Chapter 13

GAS MIXTURES

U p to this point, we have limited our consideration to thermodynamic systems that involve a single pure substance such as water. Many important thermodynamic applications, however, involve *mixtures* of several pure substances rather than a single pure substance. Therefore, it is important to develop an understanding of mixtures and learn how to handle them.

In this chapter, we deal with nonreacting gas mixtures. A nonreacting gas mixture can be treated as a pure substance since it is usually a homogeneous mixture of different gases. The properties of a gas mixture obviously depend on the properties of the individual gases (called *components* or *constituents*) as well as on the amount of each gas in the mixture. Therefore, it is possible to prepare tables of properties for mixtures. This has been done for common mixtures such as air. It is not practical to prepare property tables for every conceivable mixture composition, however, since the number of possible compositions is endless. Therefore, we need to develop rules for determining mixture properties from a knowledge of mixture composition and the properties of the individual components. We do this first for ideal-gas mixtures and then for real-gas mixtures. The basic principles involved are also applicable to liquid or solid mixtures, called *solutions*.

Objectives

The objectives of Chapter 13 are to:

- Develop rules for determining nonreacting gas mixture properties from knowledge of mixture composition and the properties of the individual components.
- Define the quantities used to describe the composition of a mixture, such as mass fraction, mole fraction, and volume fraction.
- Apply the rules for determining mixture properties to ideal-gas mixtures and real-gas mixtures.
- Predict the *P-v-T* behavior of gas mixtures based on Dalton's law of additive pressures and Amagat's law of additive volumes.
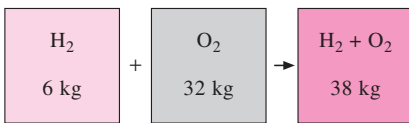- Perform energy and exergy analysis of mixing processes.

FIGURE 13–1

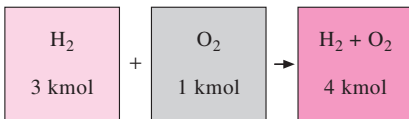The mass of a mixture is equal to the sum of the masses of its components.

FIGURE 13–2

The number of moles of a nonreacting mixture is equal to the sum of the number of moles of its components.
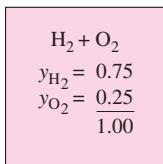

FIGURE 13–3

The sum of the mole fractions of a mixture is equal to 1.

13–1 · COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

To determine the properties of a mixture, we need to know the *composition* of the mixture as well as the properties of the individual components. There are two ways to describe the composition of a mixture: either by specifying the number of moles of each component, called **molar analysis,** or by specifying the mass of each component, called **gravimetric analysis.**

Consider a gas mixture composed of k components. The mass of the mixture m_m is the sum of the masses of the individual components, and the mole number of the mixture N_m is the sum of the mole numbers of the individual components* (Figs. 13–1 and 13–2). That is,

$$m_m = \sum_{i=1}^{k} m_i \quad \text{and} \quad N_m = \sum_{i=1}^{k} N_i \qquad \textbf{(13–1}a, b\textbf{)}$$

The ratio of the mass of a component to the mass of the mixture is called the **mass fraction** mf, and the ratio of the mole number of a component to the mole number of the mixture is called the **mole fraction** y:

$$\text{mf}_i = \frac{m_i}{m_m} \quad \text{and} \quad y_i = \frac{N_i}{N_m} \qquad \textbf{(13–2}a, b\textbf{)}$$

Dividing Eq. 13–1a by m_m or Eq. 13–1b by N_m, we can easily show that the sum of the mass fractions or mole fractions for a mixture is equal to 1 (Fig. 13–3):

$$\sum_{i=1}^{k} \text{mf}_i = 1 \quad \text{and} \quad \sum_{i=1}^{k} y_i = 1$$

The mass of a substance can be expressed in terms of the mole number N and molar mass M of the substance as $m = NM$. Then the **apparent** (or **average**) **molar mass** and the **gas constant** of a mixture can be expressed as

$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_{i=1}^{k} y_i M_i \quad \text{and} \quad R_m = \frac{R_u}{M_m} \quad \textbf{(13–3}a, b\textbf{)}$$

The molar mass of a mixture can also be expressed as

$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i/M_i} = \frac{1}{\sum m_i/(m_m M_i)} = \frac{1}{\sum_{i=1}^{k} \dfrac{\text{mf}_i}{M_i}} \qquad \textbf{(13–4)}$$

Mass and mole fractions of a mixture are related by

$$\text{mf}_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m} \qquad \textbf{(13–5)}$$

---

*Throughout this chapter, the subscript m denotes the gas mixture and the subscript i denotes any single component of the mixture.

EXAMPLE 13–1   Mass and Mole Fractions of a Gas Mixture

Consider a gas mixture that consists of 3 kg of O_2, 5 kg of N_2, and 12 kg of CH_4, as shown in Fig. 13–4. Determine (a) the mass fraction of each component, (b) the mole fraction of each component, and (c) the average molar mass and gas constant of the mixture.

Solution The masses of components of a gas mixture are given. The mass fractions, the mole fractions, the molar mass, and the gas constant of the mixture are to be determined.

Analysis (a) The total mass of the mixture is

$$m_m = m_{O_2} + m_{N_2} + m_{CH_4} = 3 + 5 + 12 = 20 \text{ kg}$$

Then the mass fraction of each component becomes

$$\text{mf}_{O_2} = \frac{m_{O_2}}{m_m} = \frac{3 \text{ kg}}{20 \text{ kg}} = \textbf{0.15}$$

$$\text{mf}_{N_2} = \frac{m_{N_2}}{m_m} = \frac{5 \text{ kg}}{20 \text{ kg}} = \textbf{0.25}$$

$$\text{mf}_{CH_4} = \frac{m_{CH_4}}{m_m} = \frac{12 \text{ kg}}{20 \text{ kg}} = \textbf{0.60}$$

(b) To find the mole fractions, we need to determine the mole numbers of each component first:

$$N_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{3 \text{ kg}}{32 \text{ kg/kmol}} = 0.094 \text{ kmol}$$

$$N_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{5 \text{ kg}}{28 \text{ kg/kmol}} = 0.179 \text{ kmol}$$

$$N_{CH_4} = \frac{m_{CH_4}}{M_{CH_4}} = \frac{12 \text{ kg}}{16 \text{ kg/kmol}} = 0.750 \text{ kmol}$$

Thus,

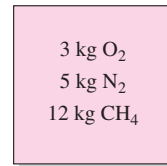$$N_m = N_{O_2} + N_{N_2} + N_{CH_4} = 0.094 + 0.179 + 0.750 = 1.023 \text{ kmol}$$

and

$$y_{O_2} = \frac{N_{O_2}}{N_m} = \frac{0.094 \text{ kmol}}{1.023 \text{ kmol}} = \textbf{0.092}$$

$$y_{N_2} = \frac{N_{N_2}}{N_m} = \frac{0.179 \text{ kmol}}{1.023 \text{ kmol}} = \textbf{0.175}$$

$$y_{CH_4} = \frac{N_{CH_4}}{N_m} = \frac{0.750 \text{ kmol}}{1.023 \text{ kmol}} = \textbf{0.733}$$

(c) The average molar mass and gas constant of the mixture are determined from their definitions,

$$M_m = \frac{m_m}{N_m} = \frac{20 \text{ kg}}{1.023 \text{ kmol}} = \textbf{19.6 kg/kmol}$$

3 kg O_2
5 kg N_2
12 kg CH_4

FIGURE 13–4
Schematic for Example 13–1.

or

$$M_m = \sum y_i M_i = y_{O_2} M_{O_2} + y_{N_2} M_{N_2} + y_{CH_4} M_{CH_4}$$
$$= (0.092)(32) + (0.175)(28) + (0.733)(16)$$
$$= 19.6 \text{ kg/kmol}$$

Also,

$$R_m = \frac{R_u}{M_m} = \frac{8.314 \text{ kJ/(kmol} \cdot \text{K)}}{19.6 \text{ kg/kmol}} = \textbf{0.424 kJ/kg} \cdot \textbf{K}$$

Discussion When mass fractions are available, the molar mass and mole fractions could also be determined directly from Eqs. 13–4 and 13–5.

13–2 ▪ *P-v-T* BEHAVIOR OF GAS MIXTURES: IDEAL AND REAL GASES

An ideal gas is defined as a gas whose molecules are spaced far apart so that the behavior of a molecule is not influenced by the presence of other molecules—a situation encountered at low densities. We also mentioned that real gases approximate this behavior closely when they are at a low pressure or high temperature relative to their critical-point values. The *P-v-T* behavior of an ideal gas is expressed by the simple relation $Pv = RT$, which is called the *ideal-gas equation of state*. The *P-v-T* behavior of real gases is expressed by more complex equations of state or by $Pv = ZRT$, where Z is the compressibility factor.
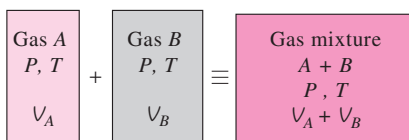
When two or more ideal gases are mixed, the behavior of a molecule normally is not influenced by the presence of other similar or dissimilar molecules, and therefore a nonreacting mixture of ideal gases also behaves as an ideal gas. Air, for example, is conveniently treated as an ideal gas in the range where nitrogen and oxygen behave as ideal gases. When a gas mixture consists of real (nonideal) gases, however, the prediction of the *P-v-T* behavior of the mixture becomes rather involved.

