reactor operations. We also describe a procedure to determine the number of independent reactions and how to identify a set of independent reactions.

To develop insight into the concept of independent reactions, consider the following reversible chemical reaction:



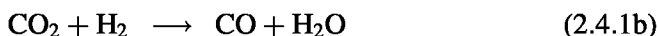
According to the stoichiometric methodology adopted here, reversible reactions are represented as two distinct reactions, a forward and a reverse. Hence, Reaction 2.4.1 is described by two chemical reactions: a forward reaction,



whose stoichiometric coefficients are

$$s_{\text{CO}} = -1 \quad s_{\text{H}_2\text{O}} = -1 \quad s_{\text{CO}_2} = 1 \quad s_{\text{H}_2} = 1$$

and a backward reaction,



whose stoichiometric coefficients are

$$s_{\text{CO}} = 1 \quad s_{\text{H}_2\text{O}} = 1 \quad s_{\text{CO}_2} = -1 \quad s_{\text{H}_2} = -1$$

Although two chemical reactions take place here, both of them provide the same information on the proportions among the individual species. This is because Reaction 2.4.1b is the reverse of Reaction 2.4.1a, and its stoichiometric coefficients have the negative values of those of Reaction 2.4.1a. In mathematical terms, we say that the two reactions are linearly dependent. Hence, only one chemical reaction (stoichiometric relation) is needed to determine the species compositions.

For more complex reaction systems, the dependency between the chemical reactions may be due to a linear combination of two (or more) independent reactions. Consider, for example, the following simultaneous chemical reactions:



A close examination of these reactions reveals that Reaction 2.4.2c is the sum of Reaction 2.4.2a and Reaction 2.4.2b. Hence, there are only two independent chemical reactions, and, to determine any state quantity, we have to consider only a set of two independent reactions. In this case, any two reactions among the three form a set of independent reactions.

To determine the number of independent reactions in a set of multiple chemical reactions, we construct the matrix of the stoichiometric coefficients for the chemical reactions. We designate a row for each chemical reaction and a column for each chemical species and write the stoichiometric coefficient of each species in the respective reaction in the corresponding matrix element. The order that the reactions (rows) or the species (columns) are assigned in the matrix is not important. However, to avoid forming ill-behaved matrices, it is prudent to consider the important (dominant) reactions first and write the species in the order they appear in the reactions. Once a column is assigned to a specific species, it should not be changed. For example, for Reaction 2.4.1, the matrix of stoichiometric coefficients is constructed by listing the two individual reactions as they are given and the species in the order they appear in the respective reactions,

$$\begin{array}{cccc} \text{CO} & \text{H}_2\text{O} & \text{CO}_2 & \text{H}_2 \\ \left[\begin{array}{cccc} -1 & -1 & 1 & 1 \\ 1 & 1 & -1 & -1 \end{array} \right] \end{array} \quad (2.4.3)$$

For Reactions 2.4.2a, 2.4.2b, and 2.4.2c, the stoichiometric matrix is

$$\begin{array}{cccc} \text{C} & \text{O}_2 & \text{CO} & \text{CO}_2 \\ \left[\begin{array}{cccc} -1 & -0.5 & 1 & 0 \\ 0 & -0.5 & -1 & 1 \\ -1 & -1 & 0 & 1 \end{array} \right] \end{array} \quad (2.4.4)$$

The fact that chemical reactions are expressed as linear homogeneous equations allows us to exploit the properties of such equations and to use the associated algebraic tools. Specifically, we use elementary row operations to reduce the stoichiometric matrix to a reduced form, using Gaussian elimination. A reduced matrix is defined as a matrix where all the elements below the diagonal (elements 1,1; 2,2; 3,3; etc.) are zero. The number of nonzero rows in the reduced matrix indicates the number of independent chemical reactions. (A zero row is defined as a row in which all elements are zero.) The nonzero rows in the reduced matrix represent one set of independent chemical reactions (i.e., stoichiometric relations) for the system.

Elementary row operations are mathematical operations that can be performed on individual equations in a system of linear equations without changing the solution of the system. There are three elementary row operations: (i) interchanging any two rows, (ii) multiplying a row by a nonzero constant, and (iii) adding a scalar-multiplied row to another row. To reduce a matrix to a diagonal form, the three elementary row operations are applied to modify the matrix such that all the entries below the diagonal are zeros. First, we check if the first diagonal element (the element in the first row) is nonzero. If it is nonzero, we use the three elementary row operations to convert all the elements in the first column below it to zero. For example, in stoichiometric Matrix 2.4.3, the diagonal element in the first row is nonzero, and, to eliminate the entry below it, we add the first row to the second row and obtain

$$\begin{bmatrix} -1 & -1 & 1 & 1 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (2.4.5)$$

In general, when the diagonal element is zero, we replace it (if possible) with a nonzero element by interchanging the row with a lower row. We repeat the procedure for the diagonal element in the second column, then the third column, and so on until we obtain a reduced matrix. In Matrix 2.4.5, all the elements below the diagonal are zero, therefore, it is a reduced matrix. Since it has only one nonzero row, the system has one independent chemical reaction. Note that unlike a conventional Gaussian elimination procedure, the elements on the diagonal are not converted to 1, since by multiplying a row by a negative constant we change the corresponding chemical reaction.

To determine the number of independent reactions among Reactions 2.4.2a, 2.4.2b, and 2.4.2c, we reduce Matrix 2.4.4. Since the diagonal element in the first row is nonzero, we leave the first row unchanged and eliminate the nonzero elements in the first column below it. Similarly, since the first element in the second row is zero, leave the second row unchanged. To eliminate the nonzero element in the first column of the third row, subtract the first row from the third row and obtain the following matrix:

$$\begin{bmatrix} -1 & -0.5 & 1 & 0 \\ 0 & -0.5 & -1 & 1 \\ 0 & -0.5 & -1 & 1 \end{bmatrix} \quad (2.4.6)$$

Now check the diagonal element of the second column. Since it is nonzero, leave the second row unchanged and eliminate the nonzero elements in the second column below it. To eliminate the nonzero element in the second column of the third row, subtract the second row from the third row and obtain the following matrix:

$$\begin{bmatrix} -1 & -0.5 & 1 & 0 \\ 0 & -0.5 & -1 & 1 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (2.4.7)$$

In this matrix, all the elements below the diagonal are zero; hence, it is a reduced matrix. Since it has two nonzero rows, there are two independent reactions.

Once a reduced stoichiometric matrix is obtained, we can identify one set of independent chemical reactions from the nonzero rows of the reduced matrix. In the case of Matrix 2.4.5, the nonzero row represents Reaction 2.4.1a. In the case of Matrix 2.4.7, the two nonzero rows represent Reactions 2.4.2a and 2.4.2b. Note that the set of independent reactions is not unique, and other sets can be generated by replacing one or more reactions in the original set by a linear combination of some or all reactions in the original set. For example, Reaction 2.4.1b, the reverse of Reaction 2.4.1a, can serve as the independent reaction of Reactions 2.4.1a and 2.4.1b. In Matrix 2.4.7, the second row can be replaced by the sum of the first and second row to obtain Reactions 2.4.2a and 2.4.2c as a set of independent reactions. In fact, for this case, any two reactions of the original three form a set of independent reactions. In principle, the set of independent reactions may include a reaction that does not actually take place in the reactor, yet we can use the set to calculate the reactor composition and other state variables. In practice, to simplify the calculations, we select a convenient set of independent reactions. In Chapter 4, a methodology for identifying the most suitable set of independent chemical reactions for designing chemical reactors is described.

As will be discussed later, the rates at which chemical species are being formed (or depleted) depend on *all* the chemical reactions that actually take place in the reactor (reaction pathways). Hence, to design chemical reactors with multiple reactions, we consider all the chemical reactions that are taking place, including the *dependent* reactions. Therefore, it is necessary to express the dependent reactions in terms of the independent reactions. Next, we describe how to do so.

Once a set of independent reactions is selected, write each of the dependent reactions as a linear combination of the independent reactions. The total number of reactions is the sum of the independent and dependent reactions:

$$n_R = n_I + n_D \quad (2.4.8)$$

Let index m denote the m th independent reaction and index k the k th dependent reaction. For example, for Reactions 2.4.1a and 2.4.1b, there are two reactions but one independent reaction. By selecting Reaction 2.4.1a as the independent

reaction, $m = 1$, and the index of the dependent reaction is $k = 2$. For Reactions 2.4.2a, 2.4.2b, and 2.4.2c, the set consists of three reactions, but among them only two are independent reactions. If Reactions 2.4.2a and 2.4.2b are selected as the independent reactions, and Reaction 2.4.2c as the dependent reaction, then, $m = 1, 2$, and $k = 3$.

To determine the relationships between the dependent and independent reactions, let α_{km} denote the scalar factor relating the k th dependent reaction to the m th independent reaction. Thus, α_{km} is the multiplier of the m th independent reaction to obtain the k th independent reaction. To determine the numerical values of the α_{km} factors, we conduct species balances for each dependent reaction. For the k th dependent reaction, the following set of linear equations should be satisfied for each species:

$$\sum_m^{\nu_j} \alpha_{km}(s_j)_m = (s_j)_k \quad j = A, B, \dots \quad (2.4.9)$$

Hence, Eq. 2.4.9 provides a set of linear equations whose unknowns are α_{km} 's. As we will see later, these factors play an important role in formulating the design equations for chemical reactors with multiple reactions.

To illustrate how the α_{km} factors are determined, consider, for example, Reactions 2.4.1a and 2.4.1b. Selecting Reaction 2.4.1a as the independent reaction ($m = 1$) and Reaction 2.4.1b as the dependent reaction ($k = 2$), write Eq. 2.4.9 for Reaction 2.4.1b and take $j = \text{CO}$; thus,

$$\alpha_{21}(-1) = 1$$

and $\alpha_{21} = -1$. Indeed, Reaction 2.4.1b is the reverse of Reaction 2.4.1a and is obtained by multiplying the latter by -1 . To determine the relationships between dependent and independent reactions among Reactions 2.4.2a, 2.4.2b, and 2.4.2c, we select Reactions 2.4.2a and 2.4.2b as the independent reactions and Reaction 2.4.2c as the dependent reaction. Hence, $m = 1, 2$ and $k = 3$. Write Eq. 2.4.9 for Reaction 2.4.2c for two species. For $j = \text{C}$,

$$\alpha_{31}(-1) + \alpha_{32}(0) = -1$$

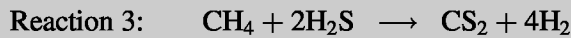
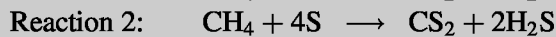
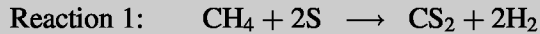
and $\alpha_{31} = 1$. For $j = \text{CO}$,

$$\alpha_{31}(1) + \alpha_{32}(-1) = 0$$

and $\alpha_{32} = 1$. Hence, Reaction 2.4.2c is the sum of Reactions 2.4.2a and 2.4.2b,



Example 2.6 Carbon disulfide is a common solvent that is produced by reacting sulfur vapor with methane. It is produced in a steady-flow reactor where the following chemical reactions take place:



Methane is fed to the reactor at a rate of 80 mol/min and vapor sulfur at a rate of 400 mol/min. The fraction of the methane converted in the reactor is 80%, and the hydrogen mole fraction in the product stream is 10.5%.