The prediction of the *P-v-T* behavior of gas mixtures is usually based on two models: *Dalton's law of additive pressures* and *Amagat's law of additive volumes*. Both models are described and discussed below.
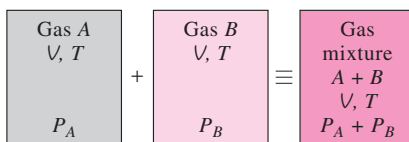
FIGURE 13–5

Dalton's law of additive pressures for a mixture of two ideal gases.

Dalton's law of additive pressures: The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at the mixture temperature and volume (Fig. 13–5).

Amagat's law of additive volumes: The volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure (Fig. 13–6).

FIGURE 13–6

Amagat's law of additive volumes for a mixture of two ideal gases.

Dalton's and Amagat's laws hold exactly for ideal-gas mixtures, but only approximately for real-gas mixtures. This is due to intermolecular forces that may be significant for real gases at high densities. For ideal gases, these two laws are identical and give identical results.

Dalton's and Amagat's laws can be expressed as follows:

Dalton's law:
$$P_m = \sum_{i=1}^{k} P_i(T_m, V_m)$$ (13–6)

Amagat's law:
$$V_m = \sum_{i=1}^{k} V_i(T_m, P_m)$$ (13–7)

exact for ideal gases, approximate for real gases

FIGURE 13–7

The volume a component would occupy if it existed alone at the mixture T and P is called the *component volume* (for ideal gases, it is equal to the partial volume $y_i V_m$).

In these relations, P_i is called the **component pressure** and V_i is called the **component volume** (Fig. 13–7). Note that V_i is the volume a component *would* occupy if it existed alone at T_m and P_m, not the actual volume occupied by the component in the mixture. (In a vessel that holds a gas mixture, each component fills the entire volume of the vessel. Therefore, the volume of each component is equal to the volume of the vessel.) Also, the ratio P_i/P_m is called the **pressure fraction** and the ratio V_i/V_m is called the **volume fraction** of component i.

Ideal-Gas Mixtures

For ideal gases, P_i and V_i can be related to y_i by using the ideal-gas relation for both the components and the gas mixture:

$$\frac{P_i(T_m, V_m)}{P_m} = \frac{N_i R_u T_m / V_m}{N_m R_u T_m / V_m} = \frac{N_i}{N_m} = y_i$$

$$\frac{V_i(T_m, P_m)}{V_m} = \frac{N_i R_u T_m / P_m}{N_m R_u T_m / P_m} = \frac{N_i}{N_m} = y_i$$

Therefore,

$$\frac{P_i}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$ (13–8)

Equation 13–8 is strictly valid for ideal-gas mixtures since it is derived by assuming ideal-gas behavior for the gas mixture and each of its components. The quantity $y_i P_m$ is called the **partial pressure** (identical to the *component pressure* for ideal gases), and the quantity $y_i V_m$ is called the **partial volume** (identical to the *component volume* for ideal gases). *Note that for an ideal-gas mixture, the mole fraction, the pressure fraction, and the volume fraction of a component are identical*.

The composition of an ideal-gas mixture (such as the exhaust gases leaving a combustion chamber) is frequently determined by a volumetric analysis (called the Orsat Analysis) and Eq. 13–8. A sample gas at a known volume, pressure, and temperature is passed into a vessel containing reagents that absorb one of the gases. The volume of the remaining gas is then measured at the original pressure and temperature. The ratio of the reduction in volume to the original volume (volume fraction) represents the mole fraction of that particular gas.

Real-Gas Mixtures

Dalton's law of additive pressures and Amagat's law of additive volumes can also be used for real gases, often with reasonable accuracy. This time, however, the component pressures or component volumes should be evaluated from relations that take into account the deviation of each component
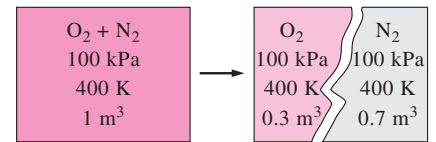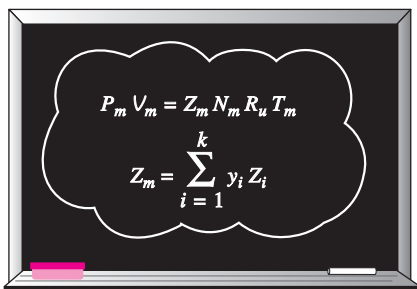
FIGURE 13–8

One way of predicting the P-v-T behavior of a real-gas mixture is to use compressibility factor.

from ideal-gas behavior. One way of doing that is to use more exact equations of state (van der Waals, Beattie–Bridgeman, Benedict–Webb–Rubin, etc.) instead of the ideal-gas equation of state. Another way is to use the compressibility factor (Fig. 13–8) as

$$PV = ZNR_u T \qquad \text{(13–9)}$$

The compressibility factor of the mixture Z_m can be expressed in terms of the compressibility factors of the individual gases Z_i by applying Eq. 13–9 to both sides of Dalton's law or Amagat's law expression and simplifying. We obtain

$$Z_m = \sum_{i=1}^{k} y_i Z_i \qquad \text{(13–10)}$$

where Z_i is determined either at T_m and V_m (Dalton's law) or at T_m and P_m (Amagat's law) for each individual gas. It may seem that using either law gives the same result, but it does not.

The compressibility-factor approach, in general, gives more accurate results when the Z_i's in Eq. 13–10 are evaluated by using Amagat's law instead of Dalton's law. This is because Amagat's law involves the use of mixture pressure P_m, which accounts for the influence of intermolecular forces between the molecules of different gases. Dalton's law disregards the influence of dissimilar molecules in a mixture on each other. As a result, it tends to underpredict the pressure of a gas mixture for a given V_m and T_m. Therefore, Dalton's law is more appropriate for gas mixtures at low pressures. Amagat's law is more appropriate at high pressures.

Note that there is a significant difference between using the compressibility factor for a single gas and for a mixture of gases. The compressibility factor predicts the P-v-T behavior of single gases rather accurately, as discussed in Chapter 3, but not for mixtures of gases. When we use compressibility factors for the components of a gas mixture, we account for the influence of like molecules on each other; the influence of dissimilar molecules remains largely unaccounted for. Consequently, a property value predicted by this approach may be considerably different from the experimentally determined value.

Another approach for predicting the P-v-T behavior of a gas mixture is to treat the gas mixture as a pseudopure substance (Fig. 13–9). One such method, proposed by W. B. Kay in 1936 and called **Kay's rule,** involves the use of a *pseudocritical pressure* $P'_{cr,m}$ and *pseudocritical temperature* $T'_{cr,m}$ for the mixture, defined in terms of the critical pressures and temperatures of the mixture components as

$$P'_{cr,m} = \sum_{i=1}^{k} y_i P_{cr,i} \quad \text{and} \quad T'_{cr,m} = \sum_{i=1}^{k} y_i T_{cr,i} \qquad \text{(13–11a, b)}$$
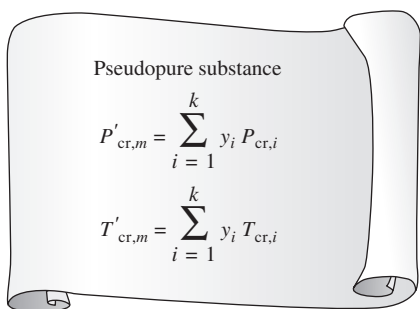

FIGURE 13–9

Another way of predicting the P-v-T behavior of a real-gas mixture is to treat it as a pseudopure substance with critical properties P'_{cr} and T'_{cr}.

The compressibility factor of the mixture Z_m is then easily determined by using these pseudocritical properties. The result obtained by using Kay's rule is accurate to within about 10 percent over a wide range of temperatures and pressures, which is acceptable for most engineering purposes.

Another way of treating a gas mixture as a pseudopure substance is to use a more accurate equation of state such as the van der Waals, Beattie–Bridgeman, or Benedict–Webb–Rubin equation for the mixture, and to determine the constant coefficients in terms of the coefficients of the components.

In the van der Waals equation, for example, the two constants for the mixture are determined from

$$a_m = \left(\sum_{i=1}^{k} y_i a_i^{1/2} \right)^2 \quad \text{and} \quad b_m = \sum_{i=1}^{k} y_i b_i \qquad \text{(13–12a, b)}$$

where expressions for a_i and b_i are given in Chapter 3.

EXAMPLE 13–2   *P-v-T* **Behavior of Nonideal Gas Mixtures**

A rigid tank contains 2 kmol of N_2 and 6 kmol of CO_2 gases at 300 K and 15 MPa (Fig. 13–10). Estimate the volume of the tank on the basis of (*a*) the ideal-gas equation of state, (*b*) Kay's rule, (*c*) compressibility factors and Amagat's law, and (*d*) compressibility factors and Dalton's law.

Solution   The composition of a mixture in a rigid tank is given. The volume of the tank is to be determined using four different approaches.
Assumptions   Stated in each section.
Analysis   (*a*) When the mixture is assumed to behave as an ideal gas, the volume of the mixture is easily determined from the ideal-gas relation for the mixture:

$$V_m = \frac{N_m R_u T_m}{P_m} = \frac{(8 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(300 \text{ K})}{15{,}000 \text{ kPa}} = \textbf{1.330 m}^3$$

since

$$N_m = N_{N_2} + N_{CO_2} = 2 + 6 = 8 \text{ kmol}$$

(*b*) To use Kay's rule, we need to determine the pseudocritical temperature and pseudocritical pressure of the mixture by using the critical-point properties of N_2 and CO_2 from Table A–1. However, first we need to determine the mole fraction of each component:

$$y_{N_2} = \frac{N_{N_2}}{N_m} = \frac{2 \text{ kmol}}{8 \text{ kmol}} = 0.25 \quad \text{and} \quad y_{CO_2} = \frac{N_{CO_2}}{N_m} = \frac{6 \text{ kmol}}{8 \text{ kmol}} = 0.75$$

$$T'_{cr,m} = \sum y_i T_{cr,i} = y_{N_2} T_{cr,N_2} + y_{CO_2} T_{cr,CO_2}$$
$$= (0.25)(126.2 \text{ K}) + (0.75)(304.2 \text{ K}) = 259.7 \text{ K}$$

$$P'_{cr,m} = \sum y_i P_{cr,i} = y_{N_2} P_{cr,N_2} + y_{CO_2} P_{cr,CO_2}$$
$$= (0.25)(3.39 \text{ MPa}) + (0.75)(7.39 \text{ MPa}) = 6.39 \text{ MPa}$$

Then,

$$\left. \begin{array}{l} T_R = \dfrac{T_m}{T'_{cr,m}} = \dfrac{300 \text{ K}}{259.7 \text{ K}} = 1.16 \\[2mm] P_R = \dfrac{P_m}{P'_{cr,m}} = \dfrac{15 \text{ MPa}}{6.39 \text{ MPa}} = 2.35 \end{array} \right\} Z_m = 0.49 \qquad \text{(Fig. A–15b)}$$

Thus,

$$V_m = \frac{Z_m N_m R_u T_m}{P_m} = Z_m V_{ideal} = (0.49)(1.330 \text{ m}^3) = \textbf{0.652 m}^3$$

---

2 kmol N_2
6 kmol CO_2
300 K
15 MPa
V_m = ?

FIGURE 13–10
Schematic for Example 13–2.

(c) When Amagat's law is used in conjunction with compressibility factors, Z_m is determined from Eq. 13–10. But first we need to determine the Z of each component on the basis of Amagat's law:

$$N_2: \quad T_{R,N_2} = \frac{T_m}{T_{cr,N_2}} = \frac{300 \text{ K}}{126.2 \text{ K}} = 2.38 \left.\begin{array}{l} \\ \\ \end{array}\right\} \quad Z_{N_2} = 1.02 \quad (\text{Fig. A–15}b)$$
$$P_{R,N_2} = \frac{P_m}{P_{cr,N_2}} = \frac{15 \text{ MPa}}{3.39 \text{ MPa}} = 4.42$$

$$CO_2: \quad T_{R,CO_2} = \frac{T_m}{T_{cr,CO_2}} = \frac{300 \text{ K}}{304.2 \text{ K}} = 0.99 \left.\begin{array}{l} \\ \\ \end{array}\right\} \quad Z_{CO_2} = 0.30 \quad (\text{Fig. A–15}b)$$
$$P_{R,CO_2} = \frac{P_m}{P_{cr,CO_2}} = \frac{15 \text{ MPa}}{7.39 \text{ MPa}} = 2.03$$

Mixture: $\quad Z_m = \sum y_i Z_i = y_{N_2} Z_{N_2} + y_{CO_2} Z_{CO_2}$
$$= (0.25)(1.02) + (0.75)(0.30) = 0.48$$

Thus,

$$V_m = \frac{Z_m N_m R_u T_m}{P_m} = Z_m V_{\text{ideal}} = (0.48)(1.330 \text{ m}^3) = \textbf{0.638 m}^3$$

The compressibility factor in this case turned out to be almost the same as the one determined by using Kay's rule.

(d) When Dalton's law is used in conjunction with compressibility factors, Z_m is again determined from Eq. 13–10. However, this time the Z of each component is to be determined at the mixture temperature and volume, which is not known. Therefore, an iterative solution is required. We start the calculations by assuming that the volume of the gas mixture is 1.330 m³, the value determined by assuming ideal-gas behavior.

The T_R values in this case are identical to those obtained in part (c) and remain constant. The pseudoreduced volume is determined from its definition in Chap. 3:

$$v_{R,N_2} = \frac{\bar{v}_{N_2}}{R_u T_{cr,N_2}/P_{cr,N_2}} = \frac{V_m/N_{N_2}}{R_u T_{cr,N_2}/P_{cr,N_2}}$$

$$= \frac{(1.33 \text{ m}^3)/(2 \text{ kmol})}{(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(126.2 \text{ K})/(3390 \text{ kPa})} = 2.15$$

Similarly,

$$v_{R,CO_2} = \frac{(1.33 \text{ m}^3)/(6 \text{ kmol})}{(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(304.2 \text{ K})/(7390 \text{ kPa})} = 0.648$$

From Fig. A–15, we read $Z_{N_2} = 0.99$ and $Z_{CO_2} = 0.56$. Thus,

$$Z_m = y_{N_2} Z_{N_2} + y_{CO_2} Z_{CO_2} = (0.25)(0.99) + (0.75)(0.56) = 0.67$$

and

$$V_m = \frac{Z_m N_m R T_m}{P_m} = Z_m V_{\text{ideal}} = (0.67)(1.330 \text{ m}^3) = 0.891 \text{ m}^3$$

This is 33 percent lower than the assumed value. Therefore, we should repeat the calculations, using the new value of V_m. When the calculations are repeated we obtain 0.738 m³ after the second iteration, 0.678 m³ after the third iteration, and 0.648 m³ after the fourth iteration. This value does not change with more iterations. Therefore,

$$V_m = \mathbf{0.648\ m^3}$$

Discussion   Notice that the results obtained in parts (b), (c), and (d) are very close. But they are very different from the ideal-gas values. Therefore, treating a mixture of gases as an ideal gas may yield unacceptable errors at high pressures.

13–3 ▪ PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

Consider a gas mixture that consists of 2 kg of N_2 and 3 kg of CO_2. The total mass (an *extensive property*) of this mixture is 5 kg. How did we do it? Well, we simply added the mass of each component. This example suggests a simple way of evaluating the **extensive properties** of a nonreacting ideal- or real-gas mixture: *Just add the contributions of each component of the mixture* (Fig. 13–11). Then the total internal energy, enthalpy, and entropy of a gas mixture can be expressed, respectively, as

$$U_m = \sum_{i=1}^{k} U_i = \sum_{i=1}^{k} m_i u_i = \sum_{i=1}^{k} N_i \bar{u}_i \quad \text{(kJ)} \qquad \textbf{(13–13)}$$

$$H_m = \sum_{i=1}^{k} H_i = \sum_{i=1}^{k} m_i h_i = \sum_{i=1}^{k} N_i \bar{h}_i \quad \text{(kJ)} \qquad \textbf{(13–14)}$$

$$S_m = \sum_{i=1}^{k} S_i = \sum_{i=1}^{k} m_i s_i = \sum_{i=1}^{k} N_i \bar{s}_i \quad \text{(kJ/K)} \qquad \textbf{(13–15)}$$

By following a similar logic, the changes in internal energy, enthalpy, and entropy of a gas mixture during a process can be expressed, respectively, as

$$\Delta U_m = \sum_{i=1}^{k} \Delta U_i = \sum_{i=1}^{k} m_i\,\Delta u_i = \sum_{i=1}^{k} N_i\,\Delta \bar{u}_i \quad \text{(kJ)} \qquad \textbf{(13–16)}$$

$$\Delta H_m = \sum_{i=1}^{k} \Delta H_i = \sum_{i=1}^{k} m_i\,\Delta h_i = \sum_{i=1}^{k} N_i\,\Delta \bar{h}_i \quad \text{(kJ)} \qquad \textbf{(13–17)}$$

$$\Delta S_m = \sum_{i=1}^{k} \Delta S_i = \sum_{i=1}^{k} m_i\,\Delta s_i = \sum_{i=1}^{k} N_i\,\Delta \bar{s}_i \quad \text{(kJ/K)} \qquad \textbf{(13–18)}$$

Now reconsider the same mixture, and assume that both N_2 and CO_2 are at 25°C. The temperature (an *intensive* property) of the mixture is, as you would expect, also 25°C. Notice that we did not add the component temperatures to determine the mixture temperature. Instead, we used some kind of averaging scheme, a characteristic approach for determining the **intensive properties** of a mixture. The internal energy, enthalpy, and entropy of a mixture *per unit mass* or *per unit mole* of the mixture can be determined by dividing the equations above by the mass or the mole number of the mixture (m_m or N_m). We obtain (Fig. 13–12)
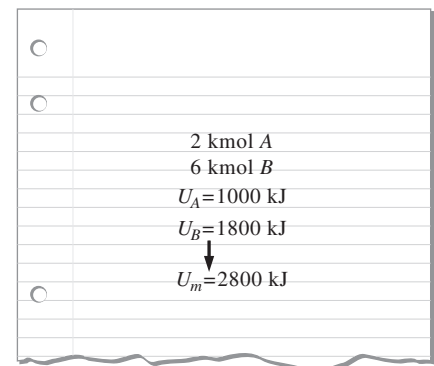
FIGURE 13–11
The extensive properties of a mixture are determined by simply adding the properties of the components.