- Identify a set of independent reactions.
- Determine the production rate of carbon disulfide.
- Determine the composition of the outlet stream.
- Express each of the dependent reactions in terms of the independent reactions.

Solution

- To determine the number of independent reactions, first construct a matrix of stoichiometric coefficients for the given reactions.

$$\begin{array}{ccccc}
 \text{CH}_4 & \text{S} & \text{CS}_2 & \text{H}_2 & \text{H}_2\text{S} \\
 \left[\begin{array}{ccccc}
 -1 & -2 & 1 & 2 & 0 \\
 -1 & -4 & 1 & 0 & 2 \\
 -1 & 0 & 1 & 4 & -2
 \end{array} \right] & & & & \text{(a)}
 \end{array}$$

The diagonal element in the first column is nonzero, so the first row is left unchanged. To eliminate the nonzero elements below the diagonal in the first column, we subtract the first row from the second row and the first row from the third row. Matrix (a) reduces to

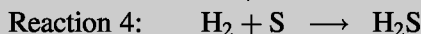
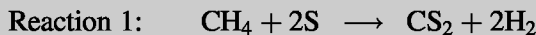
$$\left[\begin{array}{ccccc}
 -1 & -2 & 1 & 2 & 0 \\
 0 & -2 & 0 & -2 & 2 \\
 0 & 2 & 0 & 2 & -2
 \end{array} \right] \quad \text{(b)}$$

Now all the elements in the first column below the diagonal element are zero, and we proceed to the second column. The diagonal element in the second column (in the second row) is nonzero, so the second row is left unchanged. To eliminate the nonzero elements below the diagonal in the second column in Matrix (b), we add the second row to the third row. To simplify the reduced

matrix, we divide the second row by 2, and the matrix reduces to

$$\begin{bmatrix} -1 & -2 & 1 & 2 & 0 \\ 0 & -1 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (\text{c})$$

Since all the elements under the diagonal in Matrix (c) are zero, this matrix is a *reduced* matrix. Since Matrix (c) has two nonzero rows, there are two independent chemical reactions. In this case, we can select any two reactions of the original system as a set of independent reactions. The nonzero rows in Matrix (c) represent another set of independent reactions:



Note that the second row in Matrix (c) represents a chemical reaction (or more accurately a stoichiometric relation) that is not among the original reactions, and we denote it as Reaction 4. Hence, in this case, there are four plausible stoichiometric relations among the species, but only two of them are independent. Also, only Reactions 1, 2, and 3 actually take place in the reactor (i.e., reaction pathways).

- b. To determine the species flow rates at the reactor outlet, a set of two independent reactions is selected and its extents calculated. We select Reactions 1 and 4 as the set of independent reactions; Hence, the indices of the independent reactions are $m = 1, 4$, and the indices of the dependent reactions are $k = 2, 3$. The stoichiometric coefficients of the two independent reactions are

$$(s_{\text{CH}_4})_1 = -1 \quad (s_{\text{S}})_1 = -2 \quad (s_{\text{CS}_2})_1 = 1 \quad (s_{\text{H}_2})_1 = 2 \quad (s_{\text{H}_2\text{S}})_1 = 0 \quad \Delta_1 = 0$$

$$(s_{\text{CH}_4})_4 = 0 \quad (s_{\text{S}})_4 = -1 \quad (s_{\text{CS}_2})_4 = 0 \quad (s_{\text{H}_2})_4 = -1 \quad (s_{\text{H}_2\text{S}})_4 = 1 \quad \Delta_4 = -1$$

To determine the required quantities, we express the molar flow rates of the individual species in terms of the extents of Reactions 1 and 4. Selecting the given inlet flow rates as a basis for the calculation,

$$(F_{\text{CH}_4})_{\text{in}} = 80 \text{ mol/min} \quad (F_{\text{S}})_{\text{in}} = 400 \text{ mol/min} \quad (F_{\text{tot}})_{\text{in}} = 480 \text{ mol/min}$$

To express the molar flow rates of the individual species in the product stream, we use Eq. 2.3.11 for the individual species:

$$(F_{\text{CH}_4})_{\text{out}} = 80 + (-1)\dot{X}_1 + (0)\dot{X}_4 = 80 - \dot{X}_1 \quad (\text{d})$$

$$(F_{\text{S}})_{\text{out}} = 400 + (-2)\dot{X}_1 + (-1)\dot{X}_4 = 400 - 2\dot{X}_1 - \dot{X}_4 \quad (\text{e})$$

$$(F_{\text{CS}_2})_{\text{out}} = 0 + (1)\dot{X}_1 + (0)\dot{X}_4 = \dot{X}_1 \quad (\text{f})$$

$$(F_{\text{H}_2})_{\text{out}} = 0 + (2)\dot{X}_1 + (-1)\dot{X}_4 = 2\dot{X}_1 - \dot{X}_4 \quad (\text{g})$$

$$(F_{\text{H}_2\text{S}})_{\text{out}} = 0 + (0)\dot{X}_1 + (1)\dot{X}_4 = \dot{X}_4 \quad (\text{h})$$

and, using Eq. 2.3.12,

$$(F_{\text{tot}})_{\text{out}} = 480 + (0)\dot{X}_1 + (-1)\dot{X}_4 = 480 - \dot{X}_4 \quad (\text{i})$$

Expressing the fraction of CH_4 that is converted,

$$\frac{(F_{\text{CH}_4})_{\text{in}} - (F_{\text{CH}_4})_{\text{out}}}{(F_{\text{CH}_4})_{\text{in}}} = \frac{80 - (80 - \dot{X}_1)}{80} = 0.8$$

and we obtain $\dot{X}_1 = 64 \text{ kmol/min}$. Using (g) and (i), the fraction of H_2 in the outlet stream is

$$(y_{\text{H}_2})_{\text{out}} = \frac{(F_{\text{H}_2})_{\text{out}}}{(F_{\text{tot}})_{\text{out}}} = \frac{2\dot{X}_1 - \dot{X}_4}{480 - \dot{X}_4} = 0.105 \quad (\text{j})$$

Substituting $\dot{X}_1 = 64 \text{ mol/min}$ into (j), $\dot{X}_4 = 86.7 \text{ mol/min}$. Now that the extents of the two independent reactions are known, we calculate the species molar flow rates of the effluent stream using (d) through (h):

$$\begin{aligned} (F_{\text{CH}_4})_{\text{out}} &= 16 & (F_{\text{S}})_{\text{out}} &= 185.3 & (F_{\text{CS}_2})_{\text{out}} &= 64 \\ (F_{\text{H}_2})_{\text{out}} &= 41.3 & (F_{\text{H}_2\text{S}})_{\text{out}} &= 86.7 & (F_{\text{tot}})_{\text{out}} &= 393.3 \text{ mol/min} \end{aligned}$$

The production rate of CS_2 is 64 mol/min .

- c. Now that the molar flow rates of the individual species in the outlet stream are known, the stream's composition can be calculated using (j). The respective mole fractions are

$$\begin{aligned} (y_{\text{CH}_4})_{\text{out}} &= 0.041 & (y_{\text{S}})_{\text{out}} &= 0.471 & (y_{\text{CS}_2})_{\text{out}} &= 0.163 \\ (y_{\text{H}_2})_{\text{out}} &= 0.105 & (y_{\text{H}_2\text{S}})_{\text{out}} &= 0.220 \end{aligned}$$

The reader is challenged to verify that the same outlet species molar flow rates are obtained when a different set of independent reactions is selected, say Reactions 1 and 2.

- d. To determine the relations between the two dependent reactions (Reactions 2 and 3) and the two independent reactions (Reactions 1 and 4), write Eq. 2.4.9 for each dependent reaction. We start with the first dependent reaction ($k = 2$):

$$\sum_m^{n_l} \alpha_{2m}(s_j)_m = \alpha_{21}(s_j)_1 + \alpha_{24}(s_j)_4 = (s_j)_2 \quad (\text{k})$$

Write (k) for $j = \text{CH}_4$:

$$\alpha_{21}(-1) + \alpha_{24}(0) = -1 \quad (\text{l})$$

and obtain $\alpha_{21} = 1$. Next, we write (k) for $j = \text{H}_2\text{S}$:

$$\alpha_{21}(0) + \alpha_{24}(1) = 2 \quad (\text{m})$$

and obtain $\alpha_{24} = 2$. Thus, Reaction 2 relates to the two independent reactions by

$$\text{Reaction 2} = \text{Reaction 1} + 2(\text{Reaction 4})$$

Consider now the second dependent reaction and write Eq. 2.4.9 for $k = 3$:

$$\sum_m^{n_r} \alpha_{3m}(s_j)_m = \alpha_{31}(s_j)_1 + \alpha_{34}(s_j)_4 = (s_j)_3 \quad (\text{n})$$

First, we write (n) for $j = \text{CH}_4$:

$$\alpha_{31}(-1) + \alpha_{34}(0) = -1 \quad (\text{o})$$

and obtain $\alpha_{31} = 1$. Then we write (n) for $j = \text{H}_2\text{S}$:

$$\alpha_{31}(0) + \alpha_{34}(1) = -2 \quad (\text{p})$$

and obtain $\alpha_{34} = -2$. Thus, Reaction 3 relates to the two independent reactions by

$$\text{Reaction 3} = \text{Reaction 1} - 2(\text{Reaction 4})$$

The previous example illustrates that the composition of a reactor can be determined by using a set of independent chemical reactions (stoichiometric relations) that includes one or more reactions that do not actually take place in the reactor.

2.5 CHARACTERIZATION OF THE REACTOR FEED

As indicated by Section 2.3, to determine the content of a batch reactor, or the outlet composition of a flow reactor, the composition of the initial state, or the inlet stream should be specified. So far, the initial contents of a batch reactor $N_j(0)$, or the inlet stream of a flow reactor, $F_{j\text{in}}$, have been specified. However, in some instances it is convenient to characterize the reactor feed in terms of stoichiometric parameters of the chemical reactions that take place in the reactor. Also, as illustrated in Example 2.1, it is useful to identify the limiting reactant. This section covers the common quantities used to characterize the reactor feed.

2.5.1 Limiting Reactant

Let A and B be two reactants of a chemical reaction taking place in a batch reactor. Using Eq. 2.3.6, at any time t , the molar contents of the two reactants are related by

$$\frac{N_A(t) - N_A(0)}{s_A} = \frac{N_B(t) - N_B(0)}{s_B}$$

If reactant A is indeed the limiting reactant, $N_A(t)$ vanishes before $N_B(t)$, therefore, the following relation should be satisfied:

$$\left| \frac{N_A(0)}{s_A} \right| \leq \left| \frac{N_B(0)}{s_B} \right| \quad (2.5.1a)$$

Note that because the stoichiometric coefficients of reactants are negative, absolute values are used. Similarly, for steady-flow reactors, using Eq. 2.3.15, the species molar flow rates of the two reactants are related by

$$\frac{F_{A_{out}} - F_{A_{in}}}{s_A} = \frac{F_{B_{out}} - F_{B_{in}}}{s_B}$$

and if A is the limiting reactant, the following condition should be satisfied:

$$\left| \frac{F_{A_{in}}}{s_A} \right| \leq \left| \frac{F_{B_{in}}}{s_B} \right| \quad (2.5.1b)$$

When reactants A and B are in stoichiometric proportion, Eqs. 2.5.1a and 2.5.1b reduce, respectively, to

$$\frac{N_A(0)}{s_A} = \frac{N_B(0)}{s_B} \quad \text{or} \quad \frac{F_{A_{in}}}{s_A} = \frac{F_{B_{in}}}{s_B} \quad (2.5.2)$$

Equation 2.5.2 is the mathematical condition for stoichiometric proportion of the reactants in the reactor feed.

When multiple chemical reactions take place, the chemical reaction whose stoichiometric coefficients are used in Eqs. 2.5.1a and 2.5.1b is the stoichiometric relation that ties the reactants fed to the desirable product. This is illustrated in Example 2.11.

The procedure for identifying the limiting reactant of a chemical reaction is quite simple. For each reactant calculate

$$\left| \frac{N_j(0)}{s_j} \right| \quad \text{or} \quad \left| \frac{F_{j_{in}}}{s_j} \right| \quad j = A, B, \dots \quad (2.5.3)$$

The reactant with the smallest value is the limiting reactant. Since very rarely a chemical reaction has more than three reactants, the procedure is rather short. When the reactants are in stoichiometric proportion, any reactant can be considered as

the limiting reactant. In the remainder of the text, the subscript A denotes the limiting reactant; other species, either reactants or products, are labeled by other letters.

2.5.2 Excess Reactant

Excess reactant is a quantity indicating the surplus amount of a reactant over the stoichiometric amount. It is usually used in combustion reactions to indicate the surplus amount of oxygen provided, which characterizes the combustion conditions. The excess amount of reactant B is defined by

$$\left(\begin{array}{c} \text{Excess} \\ \text{reactant} \\ B \end{array} \right) \equiv \frac{\text{Amount of } B \text{ fed} - \text{Stoichiometric amount of } B \text{ needed}}{\text{Stoichiometric amount of } B \text{ needed}} \quad (2.5.4)$$

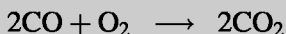
The stoichiometric amount of reactant B is determined for the specific chemical reaction or reactions under consideration. For combustion reactions, the convention is to select the chemical reactions that provide complete oxidation of all the fuel components to their highest oxidation level (all carbon atoms to CO_2 , all sulfur atoms to SO_2 , etc.). Hence, although other chemical reactions may take place during the operation, generating CO and other products, the excess oxygen is defined and calculated on the basis of *complete* oxidation reactions.

In practice, combustion operations involve the introduction of external source of oxygen, usually in the form of air. Also, in most instances, combustion involves multiple reactions. To characterize combustion operations, a quantity called “excess air” is defined by

$$\left\{ \begin{array}{c} \text{Excess} \\ \text{air} \end{array} \right\} \equiv \frac{\text{External air supplied} - \text{Stoichiometric external air required}}{\text{Stoichiometric external air required}} \quad (2.5.5)$$

Excess air is commonly used to characterize the operating conditions of burners. Note that in Eq. 2.5.5 only *external* oxygen is considered (with the exclusion of oxygen that might be in the fuel) and that the stoichiometric amount required is determined on the basis of all complete combustion reactions that might take place.

Example 2.7 The gas-phase reaction



takes place in a closed, constant-volume batch reactor at isothermal conditions. Initially, the reactor contains 1.5 kmol of CO , 1 kmol of O_2 , 1 kmol of CO_2 , and 0.5 kmol of N_2 , and its pressure is 5 atm. At time t , the reactor pressure is $P(t) = 4.5$ atm. Assume ideal-gas behavior.

- Identify the limiting reactant.
- Determine the excess amount of the other reactant.
- Determine the reactor pressure when the reaction goes to completion.

- d. Determine the extent of the reaction at time t .
 e. Determine the reactor content (in moles) at time t .

Solution We select the given chemical reaction as the chemical formula, and the stoichiometric coefficients are

$$s_{\text{CO}} = -2 \quad s_{\text{O}_2} = -1 \quad s_{\text{CO}_2} = 2 \quad s_{\text{N}_2} = 0 \quad \Delta = -1$$

- a. To identify the limiting reactant, apply Eq. 2.5.3 for each reactant:

$$\left| \frac{N_{\text{CO}}(0)}{s_{\text{CO}}} \right| = \left| \frac{1.5}{-2} \right| = 0.75 \quad \left| \frac{N_{\text{O}_2}(0)}{s_{\text{O}_2}} \right| = \left| \frac{1.0}{-1} \right| = 1.0 \quad (\text{a})$$

Hence, CO is the limiting reactant.

- b. Now that the limiting reactant is identified, the stoichiometric amount of O_2 is readily determined using Eq. 2.5.2:

$$(N_{\text{O}_2})_{\text{stoich}} = \frac{s_{\text{O}_2}}{s_{\text{CO}}} N_{\text{CO}}(0) = \frac{-1}{-2} (1.5 \text{ kmol}) = 0.75 \text{ kmol} \quad (\text{b})$$

Using Eq. 2.5.4, the excess O_2 is

$$\left\{ \begin{array}{l} \text{Excess} \\ \text{O}_2 \end{array} \right\} \equiv \frac{(1 \text{ kmol}) - (0.75 \text{ kmol})}{0.75 \text{ kmol}} = 0.33 \quad (\text{c})$$

- c. At completion, $N_{\text{CO}}(t) = 0$, and, using Eq. 2.3.5, the extent of the reaction is

$$X(t) = \frac{N_{\text{CO}}(t) - N_{\text{CO}}(0)}{s_{\text{CO}}} = \frac{0 - 1.5}{-2} = 0.75 \text{ kmol} \quad (\text{d})$$

To determine the pressure, we derive a relationship between the pressure and the extent of reaction. For ideal-gas behavior,

$$P(t) = \frac{RT}{V} N_{\text{tot}}(t) \quad (\text{e})$$

where $N_{\text{tot}}(t)$ is given by Eq. 2.3.7. Hence, for isothermal operation,

$$\frac{P(t)}{P(0)} = \frac{N_{\text{tot}}(t)}{N_{\text{tot}}(0)} = \frac{N_{\text{tot}}(0) + \Delta X(t)}{N_{\text{tot}}(0)} \quad (\text{f})$$

and, in this case, and, at $t = 0$, $N_{\text{tot}}(0) = 4 \text{ kmol}$, so

$$\frac{P(t)}{P(0)} = \frac{4 - X(t)}{4} \quad (\text{g})$$

The reactor pressure at completion is

$$P = (5 \text{ atm}) \frac{4 - 0.75}{4} = 4.06 \text{ atm}$$

d. Rearranging (f), the reaction extent when $P = 4.5 \text{ atm}$ is

$$X(t) = \left[1 - \frac{P(t)}{P(0)} \right] N_{\text{tot}}(0) = \left(1 - \frac{4.5}{5} \right) (4) = 0.4 \text{ kmol} \quad (\text{h})$$

e. Now that the extent at time t is known, we can determine the amounts of each species, using Eq. 2.3.5:

$$N_{\text{CO}}(t) = N_{\text{CO}}(0) + s_{\text{CO}}X(t) = 1.5 + (-2)(0.4) = 0.7 \text{ kmol}$$

$$N_{\text{O}_2}(t) = N_{\text{O}_2}(0) + s_{\text{O}_2}X(t) = 1.0 + (-1)(0.4) = 0.6 \text{ kmol}$$

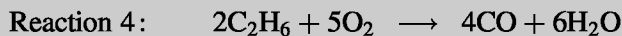
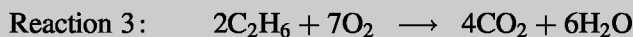
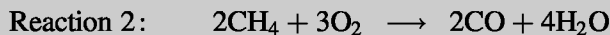
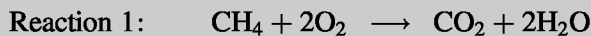
$$N_{\text{CO}_2}(t) = N_{\text{CO}_2}(0) + s_{\text{CO}_2}X(t) = 1.0 + (2)(0.4) = 1.8 \text{ kmol}$$

$$N_{\text{N}_2}(t) = N_{\text{N}_2}(0) + s_{\text{N}_2}X(t) = 0.5 + (0)(0.4) = 0.5 \text{ kmol}$$

and, using Eq. 2.3.7,

$$N_{\text{tot}}(t) = N_{\text{tot}}(0) + \Delta X(t) = 4.0 + (-1)(0.4) = 3.6 \text{ kmol}$$

Example 2.8 A gaseous fuel consisting of 72% CH_4 , 24% C_2H_6 , 3% N_2 , and 1% O_2 (mole percent) is fed into a combustion chamber at a rate of 10 g-mol/min. A stream of external air is mixed with the fuel, and the following chemical reactions are believed to take place in the combustion chamber:



An analysis of the effluent stream indicates that all the ethane has been converted and that, on a dry basis, its composition is 83.96% N_2 , 7.05% CO_2 , 0.18% CO , and 8.69% O_2 (mole percent). Determine:

- The flow rate of the air fed to the reactor
- The excess air

Solution First, we determine the number of independent reactions. We construct a matrix of stoichiometric coefficients for the given reactions:

$$\begin{array}{cccccc}
 \text{CH}_4 & \text{O}_2 & \text{CO}_2 & \text{H}_2\text{O} & \text{CO} & \text{C}_2\text{H}_6 \\
 \left[\begin{array}{cccccc}
 -1 & -2 & 1 & 2 & 0 & 0 \\
 -2 & -3 & 0 & 4 & 2 & 0 \\
 0 & -7 & 4 & 6 & 0 & -2 \\
 0 & -5 & 0 & 6 & 4 & -2 \\
 0 & -1 & 2 & 0 & -2 & 0
 \end{array} \right] & & & & & & \text{(a)}
 \end{array}$$