2 kmol A
6 kmol B
$U_A = 1000$ kJ
$U_B = 1800$ kJ
$U_m = 2800$ kJ
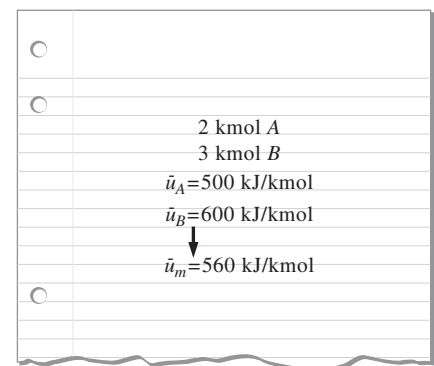
FIGURE 13–12
The intensive properties of a mixture are determined by weighted averaging.

2 kmol A
3 kmol B
$\bar{u}_A = 500$ kJ/kmol
$\bar{u}_B = 600$ kJ/kmol
$\bar{u}_m = 560$ kJ/kmol

$$u_m = \sum_{i=1}^{k} \mathrm{mf}_i u_i \quad (\mathrm{kJ/kg}) \qquad \text{and} \qquad \bar{u}_m = \sum_{i=1}^{k} y_i \bar{u}_i \quad (\mathrm{kJ/kmol}) \tag{13–19}$$

$$h_m = \sum_{i=1}^{k} \mathrm{mf}_i h_i \quad (\mathrm{kJ/kg}) \qquad \text{and} \qquad \bar{h}_m = \sum_{i=1}^{k} y_i \bar{h}_i \quad (\mathrm{kJ/kmol}) \tag{13–20}$$

$$s_m = \sum_{i=1}^{k} \mathrm{mf}_i s_i \quad (\mathrm{kJ/kg \cdot K}) \quad \text{and} \quad \bar{s}_m = \sum_{i=1}^{k} y_i \bar{s}_i \quad (\mathrm{kJ/kmol \cdot K}) \tag{13–21}$$

Similarly, the specific heats of a gas mixture can be expressed as

$$c_{v,m} = \sum_{i=1}^{k} \mathrm{mf}_i c_{v,i} \quad (\mathrm{kJ/kg \cdot K}) \quad \text{and} \quad \bar{c}_{v,m} = \sum_{i=1}^{k} y_i \bar{c}_{v,i} \quad (\mathrm{kJ/kmol \cdot K}) \tag{13–22}$$

$$c_{p,m} = \sum_{i=1}^{k} \mathrm{mf}_i c_{p,i} \quad (\mathrm{kJ/kg \cdot K}) \quad \text{and} \quad \bar{c}_{p,m} = \sum_{i=1}^{k} y_i \bar{c}_{p,i} \quad (\mathrm{kJ/kmol \cdot K}) \tag{13–23}$$

Notice that *properties per unit mass involve mass fractions* (mf_i) *and properties per unit mole involve mole fractions* (y_i).

The relations given above are exact for ideal-gas mixtures, and approximate for real-gas mixtures. (In fact, they are also applicable to nonreacting liquid and solid solutions especially when they form an "ideal solution.") The only major difficulty associated with these relations is the determination of properties for each individual gas in the mixture. The analysis can be simplified greatly, however, by treating the individual gases as ideal gases, if doing so does not introduce a significant error.

Ideal-Gas Mixtures

The gases that comprise a mixture are often at a high temperature and low pressure relative to the critical-point values of individual gases. In such cases, the gas mixture and its components can be treated as ideal gases with negligible error. Under the ideal-gas approximation, the properties of a gas are not influenced by the presence of other gases, and each gas component in the mixture behaves as if it exists alone at the mixture temperature T_m and mixture volume V_m. This principle is known as the **Gibbs–Dalton law,** which is an extension of Dalton's law of additive pressures. Also, the h, u, c_v, and c_p of an ideal gas depend on temperature only and are independent of the pressure or the volume of the ideal-gas mixture. The partial pressure of a component in an ideal-gas mixture is simply $P_i = y_i P_m$, where P_m is the mixture pressure.

Evaluation of Δu or Δh of the components of an ideal-gas mixture during a process is relatively easy since it requires only a knowledge of the initial and final temperatures. Care should be exercised, however, in evaluating the Δs of the components since the entropy of an ideal gas depends on the pressure or volume of the component as well as on its temperature. The entropy change of individual gases in an ideal-gas mixture during a process can be determined from

$$\Delta s_i = s_{i,2}^{\circ} - s_{i,1}^{\circ} - R_i \ln \frac{P_{i,2}}{P_{i,1}} \cong c_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_i \ln \frac{P_{i,2}}{P_{i,1}} \tag{13–24}$$

or

$$\Delta \bar{s}_i = \bar{s}_{i,2}^{\circ} - \bar{s}_{i,1}^{\circ} - R_u \ln \frac{P_{i,2}}{P_{i,1}} \cong \bar{c}_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_u \ln \frac{P_{i,2}}{P_{i,1}} \tag{13–25}$$

where $P_{i,2} = y_{i,2}P_{m,2}$ and $P_{i,1} = y_{i,1}P_{m,1}$. Notice that the partial pressure P_i of each component is used in the evaluation of the entropy change, not the mixture pressure P_m (Fig. 13–13).

EXAMPLE 13–3   Mixing Two Ideal Gases in a Tank

An insulated rigid tank is divided into two compartments by a partition, as shown in Fig. 13–14. One compartment contains 7 kg of oxygen gas at 40°C and 100 kPa, and the other compartment contains 4 kg of nitrogen gas at 20°C and 150 kPa. Now the partition is removed, and the two gases are allowed to mix. Determine (a) the mixture temperature and (b) the mixture pressure after equilibrium has been established.

Solution   A rigid tank contains two gases separated by a partition. The pressure and temperature of the mixture are to be determined after the partition is removed.

Assumptions   **1** We assume both gases to be ideal gases, and their mixture to be an ideal-gas mixture. This assumption is reasonable since both the oxygen and nitrogen are well above their critical temperatures and well below their critical pressures. **2** The tank is insulated and thus there is no heat transfer. **3** There are no other forms of work involved.

Properties   The constant-volume specific heats of N_2 and O_2 at room temperature are $c_{v,N_2} = 0.743$ kJ/kg · K and $c_{v,O_2} = 0.658$ kJ/kg · K (Table A–2a).

Analysis   We take the entire contents of the tank (both compartments) as the system. This is a *closed system* since no mass crosses the boundary during the process. We note that the volume of a rigid tank is constant and thus there is no boundary work done.

(a) Noting that there is no energy transfer to or from the tank, the energy balance for the system can be expressed as

$$E_{in} - E_{out} = \Delta E_{system}$$

$$0 = \Delta U = \Delta U_{N_2} + \Delta U_{O_2}$$

$$\left[mc_v(T_m - T_1) \right]_{N_2} + \left[mc_v(T_m - T_1) \right]_{O_2} = 0$$

By using c_v values at room temperature, the final temperature of the mixture is determined to be

$$(4 \text{ kg})(0.743 \text{ kJ/kg} \cdot \text{K})(T_m - 20°\text{C}) + (7 \text{ kg})(0.658 \text{ kJ/kg} \cdot \text{K})(T_m - 40°\text{C}) = 0$$

$$T_m = \mathbf{32.2°C}$$

(b) The final pressure of the mixture is determined from the ideal-gas relation

$$P_m V_m = N_m R_u T_m$$

where

$$N_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{7 \text{ kg}}{32 \text{ kg/kmol}} = 0.219 \text{ kmol}$$

$$N_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{4 \text{ kg}}{28 \text{ kg/kmol}} = 0.143 \text{ kmol}$$

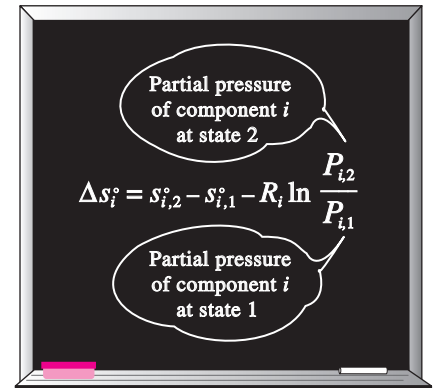$$N_m = N_{O_2} + N_{N_2} = 0.219 + 0.143 = 0.362 \text{ kmol}$$