Applying Gaussian elimination, Matrix (a) reduces to

$$\left[\begin{array}{cccccc}
 -1 & -2 & 1 & 2 & 0 & 0 \\
 0 & 1 & -2 & 0 & 2 & 0 \\
 0 & 0 & -5 & 3 & 7 & -1 \\
 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0
 \end{array} \right] \quad \text{(b)}$$

Since Matrix (b) has three nonzero rows, there are three independent chemical reactions. We select Reactions 1, 3, and 5 as a set of independent reactions, and their stoichiometric coefficients are

$$\begin{array}{l}
 (s_{\text{CH}_4})_1 = -1 \quad (s_{\text{O}_2})_1 = -2 \quad (s_{\text{CO}_2})_1 = 1 \quad (s_{\text{H}_2\text{O}})_1 = 2 \quad (s_{\text{CO}})_1 = 0 \quad (s_{\text{C}_2\text{H}_6})_1 = 0 \\
 (s_{\text{CH}_4})_3 = 0 \quad (s_{\text{O}_2})_3 = -7 \quad (s_{\text{CO}_2})_3 = 4 \quad (s_{\text{H}_2\text{O}})_3 = 6 \quad (s_{\text{CO}})_3 = 0 \quad (s_{\text{C}_2\text{H}_6})_3 = 0 \\
 (s_{\text{CH}_4})_5 = 0 \quad (s_{\text{O}_2})_5 = -1 \quad (s_{\text{CO}_2})_5 = 2 \quad (s_{\text{H}_2\text{O}})_5 = 0 \quad (s_{\text{CO}})_5 = -2 \quad (s_{\text{C}_2\text{H}_6})_5 = 2 \\
 \Delta_1 = 0 \quad \Delta_3 = 1 \quad \Delta_5 = -1
 \end{array}$$

We select the fuel feed as a basis for the calculation ($F_1 = 10$ mol/min) and denote the fed air stream by F_2 . The inlet stream is $F_1 + F_2$.

a. First we want to determine the extents of the three independent reactions (i.e., Reactions 1, 3, and 5), using the given dry-basis compositions. Using Eq. 2.3.12, the total molar flow rate of the flue gas is

$$(F_{\text{tot}})_{\text{out}} = (10 + F_2) + \dot{X}_3 - \dot{X}_5 \quad \text{(c)}$$

Using Eq. 2.3.11, the molar flow rate of H_2O in the flue gas is

$$(F_{\text{H}_2\text{O}})_{\text{out}} = (0) + 2\dot{X}_1 + 6\dot{X}_3 \quad \text{(d)}$$

Combining (c) and (d), the total molar flow rate of the dry flue gas is

$$(F_{\text{tot}})_{\text{dry}} = (F_{\text{tot}})_{\text{out}} - (F_{\text{H}_2\text{O}})_{\text{out}} = 10 + F_2 - 2\dot{X}_1 - 5\dot{X}_3 - \dot{X}_5 \quad \text{(e)}$$

Using Eqs. 2.3.11 and (e) for each of the given dry compositions, we obtain

$$y_{\text{N}_2} = \frac{0.3 + 0.79F_2}{10 + F_2 - 2\dot{X}_1 - 5\dot{X}_3 - \dot{X}_5} = 0.8399 \quad (\text{f})$$

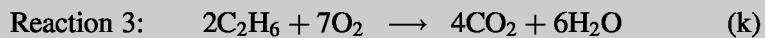
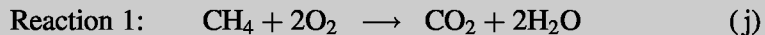
$$y_{\text{O}_2} = \frac{0.1 + 0.21F_2 - 2\dot{X}_1 - 7\dot{X}_3 - \dot{X}_5}{10 + F_2 - 2\dot{X}_1 - 5\dot{X}_3 - \dot{X}_5} = 0.0865 \quad (\text{g})$$

$$y_{\text{CO}_2} = \frac{\dot{X}_1 + 4\dot{X}_3 + 2\dot{X}_5}{10 + F_2 - 2\dot{X}_1 - 5\dot{X}_3 - \dot{X}_5} = 0.0708 \quad (\text{h})$$

$$y_{\text{CO}} = \frac{-2\dot{X}_5}{10 + F_2 - 2\dot{X}_1 - 5\dot{X}_3 - \dot{X}_5} = 0.0018 \quad (\text{i})$$

Solving (f), (g), (h), and (i), we obtain $F_2 = 172.9$ mol/min, $\dot{X}_1 = 7.03$ mol/min, $\dot{X}_3 = 1.2$ mol/min, and $\dot{X}_5 = -0.147$ mol/min. The molar feed rate of the air stream is 172.9 mol/min. The amount of external oxygen fed is $0.21F_2 = 36.31$ mol/min. The total amount of oxygen fed to the combustor is $0.01(10) + 36.31 = 36.41$ mol/min.

- b. To determine the excess amount of external oxygen, we first have to determine the stoichiometric amount needed. For methane and ethane, the stoichiometric amount is determined on the basis of the reactions for *complete* combustion:



Note that we do not consider Reaction 5 because CO is not a species in the fuel. Using Eq. 2.5.2, the stoichiometric amount of oxygen needed for complete combustion is

$$(F_{\text{O}_2})_{\text{stoich}} = \frac{(s_{\text{O}_2})_1}{(s_{\text{CH}_4})_1} (F_{\text{CH}_4})_{\text{in}} + \frac{(s_{\text{O}_2})_3}{(s_{\text{C}_2\text{H}_6})_3} (F_{\text{C}_2\text{H}_6})_{\text{in}} \quad (\text{l})$$

The total stoichiometric amount of oxygen needed is 22.8 mol/min, but 0.1 mol/min is fed in the fuel stream itself. Hence, the stoichiometric amount of external oxygen needed is 22.7 mol/min. Using Eq. 2.5.5, the excess air is

$$\left\{ \begin{array}{c} \text{Excess} \\ \text{air} \end{array} \right\} = \left\{ \begin{array}{c} \text{Excess} \\ \text{external O}_2 \end{array} \right\} = \frac{36.41 - 22.7}{22.7} = 0.604 \quad (\text{m})$$

2.6 CHARACTERIZATION OF REACTOR PERFORMANCE

In the preceding sections, the stoichiometric relationships used to quantify the operation of chemical reactors were expressed in terms of extensive quantities (moles, molar flow rates, reaction extents, etc.) whose numerical values depend on the basis selected for the calculation. In most applications, it is convenient to define intensive dimensionless quantities that characterize the operation of chemical reactors and provide quick measures of the reactor performance. In this section, we define and discuss some common stoichiometric quantities used in reactor analysis.

2.6.1 Reactant Conversion

The conversion is defined as the fraction of a reactant that has been consumed. For batch reactors, the conversion of reactant A at time t , $f_A(t)$, is defined by

$$f_A(t) \equiv \frac{\text{Moles of reactant A consumed in time } t}{\text{Moles of reactant A charged to the reactor}} = \frac{N_A(0) - N_A(t)}{N_A(0)} \quad (2.6.1a)$$

For flow reactors operating at steady state, the conversion of reactant A in the reactor is defined by

$$f_{A_{\text{out}}} \equiv \frac{\text{Rate reactant A is consumed in the system}}{\text{Rate reactant A is fed to the system}} = \frac{F_{A_{\text{in}}} - F_{A_{\text{out}}}}{F_{A_{\text{in}}}} \quad (2.6.1b)$$

Three points concerning the conversion should be noted:

1. The conversion is defined only for *reactants*, and, by definition, its value is between 0 and 1.
2. The conversion is related to the composition (or flow rate) of a reactant, and it is not defined on the basis of any specific chemical reaction. When multiple chemical reactions take place, a reactant may be consumed in several chemical reactions. However, if reactant A is produced by any independent chemical reaction, its conversion is not defined.
3. The conversion depends on the initial state selected, $N_A(0)$ (for batch reactors) and on the boundaries of the system, “in” and “out” (for flow reactors)—see Example 2.9.

When a *single* chemical reaction takes place, the conversion of a reactant relates to the extent of the reaction. For batch reactors, from Eq. 2.3.5,

$$N_A(0) - N_A(t) = -s_A X_1(t)$$

and, substituting in Eq. 2.6.1a, the relationship between the conversion of reactant A and the reaction extent is

$$f_A(t) = -\frac{s_A}{N_A(0)} X(t) \quad (2.6.2)$$

To express the number of moles of any species in terms of the conversion of reactant A, substitute $X(t)$ from Eq. 2.6.2 into Eq. 2.3.6 and obtain

$$N_j(t) = N_j(0) - \frac{S_j}{s_A} N_A(0) f_A(t) \quad (2.6.3)$$

To express the total number of moles in the reactor in terms of the conversion of reactant A, substitute $X(t)$ from Eq. 2.3.5 into Eq. 2.3.7 and obtain

$$N_{\text{tot}}(t) = N_{\text{tot}}(0) - \frac{\Delta}{s_A} N_A(0) f_A(t) \quad (2.6.4)$$

where Δ , defined by Eq. 2.2.5, denotes the change in the number of moles per unit extent.

To obtain a relationship between the conversion and the reaction extent in steady-flow reactors with *single* chemical reactions, we write Eq. 2.3.13 for reactant A and substitute it in Eq. 2.6.1b,

$$f_{A_{\text{out}}} = -\frac{s_A}{F_{A_{\text{in}}}} \dot{X}_{\text{out}} \quad (2.6.5)$$

To express the molar flow rate of any species at the reactor outlet in terms of the conversion of reactant A, substitute Eq. 2.6.5 into Eq. 2.3.13 and obtain

$$F_{j_{\text{out}}} = F_{j_{\text{in}}} - \frac{S_j}{s_A} F_{A_{\text{in}}} f_{A_{\text{out}}} \quad (2.6.6)$$

To relate the total molar flow rate at the reactor exit to the conversion, substitute Eq. 2.6.6 into Eq. 2.3.14 and obtain

$$F_{\text{tot}_{\text{out}}} = F_{\text{tot}_{\text{in}}} - \frac{\Delta}{s_A} F_{A_{\text{in}}} f_{A_{\text{out}}} \quad (2.6.7)$$

When species A is a reactant in several chemical reactions, the term $N_A(0) - N_A(t)$ in Eq. 2.6.1a should account for the consumption of reactant A by all the *independent* reactions. Using Eq. 2.3.3 for reactant A,

$$f_A(t) \equiv \frac{N_A(0) - N_A(t)}{N_A(0)} = -\frac{1}{N_A(0)} \sum_m^{n_r} (s_A)_m X_m(t)$$

or

$$f_A(t) = \sum_m^{n_r} f_{A_m}(t) \quad (2.6.8)$$

where $f_{A_m}(t)$ is the conversion of reactant A by the m th independent reaction, defined by

$$f_{A_m}(t) \equiv -\frac{(s_A)_m}{N_A(0)} X_m(t) \quad (2.6.9)$$

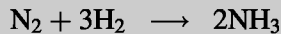
Similarly, for steady-flow reactors

$$f_A = \sum_m^{n_I} f_{A_m} \quad (2.6.10)$$

where f_{A_m} is the conversion of A by the m th independent reaction defined by

$$f_{A_m} \equiv -\frac{(s_A)_m}{F_{A_{in}}} \dot{X}_m \quad (2.6.11)$$

Example 2.9 Ammonia is produced in a continuous catalytic reactor according to the reaction



A synthesis gas stream (stream 1) consisting of 24.5% N_2 , 73.5% H_2 , and 2% argon is fed at a rate of 60 mol/min. At the operating conditions, the conversion per pass in the reactor is 12%. To enhance the operation, a portion of the reactor effluent stream (stream 3) is recycled and combined with the fresh synthesis gas as illustrated in Figure E2.9.1. If the mole fraction of the argon in the product stream (stream 4) is 3%, determine:

- The ammonia production rate
- The overall nitrogen conversion in the process
- The recycle ratio (F_5/F_4)

Solution The stoichiometric coefficients of the chemical reaction are

$$s_{\text{N}_2} = -1 \quad s_{\text{H}_2} = -3 \quad s_{\text{NH}_3} = 2 \quad s_{\text{Ar}} = 0 \quad \Delta = -2$$

Note that the argon is an inert species, and its stoichiometric coefficient is zero.

- Selecting the entire process as the system (the inlet is stream 1 and the outlet is stream 4); hence, $(F_{\text{tot}})_{\text{in}} = F_1 = 60$ mol/min and $(F_{\text{tot}})_{\text{out}} = F_4$. Writing an argon balance using Eq. 2.3.3,

$$(F_{\text{Ar}})_4 = (F_{\text{Ar}})_1 + s_{\text{Ar}} \dot{X} \quad (a)$$

$$(0.03)(F_{\text{tot}})_4 = (0.02)(F_{\text{tot}})_1 = (0.02)(60 \text{ mol/min})$$

Solving (a), $(F_{\text{tot}})_4 = 40$ mol/min. Using Eq. 2.3.14 to relate the total molar flow rate of the outlet stream to the extent,

$$(F_{\text{tot}})_4 = (F_{\text{tot}})_1 + \Delta \dot{X} \quad (b)$$

$$40 = 60 + (-2)\dot{X}$$

and $\dot{X} = 10$ mol/min. Now that the extent of the reaction is known, the production rate of ammonia can be calculated by using Eq. 2.3.13,

$$(F_{\text{NH}_3})_4 = (F_{\text{NH}_3})_1 + s_{\text{NH}_3} \dot{X} = 0 + (2)(10) = 20 \text{ mol/min} \quad (c)$$

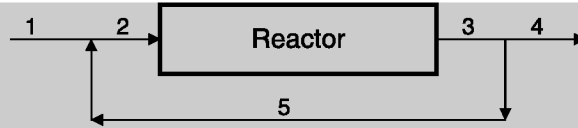


Figure E2.9.1 Recycle of ammonia reactor.

- b. To calculate the nitrogen molar flow rate at the outlet stream, we write Eq. 2.3.13 for nitrogen:

$$(F_{\text{N}_2})_4 = (F_{\text{N}_2})_1 + s_{\text{N}_2}\dot{X} = (0.245)(60) + (-1)(10) = 4.70 \text{ mol/min} \quad (\text{d})$$

The overall nitrogen conversion in the process, defined by Eq. 2.6.1b, is

$$f_{\text{N}_2} \equiv \frac{(F_{\text{N}_2})_1 - (F_{\text{N}_2})_4}{(F_{\text{N}_2})_1} = \frac{14.7 - 4.7}{14.7} = 0.680 \quad (\text{e})$$

Note that the same conversion is obtained by using Eq. 2.6.5.

- c. To calculate the recycle ratio, we select the reactor itself as the system (the inlet stream is stream 2 and the outlet stream is stream 3). Using the given conversion per pass,

$$f_{\text{N}_2} \equiv \frac{(F_{\text{N}_2})_2 - (F_{\text{N}_2})_3}{(F_{\text{N}_2})_2} = 0.12$$

or

$$(F_{\text{N}_2})_3 = 0.880(F_{\text{N}_2})_2 \quad (\text{f})$$

Using Eq. 2.3.13 to express $(F_{\text{N}_2})_3$ and $(F_{\text{N}_2})_2$ in terms of the extent,

$$(F_{\text{N}_2})_3 = (F_{\text{N}_2})_2 + s_{\text{N}_2}\dot{X} = (F_{\text{N}_2})_2 + (-1)(10) \quad (\text{g})$$

and substituting (f),

$$(0.880)(F_{\text{N}_2})_2 = (F_{\text{N}_2})_2 + (-1)(10) \quad (\text{h})$$

Solving (h), $(F_{\text{N}_2})_2 = 83.33 \text{ mol/min}$, and, from (f), $(F_{\text{N}_2})_3 = 73.33 \text{ mol/min}$. Now, writing a nitrogen balance over the mixing point,

$$\begin{aligned} (F_{\text{N}_2})_2 &= (F_{\text{N}_2})_1 + (F_{\text{N}_2})_5 = 0.880(F_{\text{N}_2})_2 \\ 83.33 &= (0.245)(60) + (F_{\text{N}_2})_5 \end{aligned} \quad (\text{i})$$

Solving (i), $(F_{\text{N}_2})_5 = 68.63 \text{ mol/min}$. Thus, the recycle ratio is

$$R \equiv \frac{(F_{\text{N}_2})_5}{(F_{\text{N}_2})_4} = \frac{68.63}{4.70} = 14.6$$

2.6.2 Product Yield and Selectivity

When several simultaneous chemical reactions take place producing both desired and undesired products, it is convenient to define parameters that indicate what portion of the reactant was converted to valuable products. Below, we define and discuss two quantities that are commonly used: yield and selectivity of the desirable product.

Yield is a measure of the portion of a reactant converted to the desired product by the *desirable* chemical reaction. It indicates the amount of the desirable product, species V, produced relative to the amount of V that could have been produced if only the desirable reaction took place. The yield is defined such that its value is between zero and one.

For *batch reactors*, the yield of product V at time t is

$$\eta_V(t) \equiv \left(\begin{array}{c} \text{Stoichiometric} \\ \text{factor} \end{array} \right) \frac{\text{Moles of product V formed in time } t}{\text{Moles of reactant A initially in the reactor}}$$

and in mathematical terms

$$\eta_V(t) \equiv - \left(\frac{s_A}{s_V} \right)_{\text{des}} \frac{N_V(t) - N_V(0)}{N_A(0)} \quad (2.6.12)$$

where s_A and s_V are, respectively, the stoichiometric coefficients of A and V in the *desirable* chemical reaction. Using stoichiometric relations (Eq. 2.3.3), the yield relates to the extents of the independent chemical reactions by

$$\eta_V(t) = - \left(\frac{s_A}{s_V} \right)_{\text{des}} \frac{1}{N_A(0)} \left[\sum_m^{n_I} (s_V)_m X_m(t) \right] \quad (2.6.13)$$

For *flow reactors*, the yield of product V at the reactor outlet is

$$\eta_{V_{\text{out}}} \equiv \left(\begin{array}{c} \text{Stoichiometric} \\ \text{factor} \end{array} \right) \frac{\text{Rate product V is formed in the reactor}}{\text{Rate of reactant A is fed into the reactor}}$$

and in mathematical terms

$$\eta_{V_{\text{out}}} \equiv - \left(\frac{s_A}{s_V} \right)_{\text{des}} \frac{F_{V_{\text{out}}} - F_{V_{\text{in}}}}{F_{A_{\text{in}}}} \quad (2.6.14)$$

Using Eq. 2.3.11, the yield relates to the extents of the independent chemical reactions by

$$\eta_{V_{\text{out}}} = - \left(\frac{s_A}{s_V} \right)_{\text{des}} \frac{1}{F_{A_{\text{in}}}} \left[\sum_m^{n_I} (s_V)_m \dot{X}_m \right] \quad (2.6.15)$$

Product selectivity indicates the amount of product V produced relative to the theoretical amount of V that could be produced if all reactant A *consumed* were reacted by the desirable chemical reaction. For batch reactors, the selectivity of product V at time t is defined by

$$\sigma_V(t) \equiv \left(\begin{array}{c} \text{Stoichiometric} \\ \text{factor} \end{array} \right) \frac{\text{Moles of product V formed in time } t}{\text{Moles of reactant A consumed in time } t}$$

In mathematical terms

$$\sigma_V(t) \equiv - \left(\frac{s_A}{s_V} \right)_{\text{des}} \frac{N_V(t) - N_V(0)}{N_A(0) - N_A(t)} \quad (2.6.16)$$

Using Eq. 2.3.3,

$$\sigma_V(t) = - \left(\frac{s_A}{s_V} \right)_{\text{des}} \frac{\sum_m^{n_I} (s_V)_m X_m(t)}{\sum_m^{n_I} (s_A)_m X_m(t)} \quad (2.6.17)$$

For steady-flow reactors, the selectivity of product V is defined by

$$\sigma_V(t) \equiv \left(\begin{array}{c} \text{Stoichiometric} \\ \text{factor} \end{array} \right) \frac{\text{Rate Product V is formed in the reactor}}{\text{Rate Reactant A is consumed in the reactor}}$$

In mathematical terms

$$\sigma_V \equiv - \left(\frac{s_A}{s_V} \right)_{\text{des}} \frac{F_{V_{\text{out}}} - F_{V_{\text{in}}}}{F_{A_{\text{in}}} - F_{A_{\text{out}}}} \quad (2.6.18)$$

Using Eq. 2.3.11, the yield relates to the extents of the independent chemical reactions:

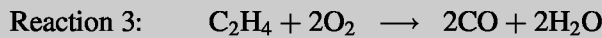
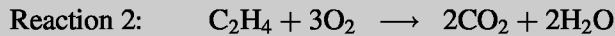
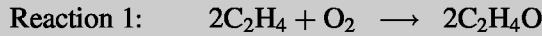
$$\sigma_V = - \left(\frac{s_A}{s_V} \right)_{\text{des}} \frac{\sum_m^{n_I} (s_V)_m \dot{X}_m}{\sum_m^{n_I} (s_A)_m \dot{X}_m} \quad (2.6.19)$$

Several points should be noted:

1. Both the yield and the selectivity are defined such that their numerical values are between 0 and 1.
2. The subscript "des" in the definitions refers to the chemical formula that ties reactant A to the product V (the desirable reaction). In some cases (e.g., in sequential reactions) the desirable reaction does not actually take place, but rather it is merely stoichiometric relations (see Example 2.11).
3. There is a simple relationship between the yield and the selectivity. Using the conversion definition, Eq. 2.6.1a or 2.6.1b,

$$\eta_V(t) = \sigma_V(t) f_A(t) \quad \text{or} \quad \eta_V = \sigma_V f_A \quad (2.6.20)$$