FIGURE 13–13

Partial pressures (not the mixture pressure) are used in the evaluation of entropy changes of ideal-gas mixtures.
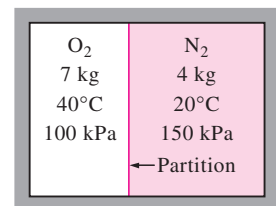
$$\Delta s_i^\circ = s_{i,2}^\circ - s_{i,1}^\circ - R_i \ln \frac{P_{i,2}}{P_{i,1}}$$

Partial pressure of component i at state 2

Partial pressure of component i at state 1

O_2	N_2
7 kg	4 kg
40°C	20°C
100 kPa	150 kPa
	←Partition

FIGURE 13–14

Schematic for Example 13–3.

and

$$V_{O_2} = \left(\frac{NR_u T_1}{P_1}\right)_{O_2} = \frac{(0.219 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(313 \text{ K})}{100 \text{ kPa}} = 5.70 \text{ m}^3$$

$$V_{N_2} = \left(\frac{NR_u T_1}{P_1}\right)_{N_2} = \frac{(0.143 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(293 \text{ K})}{150 \text{ kPa}} = 2.32 \text{ m}^3$$

$$V_m = V_{O_2} + V_{N_2} = 5.70 + 2.32 = 8.02 \text{ m}^3$$

Thus,

$$P_m = \frac{N_m R_u T_m}{V_m} = \frac{(0.362 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(305.2 \text{ K})}{8.02 \text{ m}^3} = \textbf{114.5 kPa}$$

Discussion We could also determine the mixture pressure by using $P_m V_m = m_m R_m T_m$, where R_m is the apparent gas constant of the mixture. This would require a knowledge of mixture composition in terms of mass or mole fractions.
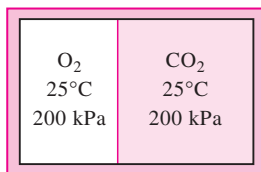

FIGURE 13–15
Schematic for Example 13–4.

EXAMPLE 13–4 Exergy Destruction during Mixing of Ideal Gases

An insulated rigid tank is divided into two compartments by a partition, as shown in Fig. 13–15. One compartment contains 3 kmol of O_2, and the other compartment contains 5 kmol of CO_2. Both gases are initially at 25°C and 200 kPa. Now the partition is removed, and the two gases are allowed to mix. Assuming the surroundings are at 25°C and both gases behave as ideal gases, determine the entropy change and exergy destruction associated with this process.

Solution A rigid tank contains two gases separated by a partition. The entropy change and exergy destroyed after the partition is removed are to be determined.
Assumptions Both gases and their mixture are ideal gases.
Analysis We take the entire contents of the tank (both compartments) as the system. This is a *closed system* since no mass crosses the boundary during the process. We note that the volume of a rigid tank is constant, and there is no energy transfer as heat or work. Also, both gases are initially at the same temperature and pressure.

When two ideal gases initially at the same temperature and pressure are mixed by removing a partition between them, the mixture will also be at the same temperature and pressure. (Can you prove it? Will this be true for non-ideal gases?) Therefore, the temperature and pressure in the tank will still be 25°C and 200 kPa, respectively, after the mixing. The entropy change of each component gas can be determined from Eqs. 13–18 and 13–25:

$$\Delta S_m = \sum \Delta S_i = \sum N_i \, \Delta \bar{s}_i = \sum N_i \left(\bar{c}_{p,i} \ln \frac{T_{i,2}}{T_{i,1}}^{\nearrow 0} - R_u \ln \frac{P_{i,2}}{P_{i,1}} \right)$$

$$= -R_u \sum N_i \ln \frac{y_{i,2} P_{m,2}}{P_{i,1}} = -R_u \sum N_i \ln y_{i,2}$$

since $P_{m,2} = P_{i,1} = 200$ kPa. It is obvious that the entropy change is independent of the composition of the mixture in this case and depends on only

the mole fraction of the gases in the mixture. What is not so obvious is that if the same gas in two different chambers is mixed at constant temperature and pressure, the entropy change is zero.

Substituting the known values, the entropy change becomes

$$N_m = N_{O_2} + N_{CO_2} = (3 + 5)\,\text{kmol} = 8\,\text{kmol}$$

$$y_{O_2} = \frac{N_{O_2}}{N_m} = \frac{3\,\text{kmol}}{8\,\text{kmol}} = 0.375$$

$$y_{CO_2} = \frac{N_{CO_2}}{N_m} = \frac{5\,\text{kmol}}{8\,\text{kmol}} = 0.625$$

$$\Delta S_m = -R_u(N_{O_2}\ln y_{O_2} + N_{CO_2}\ln y_{CO_2})$$

$$= -(8.314\,\text{kJ/kmol}\cdot\text{K})[(3\,\text{kmol})(\ln 0.375) + (5\,\text{kmol})(\ln 0.625)]$$

$$= \textbf{44.0 kJ/K}$$

The exergy destruction associated with this mixing process is determined from

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} = T_0\,\Delta S_{\text{sys}}$$

$$= (298\,\text{K})(44.0\,\text{kJ/K})$$

$$= \textbf{13.1 MJ}$$

Discussion This large value of exergy destruction shows that mixing processes are highly irreversible.

Real-Gas Mixtures

When the components of a gas mixture do not behave as ideal gases, the analysis becomes more complex because the properties of real (nonideal) gases such as u, h, c_v, and c_p depend on the pressure (or specific volume) as well as on the temperature. In such cases, the effects of deviation from ideal-gas behavior on the mixture properties should be accounted for.

Consider two nonideal gases contained in two separate compartments of an adiabatic rigid tank at 100 kPa and 25°C. The partition separating the two gases is removed, and the two gases are allowed to mix. What do you think the final pressure in the tank will be? You are probably tempted to say 100 kPa, which would be true for ideal gases. However, this is not true for nonideal gases because of the influence of the molecules of different gases on each other (deviation from Dalton's law, Fig. 13–16).

When real-gas mixtures are involved, it may be necessary to account for the effect of nonideal behavior on the mixture properties such as enthalpy and entropy. One way of doing that is to use compressibility factors in conjunction with generalized equations and charts developed in Chapter 12 for real gases.

Consider the following $T\,ds$ relation for a gas mixture:

$$dh_m = T_m\,ds_m + v_m\,dP_m$$

It can also be expressed as

$$d\left(\sum \text{mf}_i h_i\right) = T_m\,d\left(\sum \text{mf}_i s_i\right) + \left(\sum \text{mf}_i v_i\right)dP_m$$
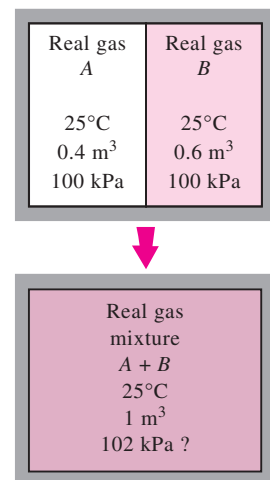
FIGURE 13–16

It is difficult to predict the behavior of nonideal-gas mixtures because of the influence of dissimilar molecules on each other.

or

$$\sum \mathrm{mf}_i(dh_i - T_m \, ds_i - v_i \, dP_m) = 0$$

which yields

$$dh_i = T_m \, ds_i + v_i \, dP_m \qquad \text{(13–26)}$$

This is an important result because Eq. 13–26 is the starting equation in the development of the generalized relations and charts for enthalpy and entropy. It suggests that the generalized property relations and charts for real gases developed in Chapter 12 can also be used for the components of real-gas mixtures. But the reduced temperature T_R and reduced pressure P_R for each component should be evaluated by using the mixture temperature T_m and mixture pressure P_m. This is because Eq. 13–26 involves the mixture pressure P_m, not the component pressure P_i.

The approach described above is somewhat analogous to Amagat's law of additive volumes (evaluating mixture properties at the mixture pressure and temperature), which holds exactly for ideal-gas mixtures and approximately for real-gas mixtures. Therefore, the mixture properties determined with this approach are not exact, but they are sufficiently accurate.

What if the mixture volume and temperature are specified instead of the mixture pressure and temperature? Well, there is no need to panic. Just evaluate the mixture pressure, using Dalton's law of additive pressures, and then use this value (which is only approximate) as the mixture pressure.

Another way of evaluating the properties of a real-gas mixture is to treat the mixture as a pseudopure substance having pseudocritical properties, determined in terms of the critical properties of the component gases by using Kay's rule. The approach is quite simple, and the accuracy is usually acceptable.
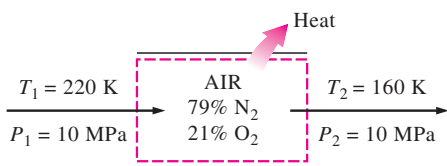

FIGURE 13–17

Schematic for Example 13–5.