Example 2.10 Ethylene oxide is produced in a catalytic steady-flow reactor. A feed consisting of 70% C₂H₄ and 30% O₂ (mole percent) is fed into the reactor at a rate of 100 mol/s. The following chemical reactions take place in the reactor:



An analysis of the exit stream indicates that its composition is 41.17% C₂H₄, 37.65% C₂H₄O, and 7.06% O₂ (mole percent). Determine:

- The conversions of ethylene and oxygen
- The yield of ethylene oxide
- The selectivity of ethylene oxide

Solution Since each chemical reaction has a species that does not participate in the other two, the three reactions are independent, and their stoichiometric coefficients are

$$\begin{aligned} (s_{\text{C}_2\text{H}_4})_1 &= -2 & (s_{\text{O}_2})_1 &= -1 & (s_{\text{C}_2\text{H}_4\text{O}})_1 &= 2 & (s_{\text{H}_2\text{O}})_1 &= 0 & (s_{\text{CO}_2})_1 &= 0 & (s_{\text{CO}})_1 &= 0 \\ (s_{\text{C}_2\text{H}_4})_2 &= -1 & (s_{\text{O}_2})_2 &= -3 & (s_{\text{C}_2\text{H}_4\text{O}})_2 &= 0 & (s_{\text{H}_2\text{O}})_2 &= 2 & (s_{\text{CO}_2})_2 &= 2 & (s_{\text{CO}})_2 &= 0 \\ (s_{\text{C}_2\text{H}_4})_3 &= -1 & (s_{\text{O}_2})_3 &= -2 & (s_{\text{C}_2\text{H}_4\text{O}})_3 &= 0 & (s_{\text{H}_2\text{O}})_3 &= 2 & (s_{\text{CO}_2})_3 &= 0 & (s_{\text{CO}})_3 &= 2 \\ \Delta_1 &= -1 & \Delta_2 &= 0 & \Delta_3 &= 1 \end{aligned}$$

To calculate the required quantities, first determine the extents of the reactions. Using Eqs. 2.3.11 and 2.3.12, the molar fraction of species *j* in the outlet stream is

$$y_j = \frac{F_{j\text{in}} + \sum_m^{n_j} (s_j)_m \dot{X}_m}{F_{\text{totin}} + \sum_m^{n_j} \Delta_m \dot{X}_m} \quad (\text{a})$$

Writing (a) for C₂H₄, C₂H₄O, and O₂,

$$y_{\text{C}_2\text{H}_4} = \frac{70 - 2\dot{X}_1 - \dot{X}_2 - \dot{X}_3}{100 - \dot{X}_1 + \dot{X}_3} = 0.4117 \quad (\text{b})$$

$$y_{\text{C}_2\text{H}_4\text{O}} = \frac{2\dot{X}_1}{100 - \dot{X}_1 + \dot{X}_3} = 0.3765 \quad (\text{c})$$

$$y_{\text{O}_2} = \frac{30 - \dot{X}_1 - 3\dot{X}_2 - 2\dot{X}_3}{100 - \dot{X}_1 + \dot{X}_3} = 0.0706 \quad (\text{d})$$

Solving (b), (c), and (d), $\dot{X}_1 = 16$, $\dot{X}_2 = 2$, and $\dot{X}_3 = 1$ mol/s. Using Eq. 2.3.11, the molar flow rates of the respective species are

$$F_{\text{C}_2\text{H}_4} = 70 - 2(16) + (-2)1 = 35 \text{ mol/s} \quad (\text{e})$$

$$F_{\text{C}_2\text{H}_4\text{O}} = 2(16) = 32 \text{ mol/s} \quad (\text{f})$$

$$F_{\text{O}_2} = 30 + (-1)16 + (-3)2 + (-2)1 = 6 \text{ mol/s} \quad (\text{g})$$

$$F_{\text{CO}_2} = 2(2) = 4 \text{ mol/s} \quad (\text{h})$$

a. Using the conversion definition (Eq. 2.6.1b) together with (e) and (g), the conversions of C_2H_4 and O_2 are, respectively,

$$f_{\text{C}_2\text{H}_4} = \frac{70 - 35}{70} = 0.50 \quad (\text{i})$$

$$f_{\text{O}_2} = \frac{30 - 6}{30} = 0.80 \quad (\text{j})$$

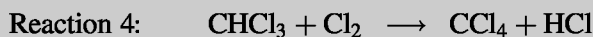
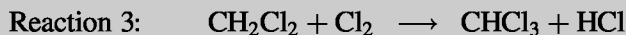
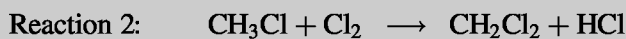
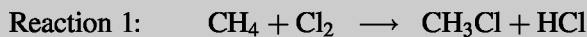
b. The desirable reaction is Reaction 1 and the limiting reactant is O_2 . Hence, using Eq. 2.6.14, the yield of ethylene oxide (on the basis of the oxygen fed) is

$$\eta_{\text{C}_2\text{H}_4\text{O}} = -\left(\frac{-1}{2}\right) \frac{32}{30} = 0.533 \quad (\text{k})$$

c. Using Eq. 2.6.18, the selectivity of ethylene oxide is

$$\sigma_{\text{C}_2\text{H}_4\text{O}} = -\left(\frac{-1}{2}\right) \frac{32}{30 - 6} = 0.667 \quad (\text{l})$$

Example 2.11 Dichloromethane is formed by reacting methane and chlorine. The following reactions take place in the reactor:

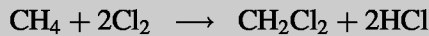


A feed consisting of 40% methane and 60% chlorine is fed to a steady-flow reactor at a rate of 100 mol/min. The desirable product is dichloromethane. At the outlet, the molar flow rate of methane is 10 mol/min and the stream contains

three times monochloromethane as dichloromethane, and the content of the latter is twice that of trichloromethane. Determine:

- The limiting reactant
- The conversions of methane and chlorine
- The yield of dichloromethane
- The selectivity of dichloromethane.

Solution The stoichiometric relation between the desirable product (dichloromethane) and the reactants is obtained by adding Reaction 1 and Reaction 2:



This stoichiometric relation represents the desirable reaction, and its stoichiometric coefficients are

$$s_{\text{CH}_4} = -1 \quad s_{\text{Cl}_2} = -2 \quad s_{\text{CH}_3\text{Cl}} = 1 \quad s_{\text{HCl}} = 2 \quad \Delta = 0$$

- To identify the limiting reactant, use Eq. 2.5.3 for the two reactants:

$$\left| \frac{F_{\text{CH}_4\text{in}}}{s_{\text{CH}_4}} \right| = \left| \frac{40}{-1} \right| = 40 \quad \text{and} \quad \left| \frac{F_{\text{Cl}_2\text{in}}}{s_{\text{Cl}_2}} \right| = \left| \frac{60}{-2} \right| = 30$$

Hence, the limiting reactant is chlorine.

- To determine the conversions, we have to calculate the extents of the given four independent reactions. The stoichiometric coefficients of the species in the four reactions are

$$\begin{array}{cccc} (s_{\text{CH}_4})_1 = -1 & (s_{\text{CH}_4})_2 = 0 & (s_{\text{CH}_4})_3 = 0 & (s_{\text{CH}_4})_4 = 0 \\ (s_{\text{Cl}_2})_1 = -1 & (s_{\text{Cl}_2})_2 = -1 & (s_{\text{Cl}_2})_3 = -1 & (s_{\text{Cl}_2})_4 = -1 \\ (s_{\text{CH}_3\text{Cl}})_1 = 1 & (s_{\text{CH}_3\text{Cl}})_2 = -1 & (s_{\text{CH}_3\text{Cl}})_3 = 0 & (s_{\text{CH}_3\text{Cl}})_4 = 0 \\ (s_{\text{CH}_2\text{Cl}_2})_1 = 0 & (s_{\text{CH}_2\text{Cl}_2})_2 = 1 & (s_{\text{CH}_2\text{Cl}_2})_3 = -1 & (s_{\text{CH}_2\text{Cl}_2})_4 = 0 \\ (s_{\text{CHCl}_3})_1 = 0 & (s_{\text{CHCl}_3})_2 = 0 & (s_{\text{CHCl}_3})_3 = 1 & (s_{\text{CHCl}_3})_4 = -1 \\ (s_{\text{CCl}_4})_1 = 0 & (s_{\text{CCl}_4})_2 = 0 & (s_{\text{CCl}_4})_3 = 0 & (s_{\text{CCl}_4})_4 = 1 \end{array}$$

Using Eq. 2.3.11, the species molar flow rates at the reactor outlet are

$$\begin{aligned} (F_{\text{CH}_4})_{\text{out}} &= 40 - \dot{X}_1 \\ (F_{\text{Cl}_2})_{\text{out}} &= 60 - \dot{X}_1 - \dot{X}_2 - \dot{X}_3 - \dot{X}_4 \end{aligned}$$

$$(F_{\text{HCl}})_{\text{out}} = \dot{X}_1 + \dot{X}_2 + \dot{X}_3 + \dot{X}_4$$

$$(F_{\text{CH}_3\text{Cl}})_{\text{out}} = \dot{X}_1 - \dot{X}_2$$

$$(F_{\text{CH}_2\text{Cl}_2})_{\text{out}} = 0 + \dot{X}_2 - \dot{X}_3$$

$$(F_{\text{CHCl}_3})_{\text{out}} = 0 + \dot{X}_3 - \dot{X}_4$$

$$(F_{\text{CCl}_4})_{\text{out}} = 0 + \dot{X}_4$$

Using the given information,

$$40 - \dot{X}_1 = 10$$

$$\frac{(F_{\text{CH}_3\text{Cl}})_{\text{out}}}{(F_{\text{CH}_2\text{Cl}_2})_{\text{out}}} = \frac{\dot{X}_1 - \dot{X}_2}{\dot{X}_2 - \dot{X}_3} = 0.5$$

$$\frac{(F_{\text{CH}_2\text{Cl}_2})_{\text{out}}}{(F_{\text{CHCl}_3})_{\text{out}}} = \frac{\dot{X}_2 - \dot{X}_3}{\dot{X}_3 - \dot{X}_4} = 2$$

$$\frac{(F_{\text{CHCl}_3})_{\text{out}}}{(F_{\text{CCl}_4})_{\text{out}}} = \frac{\dot{X}_3 - \dot{X}_4}{\dot{X}_4} = 2$$

The solution of these four equations is

$$\dot{X}_1 = 30 \quad \dot{X}_2 = 22 \quad \dot{X}_3 = 6 \quad \dot{X}_4 = 2 \text{ mol/min}$$

The species flow rates at the reactor outlet are

$$(F_{\text{CH}_3\text{Cl}})_{\text{out}} = 8 \quad (F_{\text{CH}_2\text{Cl}_2})_{\text{out}} = 16 \quad (F_{\text{CHCl}_3})_{\text{out}} = 4 \quad (F_{\text{CCl}_4})_{\text{out}} = 2 \text{ mol/min}$$

$$(F_{\text{Cl}_2})_{\text{out}} = 0 \quad (F_{\text{HCl}})_{\text{out}} = 60 \text{ mol/min}$$

Using Eq. 2.6.1b, the conversions of the two reactants are

$$f_{\text{CH}_4} \equiv \frac{(F_{\text{CH}_4})_{\text{in}} - (F_{\text{CH}_4})_{\text{out}}}{(F_{\text{CH}_4})_{\text{in}}} = \frac{40 - 10}{40} = 0.75$$

$$f_{\text{Cl}_2} \equiv \frac{(F_{\text{Cl}_2})_{\text{in}} - (F_{\text{Cl}_2})_{\text{out}}}{(F_{\text{Cl}_2})_{\text{in}}} = \frac{60 - 0}{60} = 1.0$$

c. Using Eq. 2.6.15, the yield of the dichloromethane (with respect to the methane) is

$$\eta_{\text{CH}_2\text{Cl}_2} = - \left(\frac{1}{-1} \right) \left(\frac{16 - 0}{40} \right) = 0.4$$

- d. Using Eq. 2.6.18, the selectivity of the dichloromethane (with respect to the methane) is

$$\eta_{\text{CH}_2\text{Cl}_2} = -\left(\frac{1}{-1}\right)\left(\frac{16-0}{40-30}\right) = 0.533$$

2.7 DIMENSIONLESS EXTENTS

The stoichiometric relations derived so far provide a glimpse at the key role the reaction extents play in the analysis of chemical reactors. Whenever the extents of the independent reactions are known, the reactor composition and all other stated variables (temperature, enthalpy, etc.) can be determined. Unfortunately, the extent has two deficiencies:

- It is not a measurable quantity and, consequently, must be related to other measurable quantities (concentrations, pressure, etc.).
- It is an extensive quantity depending on the amount of reactants initially in the reactor or on the inlet flow rate into the reactor.

While the use of calculated quantities may seem, at first, cumbersome and even counterproductive, it actually simplifies the analysis of chemical reactors with multiple reactions. In fact, calculated quantities such as enthalpy and free energy are commonly used in thermodynamics resulting in simplified expressions. Here too, by using the extents of independent reactions, we formulate the design of chemical reactors by the smallest number of design equations.

To characterize the generic behavior of chemical reactors, it is preferred to describe their operations in terms of intensive dimensionless quantities. To convert the reaction extents to intensive quantities, dimensionless extents are defined. For batch reactors, the dimensionless extent, Z_m , of the m th independent reaction is defined by

$$Z_m \equiv \frac{\text{Extent of the } m\text{th independent reaction}}{\text{Total number of moles of reference state}} = \frac{X_m}{(N_{\text{tot}})_0} \quad (2.7.1)$$

where $(N_{\text{tot}})_0$ is the total number of moles of a conveniently selected reference state. The selection of the reference state will be discussed below, but in most applications the initial state of the reactor is taken as the reference state.

For flow reactors, the dimensionless extent, Z_m , is defined by

$$Z_m \equiv \frac{\text{Extent per time of the } m\text{th independent reaction}}{\text{Total molar flow rate of reference stream}} = \frac{\dot{X}_m}{(F_{\text{tot}})_0} \quad (2.7.2)$$

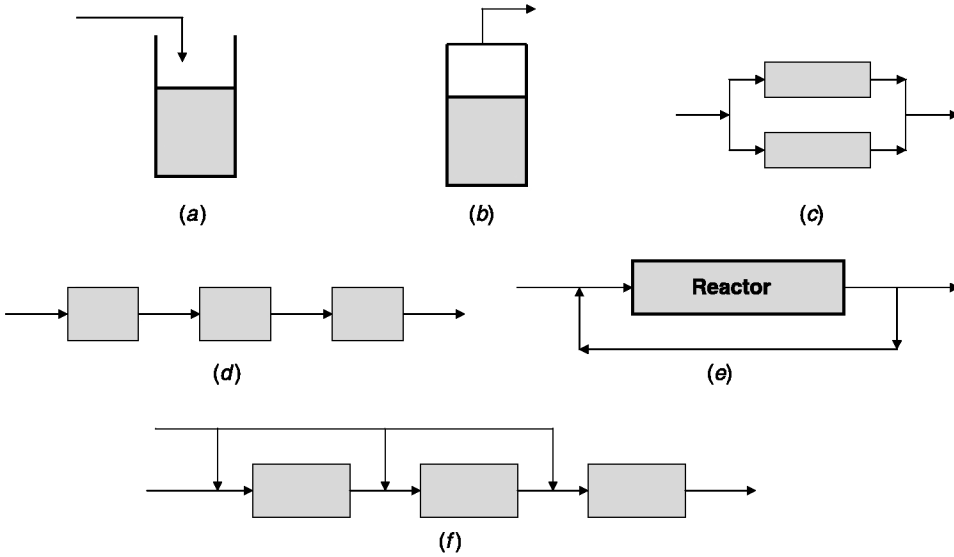


Figure 2.2 Various reactor Configurations: (a) semibatch, (b) distillation reactor, (c) split feed, (d) cascade, (e) recycle reactor, and (f) side injection.

where $(F_{\text{tot}})_0$ is the total molar flow rate of a conveniently selected reference stream. These definitions should apply for all reactor configurations; some are shown in Figure 2.2. The selection of the reference stream is discussed below. Note that the numerical values of dimensionless extents depend on the reference state or reference stream as well as on the chemical formulas used to represent the chemical transformations.

For batch reactors, using Eqs. 2.7.1 and 2.3.3, the species composition reduces to

$$N_j(t) = (N_{\text{tot}})_0 \left\{ \left[\frac{N_{\text{tot}}(0)}{(N_{\text{tot}})_0} \right] y_j(0) + \sum_m^{n_i} (s_j)_m Z_m(t) \right\} \quad (2.7.3)$$

where $y_j(0) = N_j(0)/N_{\text{tot}}(0)$ is the initial molar fraction of species j in the reactor. When the initial state is selected as the reference state, Eq. 2.7.3 reduces to

$$N_j(t) = (N_{\text{tot}})_0 \left[y_{j0} + \sum_m^{n_i} (s_j)_m Z_m(t) \right] \quad (2.7.4)$$

Similarly, using Eq. 2.3.4, the total molar content in the reactor

$$N_{\text{tot}}(t) = (N_{\text{tot}})_0 \left\{ \left[\frac{N_{\text{tot}}(0)}{(N_{\text{tot}})_0} \right] + \sum_m^{n_i} \Delta_m Z_m(t) \right\} \quad (2.7.5)$$

When the initial state is selected as the reference state, Eq. 2.7.5 reduces to

$$N_{\text{tot}}(t) = (N_{\text{tot}})_0 \left[1 + \sum_m^{n_I} \Delta_m Z_m(t) \right] \quad (2.7.6)$$

For steady-flow reactors, using Eq. 2.7.2, Eq. 2.3.11 reduces to

$$F_j = (F_{\text{tot}})_0 \left\{ \left[\frac{(F_{\text{tot}})_{\text{in}}}{(F_{\text{tot}})_0} \right] y_{j,\text{in}} + \sum_m^{n_I} (s_j)_m Z_m \right\} \quad (2.7.7)$$

where $(F_{\text{tot}})_{\text{in}}$ is the total molar flow rate of the inlet stream and $y_{j,\text{in}} = F_{j,\text{in}}/(F_{\text{tot}})_{\text{in}}$ is the molar fraction of species j in the inlet stream. When the inlet stream is selected as the reference stream, Eq. 2.7.7 reduces to

$$F_j = (F_{\text{tot}})_0 \left[y_{j0} + \sum_m^{n_I} (s_j)_m Z_m \right] \quad (2.7.8)$$

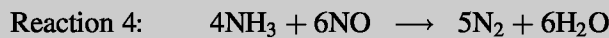
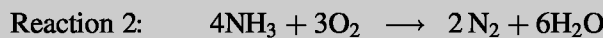
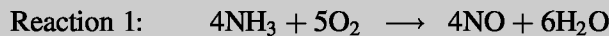
Similarly, using Eq. 2.3.12, the total molar flow rate in the reactor

$$F_{\text{tot}} = (F_{\text{tot}})_0 \left\{ \left[\frac{(F_{\text{tot}})_{\text{in}}}{(F_{\text{tot}})_0} \right] + \sum_m^{n_I} \Delta_m Z_m \right\} \quad (2.7.9)$$

When the inlet stream is selected as the reference stream, Eq. 2.7.9 reduces to

$$F_{\text{tot}} = (F_{\text{tot}})_0 \left[1 + \sum_m^{n_I} \Delta_m Z_m \right] \quad (2.7.10)$$

Example 2.12 The gas-phase catalytic oxidation of ammonia is investigated in an isothermal batch reactor. The following reactions take place in the reactor:



Initially, the reactor contains 4 mol of NH_3 and 6 mol of O_2 , and its pressure is 2 atm. At time t , the reactor pressure is 2.12 atm, and an analysis of the reactor content indicates that mole fraction of NH_3 is 0.07547, and of N_2 is 0.1132. Using the dimensionless extents, determine the reactor composition.