EXAMPLE 13–5   Cooling of a Nonideal Gas Mixture

Air is a mixture of N_2, O_2, and small amounts of other gases, and it can be approximated as 79 percent N_2 and 21 percent O_2 on mole basis. During a steady-flow process, air is cooled from 220 to 160 K at a constant pressure of 10 MPa (Fig. 13–17). Determine the heat transfer during this process per kmol of air, using (*a*) the ideal-gas approximation, (*b*) Kay's rule, and (*c*) Amagat's law.

Solution   Air at a low temperature and high pressure is cooled at constant pressure. The heat transfer is to be determined using three different approaches.

Assumptions   **1** This is a steady-flow process since there is no change with time at any point and thus $\Delta m_{CV} = 0$ and $\Delta E_{CV} = 0$. **2** The kinetic and potential energy changes are negligible.

Analysis   We take the *cooling section* as the system. This is a *control volume* since mass crosses the system boundary during the process. We note that heat is transferred out of the system.

The critical properties are $T_{cr} = 126.2$ K and $P_{cr} = 3.39$ MPa for N_2 and $T_{cr} = 154.8$ K and $P_{cr} = 5.08$ MPa for O_2. Both gases remain above their

critical temperatures, but they are also above their critical pressures. There-fore, air will probably deviate from ideal-gas behavior, and thus it should be treated as a real-gas mixture.

The energy balance for this steady-flow system can be expressed on a unit mole basis as

$$e_{in} - e_{out} = \Delta e_{system}^{\nearrow 0} = 0 \rightarrow e_{in} = e_{out} \rightarrow \bar{h}_1 = \bar{h}_2 + \bar{q}_{out}$$

$$\bar{q}_{out} = \bar{h}_1 - \bar{h}_2 = y_{N_2}(\bar{h}_1 - \bar{h}_2)_{N_2} + y_{O_2}(\bar{h}_1 - \bar{h}_2)_{O_2}$$

where the enthalpy change for either component can be determined from the generalized enthalpy departure chart (Fig. A–29) and Eq. 12–58:

$$\bar{h}_1 - \bar{h}_2 = \bar{h}_{1,ideal} - \bar{h}_{2,ideal} - R_u T_{cr}(Z_{h1} - Z_{h2})$$

The first two terms on the right-hand side of this equation represent the ideal-gas enthalpy change of the component. The terms in parentheses repre-sent the deviation from the ideal-gas behavior, and their evaluation requires a knowledge of reduced pressure P_R and reduced temperature T_R, which are calculated at the mixture temperature T_m and mixture pressure P_m.

(a) If the N_2 and O_2 mixture is assumed to behave as an ideal gas, the enthalpy of the mixture will depend on temperature only, and the enthalpy values at the initial and the final temperatures can be determined from the ideal-gas tables of N_2 and O_2 (Tables A–18 and A–19):

$$T_1 = 220 \text{ K} \rightarrow \bar{h}_{1,ideal,N_2} = 6391 \text{ kJ/kmol}$$

$$\bar{h}_{1,ideal,O_2} = 6404 \text{ kJ/kmol}$$

$$T_2 = 160 \text{ K} \rightarrow \bar{h}_{2,ideal,N_2} = 4648 \text{ kJ/kmol}$$

$$\bar{h}_{2,ideal,O_2} = 4657 \text{ kJ/kmol}$$

$$\bar{q}_{out} = y_{N_2}(\bar{h}_1 - \bar{h}_2)_{N_2} + y_{O_2}(\bar{h}_1 - \bar{h}_2)_{O_2}$$

$$= (0.79)(6391 - 4648) \text{ kJ/kmol} + (0.21)(6404 - 4657) \text{ kJ/kmol}$$

$$= \textbf{1744 kJ/kmol}$$

(b) Kay's rule is based on treating a gas mixture as a pseudopure substance whose critical temperature and pressure are

$$T'_{cr,m} = \sum y_i T_{cr,i} = y_{N_2} T_{cr,N_2} + y_{O_2} T_{cr,O_2}$$

$$= (0.79)(126.2 \text{ K}) + (0.21)(154.8 \text{ K}) = 132.2 \text{ K}$$

and

$$P'_{cr,m} = \sum y_i P_{cr,i} = y_{N_2} P_{cr,N_2} + y_{O_2} P_{cr,O_2}$$

$$= (0.79)(3.39 \text{ MPa}) + (0.21)(5.08 \text{ MPa}) = 3.74 \text{ MPa}$$

Then,

$$T_{R,1} = \frac{T_{m,1}}{T_{cr,m}} = \frac{220 \text{ K}}{132.2 \text{ K}} = 1.66$$

$$P_R = \frac{P_m}{P_{cr,m}} = \frac{10 \text{ MPa}}{3.74 \text{ MPa}} = 2.67 \left.\right\} Z_{h_1,m} = 1.0$$

$$T_{R,2} = \frac{T_{m,2}}{T_{cr,m}} = \frac{160 \text{ K}}{132.2 \text{ K}} = 1.21 \left.\right\} Z_{h_2,m} = 2.6$$

Also,

$$\bar{h}_{m_1,\text{ideal}} = y_{\text{N}_2}\bar{h}_{1,\text{ideal,N}_2} + y_{\text{O}_2}\bar{h}_{1,\text{ideal,O}_2}$$

$$= (0.79)(6391 \text{ kJ/kmol}) + (0.21)(6404 \text{ kJ/kmol})$$

$$= 6394 \text{ kJ/kmol}$$

$$\bar{h}_{m_2,\text{ideal}} = y_{\text{N}_2}\bar{h}_{2,\text{ideal,N}_2} + y_{\text{O}_2}\bar{h}_{2,\text{ideal,O}_2}$$

$$= (0.79)(4648 \text{ kJ/kmol}) + (0.21)(4657 \text{ kJ/kmol})$$

$$= 4650 \text{ kJ/kmol}$$

Therefore,

$$\bar{q}_{\text{out}} = (\bar{h}_{m_1,\text{ideal}} - \bar{h}_{m_2,\text{ideal}}) - R_u T_{\text{cr}}(Z_{h_1} - Z_{h_2})_m$$

$$= [(6394 - 4650) \text{ kJ/kmol}] - (8.314 \text{ kJ/kmol} \cdot \text{K})(132.2 \text{ K})(1.0 - 2.6)$$

$$= \textbf{3503 kJ/kmol}$$

(*c*) The reduced temperatures and pressures for both N_2 and O_2 at the initial and final states and the corresponding enthalpy departure factors are, from Fig. A–29,

N_2:

$$T_{R_1,\text{N}_2} = \frac{T_{m,1}}{T_{\text{cr,N}_2}} = \frac{220 \text{ K}}{126.2 \text{ K}} = 1.74$$

$$Z_{h_1,\text{N}_2} = 0.9$$

$$P_{R,\text{N}_2} = \frac{P_m}{P_{\text{cr,N}_2}} = \frac{10 \text{ MPa}}{3.39 \text{ MPa}} = 2.95$$

$$T_{R_2,\text{N}_2} = \frac{T_{m,2}}{T_{\text{cr,N}_2}} = \frac{160 \text{ K}}{126.2 \text{ K}} = 1.27$$

$$Z_{h_2,\text{N}_2} = 2.4$$

O_2:

$$T_{R_1,\text{O}_2} = \frac{T_{m,1}}{T_{\text{cr,O}_2}} = \frac{220 \text{ K}}{154.8 \text{ K}} = 1.42$$

$$Z_{h_1,\text{O}_2} = 1.3$$

$$P_{R,\text{O}_2} = \frac{P_m}{P_{\text{cr,O}_2}} = \frac{10 \text{ MPa}}{5.08 \text{ MPa}} = 1.97$$

$$T_{R_1,\text{O}_2} = \frac{T_{m,2}}{T_{\text{cr,O}_2}} = \frac{160 \text{ K}}{154.8 \text{ K}} = 1.03$$

$$Z_{h_2,\text{O}_2} = 4.0$$

From Eq. 12–58,

$$(\bar{h}_1 - \bar{h}_2)_{\text{N}_2} = (\bar{h}_{1,\text{ideal}} - \bar{h}_{2,\text{ideal}})_{\text{N}_2} - R_u T_{\text{cr}}(Z_{h_1} - Z_{h_2})_{\text{N}_2}$$

$$= [(6391 - 4648) \text{ kJ/kmol}] - (8.314 \text{ kJ/kmol} \cdot \text{K})(126.2 \text{ K})(0.9 - 2.4)$$

$$= 3317 \text{ kJ/kmol}$$

$$(\bar{h}_1 - \bar{h}_2)_{\text{O}_2} = (\bar{h}_{1,\text{ideal}} - \bar{h}_{2,\text{ideal}})_{\text{O}_2} - R_u T_{\text{cr}}(Z_{h_1} - Z_{h_2})_{\text{O}_2}$$

$$= [(6404 - 4657) \text{ kJ/kmol}] - (8.314 \text{ kJ/kmol} \cdot \text{K})(154.8 \text{ K})(1.3 - 4.0)$$

$$= 5222 \text{ kJ/kmol}$$

Therefore,

$$\bar{q}_{\text{out}} = y_{\text{N}_2}(\bar{h}_1 - \bar{h}_2)_{\text{N}_2} + y_{\text{O}_2}(\bar{h}_1 - \bar{h}_2)_{\text{O}_2}$$

$$= (0.79)(3317 \text{ kJ/kmol}) + (0.21)(5222 \text{ kJ/kmol})$$

$$= \textbf{3717 kJ/kmol}$$

Discussion   This result is about 6 percent greater than the result obtained in part (*b*) by using Kay's rule. But it is more than twice the result obtained by assuming the mixture to be an ideal gas.

TOPIC OF SPECIAL INTEREST*   Chemical Potential and the Separation Work of Mixtures

When two gases or two miscible liquids are brought into contact, they mix and form a homogeneous mixture or solution without requiring any work input. That is, the natural tendency of miscible substances brought into contact is to mix with each other. As such, these are irreversible processes, and thus it is impossible for the reverse process of separation to occur spontaneously. For example, pure nitrogen and oxygen gases readily mix when brought into contact, but a mixture of nitrogen and oxygen (such as air) never separates into pure nitrogen and oxygen when left unattended.

Mixing and separation processes are commonly used in practice. Separation processes require a work (or, more generally, exergy) input, and minimizing this required work input is an important part of the design process of separation plants. The presence of dissimilar molecules in a mixture affect each other, and therefore the influence of composition on the properties must be taken into consideration in any thermodynamic analysis. In this section we analyze the general mixing processes, with particular emphasis on ideal solutions, and determine the entropy generation and exergy destruction. We then consider the reverse process of separation, and determine the minimum (or reversible) work input needed for separation.

The specific Gibbs function (or Gibbs free energy) g is defined as the combination property $g = h - Ts$. Using the relation $dh = v\,dP + T\,ds$, the differential change of the Gibbs function of a pure substance is obtained by differentiation to be

$$dg = v\,dP - s\,dT \quad \text{or} \quad dG = V\,dP - S\,dT \qquad \text{(pure substance)} \quad \text{(13–27)}$$

For a mixture, the total Gibbs function is a function of two independent intensive properties as well as the composition, and thus it can be expressed as $G = G(P, T, N_1, N_2, \ldots, N_i)$. Its differential is

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \sum_i \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_j} dN_i \qquad \text{(mixture)} \quad \text{(13–28)}$$

where the subscript N_j indicates that the mole numbers of all components in the mixture other than component i are to be held constant during differentiation. For a pure substance, the last term drops out since the composition is fixed, and the equation above must reduce to the one for a pure substance. Comparing Eqs. 13–27 and 13–28 gives

$$dG = V\,dP - S\,dT + \sum_i \mu_i\,dN_i \quad \text{or} \quad d\bar{g} = \bar{v}\,dP - \bar{s}\,dT + \sum_i \mu_i\,dy_i \qquad \text{(13–29)}$$
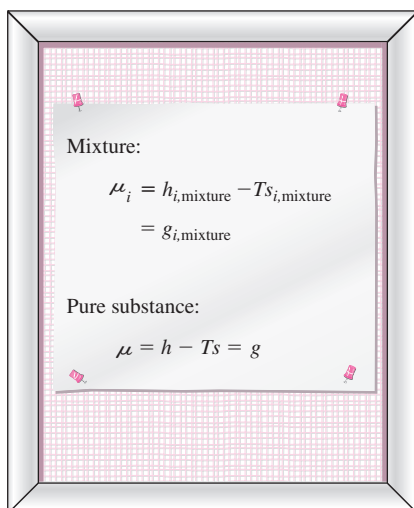
---

*This section can be skipped without a loss in continuity.

FIGURE 13–18

For a pure substance, the chemical potential is equivalent to the Gibbs function.

where $y_i = N_i/N_m$ is the mole fraction of component i (N_m is the total number of moles of the mixture) and

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_j} = \tilde{g}_i = \tilde{h}_i - T\tilde{s}_i \qquad \text{(for component } i \text{ of a mixture)}$$

(13–30)

is the **chemical potential,** which is *the change in the Gibbs function of the mixture in a specified phase when a unit amount of component i in the same phase is added as pressure, temperature, and the amounts of all other components are held constant.* The symbol tilde (as in $\tilde{v}$, $\tilde{h}$, and $\tilde{s}$) is used to denote the **partial molar properties** of the components. Note that the summation term in Eq. 13–29 is zero for a single component system and thus the chemical potential of a pure system in a given phase is equivalent to the molar Gibbs function (Fig. 13–18) since $G = Ng = N\mu$, where

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} = \bar{g} = \bar{h} - T\bar{s} \qquad \text{(pure substance)} \qquad \text{(13–31)}$$

Therefore, the difference between the chemical potential and the Gibbs function is due to the effect of dissimilar molecules in a mixture on each other. It is because of this molecular effect that the volume of the mixture of two miscible liquids may be more or less than the sum of the initial volumes of the individual liquids. Likewise, the total enthalpy of the mixture of two components at the same pressure and temperature, in general, is not equal to the sum of the total enthalpies of the individual components before mixing, the difference being the enthalpy (or heat) of mixing, which is the heat released or absorbed as two or more components are mixed isothermally. For example, the volume of an ethyl alcohol–water mixture is a few percent less than the sum of the volumes of the individual liquids before mixing. Also, when water and flour are mixed to make dough, the temperature of the dough rises noticeably due to the enthalpy of mixing released.

For reasons explained above, the partial molar properties of the components (denoted by an tilde) should be used in the evaluation of the extensive properties of a mixture instead of the specific properties of the pure components. For example, the total volume, enthalpy, and entropy of a mixture should be determined from, respectively,

$$V = \sum_i N_i\tilde{v}_i \quad H = \sum_i N_i\tilde{h}_i \quad \text{and} \quad S = \sum_i N_i\tilde{s}_i \qquad \text{(mixture)} \qquad \text{(13–32)}$$

instead of

$$V^* = \sum_i N_i\bar{v}_i \quad H^* = \sum_i N_i\bar{h}_i \quad \text{and} \quad S^* = \sum_i N_i\bar{s}_i \qquad \text{(13–33)}$$

Then the changes in these extensive properties during mixing become

$$\Delta V_{\text{mixing}} = \sum_i N_i(\tilde{v}_i - \bar{v}_i), \; \Delta H_{\text{mixing}} = \sum_i N_i(\tilde{h}_i - \bar{h}_i), \; \Delta S_{\text{mixing}} = \sum_i N_i(\tilde{s}_i - \bar{s}_i)$$

(13–34)

where ΔH_{mixing} is the **enthalpy of mixing** and ΔS_{mixing} is the **entropy of mixing** (Fig. 13–19). The enthalpy of mixing is positive for exothermic mix-
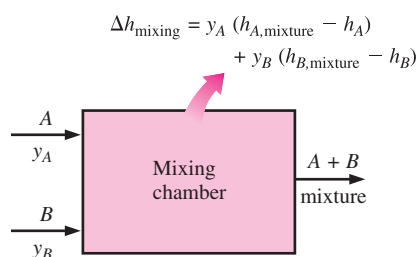

FIGURE 13–19

The amount of heat released or absorbed during a mixing process is called the enthalpy (or heat) of mixing, which is zero for ideal solutions.

ing processes, negative for endothermic mixing processes, and zero for isothermal mixing processes during which no heat is absorbed or released. Note that mixing is an irreversible process, and thus the entropy of mixing must be a positive quantity during an adiabatic process. The specific volume, enthalpy, and entropy of a mixture are determined from

$$\bar{v} = \sum_i y_i \tilde{v}_i \qquad \bar{h} = \sum_i y_i \tilde{h}_i \quad \text{and} \quad \bar{s} = \sum_i y_i \tilde{s}_i \qquad \textbf{(13–35)}$$

where y_i is the mole fraction of component i in the mixture.