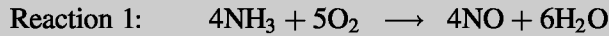
Solution First we have to determine the number of independent reactions, and to select a set of independent reactions. We construct a matrix of stoichiometric coefficients for the given reactions:

$$\begin{array}{cccccc} \text{NH}_3 & \text{O}_2 & \text{NO} & \text{H}_2\text{O} & \text{N}_2 & \text{NO}_2 \\ \left[\begin{array}{cccccc} -4 & -5 & 4 & 6 & 0 & 0 \\ -4 & -3 & 0 & 6 & 2 & 0 \\ 0 & -1 & -2 & 0 & 0 & 2 \\ -4 & 0 & -6 & 6 & 5 & 0 \end{array} \right] & & & & & \end{array} \quad (\text{a})$$

We conduct a Gaussian elimination procedure and reduce Matrix (a) to

$$\begin{array}{cccccc} \left[\begin{array}{cccccc} -4 & -5 & 4 & 6 & 0 & 0 \\ 0 & 1 & -2 & 0 & 1 & 0 \\ 0 & 0 & -4 & 0 & 1 & 2 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] & & & & & \end{array} \quad (\text{b})$$

Matrix (b) is a reduced matrix, and, since it has three nonzero rows, there are three independent chemical reactions. The nonzero rows in Matrix (b) provide the following set of independent reactions (stoichiometric relations):



Note that the second and third rows in Matrix (b) represent two chemical reactions that are not among the original reactions, and we denote them as Reactions 5 and 6. The stoichiometric coefficients of these three independent chemical reactions are

$$\begin{array}{lllll} (s_{\text{NH}_3})_1 = -4 & (s_{\text{O}_2})_1 = -5 & (s_{\text{NO}})_1 = 4 & (s_{\text{H}_2\text{O}})_1 = 6 & (s_{\text{N}_2})_1 = 0 \\ (s_{\text{NO}_2})_1 = 0 & \Delta_1 = 1 & & & \\ (s_{\text{NH}_3})_5 = 0 & (s_{\text{O}_2})_5 = 1 & (s_{\text{NO}})_5 = -2 & (s_{\text{H}_2\text{O}})_5 = 0 & (s_{\text{N}_2})_5 = 1 \\ (s_{\text{NO}_2})_5 = 0 & \Delta_5 = 0 & & & \\ (s_{\text{NH}_3})_6 = 0 & (s_{\text{O}_2})_6 = 0 & (s_{\text{NO}})_6 = -4 & (s_{\text{H}_2\text{O}})_6 = 0 & (s_{\text{N}_2})_6 = 1 \\ (s_{\text{NO}_2})_6 = 2 & \Delta_6 = -1 & & & \end{array}$$

To determine the species compositions, we express them in terms of the extents of these three independent reactions, Z_1 , Z_5 , and Z_6 . Selecting the initial state as

the reference state, and using Eq. 2.7.4,

$$\begin{aligned} N_{\text{NH}_3}(t) &= N_{\text{tot}}(0)[y_{\text{NH}_3}(0) + (s_{\text{NH}_3})_1 Z_1 + (s_{\text{NH}_3})_5 Z_5 + (s_{\text{NH}_3})_6 Z_6] \\ &= 10(0.4 - 4Z_1) \end{aligned} \quad (\text{c})$$

$$N_{\text{N}_2}(t) = N_{\text{tot}}(0)[y_{\text{N}_2}(0) + (s_{\text{N}_2})_1 Z_1 + (s_{\text{N}_2})_5 Z_5 + (s_{\text{N}_2})_6 Z_6] = 10(5Z_1 + Z_6) \quad (\text{d})$$

Using, Eq. 2.7.6,

$$N_{\text{tot}}(t) = N_{\text{tot}}(0)[1 + \Delta_1 Z_1 + \Delta_5 Z_5 + \Delta_6 Z_6] = 10(1 + Z_1 - Z_6) \quad (\text{e})$$

Using the given data, and assuming ideal gas behavior,

$$\frac{P(t)}{P(0)} = \frac{N_{\text{tot}}(t)}{N_{\text{tot}}(0)} = 1 + Z_1 - Z_6 = 1.06 \quad (\text{f})$$

$$y_{\text{NH}_3}(t) = \frac{0.4 - 4Z_1}{1 + Z_1 - Z_6} = 0.07547 \quad (\text{g})$$

$$y_{\text{N}_2}(t) = \frac{5Z_5 + Z_6}{1 + Z_1 - Z_6} = 0.1132 \quad (\text{h})$$

Solving Eqs. (f), (g), and (h), $Z_1 = 0.08$; $Z_5 = 0.10$; $Z_6 = 0.02$. Using Eqs. 2.7.4 and Eq. 2.7.6, the compositions of the other species are

$$y_{\text{NO}}(t) = \frac{4Z_1 - 2Z_5 - 4Z_6}{1 + Z_1 - Z_6} = 0.0377$$

$$y_{\text{H}_2\text{O}}(t) = \frac{6Z_1}{1 + Z_1 - Z_6} = 0.4528$$

$$y_{\text{O}_2}(t) = \frac{0.6 - 5Z_1 + Z_5}{1 + Z_1 - Z_6} = 0.283$$

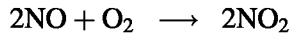
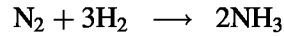
$$y_{\text{NO}_2}(t) = \frac{2Z_6}{1 + Z_1 - Z_6} = 0.0377$$

2.8 INDEPENDENT SPECIES COMPOSITION SPECIFICATIONS

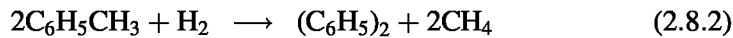
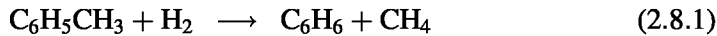
In the preceding section, we discussed how to determine the number of independent chemical reactions and how to select a set of independent reactions. The number of independent reactions indicates the number of equations that we should solve to determine the composition of the reactor. To solve these equations,

the specified species conditions should provide independent information. Below, we describe a method to determine what sets of species compositions provide independent information.

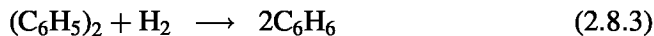
Let us examine more closely the nature of the problem. Consider first a chemical reactor where the following two reactions take place:



Since each chemical reaction has at least one species that does not participate in the other, both reactions are independent. Hence, we need to specify two species compositions to determine the extents of the two reactions. At first glance, it seems that we can specify the composition of any two species. However, a closer examination of the reactions reveals that none of the species participates in both reactions. By specifying the amount of two species from the same chemical reaction, we cannot determine the extents of the second reaction and the reactor composition. Hence, we have to specify two independent compositions such that each relates to a distinct independent chemical reaction. Similar situations may arise when we deal with more complex sets of chemical reactions, where the identification of independent compositions is not so obvious. Consider the hydrogenation of toluene where the following two reactions take place:



These two chemical reactions are independent, yet if we specify the amounts of toluene and methane, we cannot determine the composition of the other species. The reason is that, while the two reactions are independent, we cannot select any two species compositions to provide information on all other species. In this case, compositions of the toluene and methane do not provide us with a relationship on the amount of diphenyl and hydrogen. This becomes evident if we multiply Reaction 2.8.1 by 2 and subtract Reaction 2.8.2:



It is clear that specifications of the amounts of toluene and methane do not provide any information on the amounts of diphenyl and hydrogen.

Independent composition specifications depend on the relationships among individual species and the chemical reactions taking place in the reactor, but they are invariant of the specific set of independent reactions selected. Since the set of independent reactions generated by the reduced matrix of the Gaussian elimination

consists of chemical reactions with the least number of species, we apply the reduced matrix to identify independent species composition specifications. To determine the extents of the independent chemical reactions, we usually specify either the amount of individual species (moles of molar flow rates) or a quantity related to all the independent reactions (total number of moles, pressure of the system, etc.) together with compositions of certain species. Note that specifications of species mole fractions contain information on the total number of moles or, for flow reactors, on the molar flow rate.

To identify independent species composition specifications, we adopt the following procedure:

1. Construct a matrix of stoichiometric coefficients for the given reactions, and then reduce it to the reduced matrix (see Section 2.4) using Gaussian elimination.
2. Select a species (a nonzero stoichiometric coefficient) to relate to the first reaction, and then remove the column and the row from the reduced matrix.
3. Repeat step (2) for the remaining reactions until we complete the matrix. The species that we selected provide independent species compositions.
4. If the given data relates to the total number of moles rather than individual species (e.g., pressure), we add another column to the reduced matrix, containing the Δ factors (defined by Eq. 2.2.5) for each reaction in the reduced matrix. We treat the Δ column as the measurable quantity that relates to the sum of species.

For example, for Reactions 2.8.1 and 2.8.2, the reduced matrix is

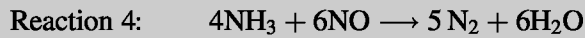
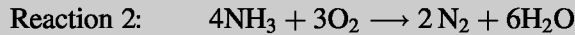
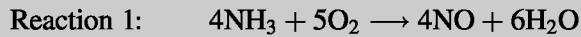
$$\begin{array}{ccccc} & \text{T} & \text{H} & \text{B} & \text{M} & \text{D} \\ \left[\begin{array}{ccccc} -1 & -1 & 1 & 1 & 0 \\ 0 & 1 & -2 & 0 & 1 \end{array} \right] & & & & & \end{array} \quad (2.8.4)$$

The two rows in Matrix 2.8.4 correspond to Reactions 2.8.1 and 2.8.3, respectively. If we select methane (M) to relate to Reaction 2.8.3, we now remove the fourth column and the first row. We can now select either H, B, or D to relate to Reaction 2.8.3. Adding the Δ factor column to Matrix 2.8.4,

$$\begin{array}{cccccc} & \text{T} & \text{H} & \text{B} & \text{M} & \text{D} & \Delta \\ \left[\begin{array}{cccccc} -1 & -1 & 1 & 1 & 0 & 0 \\ 0 & 1 & -2 & 0 & 1 & 0 \end{array} \right] & & & & & & \end{array} \quad (2.8.5)$$

Matrix 2.8.5 indicates that information on the total molar content is not useful in this case.

Example 2.13 Consider the chemical reactions of Example 2.12:



Identify a set of species compositions that can be specified to determine the extents when one of the measurable quantities is the pressure.

Solution The reduced matrix for this case was derived in Example 2.12. Adding to it the column of the Δ factors,

$$\begin{array}{ccccccc} \text{NH}_3 & \text{O}_2 & \text{NO} & \text{H}_2\text{O} & \text{N}_2 & \text{NO}_2 & \Delta \\ \left[\begin{array}{ccccccc} -4 & -5 & 4 & 6 & 0 & 0 & 1 \\ 0 & 1 & -2 & 0 & 1 & 0 & 0 \\ 0 & 0 & -4 & 0 & 1 & 2 & -1 \end{array} \right] & \text{(a)} \end{array}$$

We select NH_3 to relate to the first reaction and remove the first row and first column:

$$\begin{array}{cccccc} \text{O}_2 & \text{NO} & \text{H}_2\text{O} & \text{N}_2 & \text{NO}_2 & \Delta \\ \left[\begin{array}{cccccc} 1 & -2 & 0 & 1 & 0 & 0 \\ 0 & -4 & 0 & 1 & 2 & -1 \end{array} \right] & \text{(b)} \end{array}$$

We select the total pressure to relate to the last reaction and remove the last row and last column:

$$\begin{array}{ccccc} \text{O}_2 & \text{NO} & \text{H}_2\text{O} & \text{N}_2 & \text{NO}_2 \\ \left[\begin{array}{ccccc} 1 & -2 & 0 & 1 & 0 \end{array} \right] & \text{(c)} \end{array}$$

From Matrix (c), we can select either O_2 , NO , or N_2 to relate to the last reaction. Hence, we can specify the amount NH_3 and of any one of these species together with the total pressure to determine the composition of the reactor. The reader is challenged to check that when the amounts of NH_3 , H_2O , and the pressure are specified, we cannot determine the reactor composition.