Reconsider Eq. 13–29 for dG. Recall that properties are point functions, and they have exact differentials. Therefore, the test of exactness can be applied to the right-hand side of Eq. 13–29 to obtain some important relations. For the differential $dz = M\,dx + N\,dy$ of a function $z(x, y)$, the test of exactness is expressed as $(\partial M/\partial y)_x = (\partial N/\partial x)_y$. When the amount of component i in a mixture is varied at constant pressure or temperature while other components (indicated by j) are held constant, Eq. 13–29 simplifies to

$$dG = -S\,dT + \mu_i\,dN_i \qquad \text{(for } P = \text{constant and } N_j = \text{constant)} \qquad \textbf{(13–36)}$$

$$dG = V\,dP + \mu_i\,dN_i \qquad \text{(for } T = \text{constant and } N_j = \text{constant)} \qquad \textbf{(13–37)}$$

Applying the test of exactness to both of these relations gives

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_j} = -\tilde{s}_i \quad \text{and} \quad \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j} = \tilde{v}_i$$

$$\textbf{(13–38)}$$

where the subscript N indicates that the mole numbers of all components (and thus the composition of the mixture) is to remain constant. Taking the chemical potential of a component to be a function of temperature, pressure, and composition and thus $\mu_i = \mu_i (P, T, y_1, y_2, \ldots, y_j \ldots)$, its total differential can be expressed as

$$d\mu_i = d\tilde{g}_i = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,y} dP + \left(\frac{\partial \mu_i}{\partial T}\right)_{P,y} dT + \sum_i \left(\frac{\partial \mu_i}{\partial y_i}\right)_{P,T,y_j} dy_i \qquad \textbf{(13–39)}$$

where the subscript y indicates that the mole fractions of all components (and thus the composition of the mixture) is to remain constant. Substituting Eqs. 13–38 into the above relation gives

$$d\mu_i = \tilde{v}_i\,dP - \tilde{s}_i\,dT + \sum_i \left(\frac{\partial \mu_i}{\partial y_i}\right)_{P,T,y_j} dy_i \qquad \textbf{(13–40)}$$

For a mixture of fixed composition undergoing an isothermal process, it simplifies to

$$d\mu_i = \tilde{v}_i\,dP \qquad (T = \text{constant}, y_i = \text{constant}) \qquad \textbf{(13–41)}$$

Ideal-Gas Mixtures and Ideal Solutions

When the effect of dissimilar molecules in a mixture on each other is negligible, the mixture is said to be an **ideal mixture** or **ideal solution** and the *chemical potential of a component in such a mixture equals the Gibbs function*

of the pure component. Many liquid solutions encountered in practice, especially dilute ones, satisfy this condition very closely and can be considered to be ideal solutions with negligible error. As expected, the ideal solution approximation greatly simplifies the thermodynamic analysis of mixtures. In an ideal solution, a molecule treats the molecules of all components in the mixture the same way—no extra attraction or repulsion for the molecules of other components. This is usually the case for mixtures of similar substances such as those of petroleum products. Very dissimilar substances such as water and oil won't even mix at all to form a solution.

For an ideal-gas mixture at temperature T and total pressure P, the partial molar volume of a component i is $\widetilde{v}_i = v_i = R_u T/P$. Substituting this relation into Eq. 13–41 gives

$$d\mu_i = \frac{R_u T}{P} dP = R_u T d \ln P = R_u T d \ln P_i \quad (T = \text{constant}, \, y_i = \text{constant}, \text{ ideal gas}) \qquad \textbf{(13–42)}$$

since, from Dalton's law of additive pressures, $P_i = y_i P$ for an ideal gas mixture and

$$d \ln P_i = d \ln(y_i P) = d(\ln y_i + \ln P) = d \ln P \qquad (y_i = \text{constant}) \qquad \textbf{(13–43)}$$

for constant y_i. Integrating Eq. 13–42 at constant temperature from the total mixture pressure P to the component pressure P_i of component i gives

$$\mu_i(T, P_i) = \mu_i(T, P) + R_u T \ln \frac{P_i}{P} = \mu_i(T, P) + R_u T \ln y_i \qquad (\text{ideal gas}) \qquad \textbf{(13–44)}$$

For $y_i = 1$ (i.e., a pure substance of component i alone), the last term in the above equation drops out and we end up with $\mu_i(T, P_i) = \mu_i(T, P)$, which is the value for the pure substance i. Therefore, the term $\mu_i(T, P)$ is simply the chemical potential of the pure substance i when it exists alone at total mixture pressure and temperature, which is equivalent to the Gibbs function since the chemical potential and the Gibbs function are identical for pure substances. The term $\mu_i(T, P)$ is independent of mixture composition and mole fractions, and its value can be determined from the property tables of pure substances. Then Eq. 13–44 can be rewritten more explicitly as

$$\mu_{i,\text{mixture,ideal}}(T, P_i) = \mu_{i,\text{pure}}(T, P) + R_u T \ln y_i \qquad \textbf{(13–45)}$$

Note that *the chemical potential of a component of an ideal gas mixture depends on the mole fraction of the components as well as the mixture temperature and pressure, and is independent of the identity of the other constituent gases*. This is not surprising since the molecules of an ideal gas behave like they exist alone and are not influenced by the presence of other molecules.

Eq. 13–45 is developed for an ideal-gas mixture, but it is also applicable to mixtures or solutions that behave the same way—that is, mixtures or solutions in which the effects of molecules of different components on each other are negligible. The class of such mixtures is called *ideal solutions* (or *ideal mixtures*), as discussed before. The ideal-gas mixture described is just one cate-

gory of ideal solutions. Another major category of ideal solutions is the *dilute liquid solutions*, such as the saline water. It can be shown that the enthalpy of mixing and the volume change due to mixing are zero for ideal solutions (*see* Wark, 1995). That is,

$$\Delta V_{\text{mixing,ideal}} = \sum_i N_i(\widetilde{v}_i - \overline{v}_i) = 0 \quad \text{and} \quad \Delta H_{\text{mixing,ideal}} = \sum_i N_i(\widetilde{h}_i - \overline{h}_i) = 0$$

(13–46)

Then it follows that $\widetilde{v}_i = \overline{v}_i$ and $\widetilde{h}_i = \overline{h}_i$. That is, the partial molar volume and the partial molar enthalpy of a component in a solution equal the specific volume and enthalpy of that component when it existed alone as a pure substance at the mixture temperature and pressure. Therefore, the specific volume and enthalpy of individual components do not change during mixing if they form an ideal solution. Then the specific volume and enthalpy of an ideal solution can be expressed as (Fig. 13–20)

$$\overline{v}_{\text{mixing,ideal}} = \sum_i y_i\widetilde{v}_i = \sum_i y_i\overline{v}_{i,\text{pure}} \quad \text{and} \quad \overline{h}_{\text{mixture,ideal}} = \sum_i y_i\widetilde{h}_i = \sum_i y_i\overline{h}_{i,\text{pure}} \quad \text{(13–47)}$$

Note that this is not the case for entropy and the properties that involve entropy such as the Gibbs function, even for ideal solutions. To obtain a relation for the entropy of a mixture, we differentiate Eq. 13–45 with respect to temperature at constant pressure and mole fraction,

$$\left(\frac{\partial \mu_{i,\text{mixing}}(T, P_i)}{\partial T}\right)_{P,y} = \left(\frac{\partial \mu_{i,\text{pure}}(T, P)}{\partial T}\right)_{P,y} + R_u \ln y_i \quad \text{(13–48)}$$

We note from Eq. 13–38 that the two partial derivatives above are simply the negative of the partial molar entropies. Substituting,

$$\overline{s}_{i,\text{mixture,ideal}}(T, P_i) = \overline{s}_{i,\text{pure}}(T, P) - R_u \ln y_1 \quad \text{(ideal solution)} \quad \text{(13–49)}$$

Note that $\ln y_i$ is a negative quantity since $y_i < 1$, and thus $-R_u \ln y_i$ is always positive. Therefore, the entropy of a component in a mixture is always greater than the entropy of that component when it exists alone at the mixture temperature and pressure. Then the **entropy of mixing** of an ideal solution is determined by substituting Eq. 13–49 into Eq. 13–34 to be
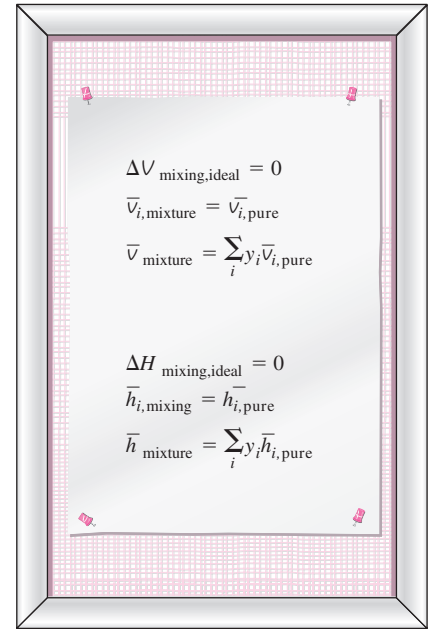
$$\Delta S_{\text{mixing,ideal}} = \sum_i N_i(\widetilde{s}_i - \overline{s}_i) = -R_u \sum_i N_i \ln y_i \quad \text{(ideal solution)} \quad \text{(13–50a)}$$

or, dividing by the total number of moles of the mixture N_m,

$$\Delta \overline{s}_{\text{mixing,ideal}} = \sum_i y_i(\widetilde{s}_i - \overline{s}_i) = -R_u \sum_i y_i \ln y_i \quad \text{(per unit mole of mixture)} \quad \text{(13–50b)}$$

Minimum Work of Separation of Mixtures

The entropy balance for a steady-flow system simplifies to $S_{\text{in}} - S_{\text{out}} + S_{\text{gen}} = 0$. Noting that entropy can be transferred by heat and mass only, the

$$\Delta V_{\text{mixing,ideal}} = 0$$
$$\overline{v}_{i,\text{mixture}} = \overline{v}_{i,\text{pure}}$$
$$\overline{v}_{\text{mixture}} = \sum_i y_i\overline{v}_{i,\text{pure}}$$

$$\Delta H_{\text{mixing,ideal}} = 0$$
$$\overline{h}_{i,\text{mixing}} = \overline{h}_{i,\text{pure}}$$
$$\overline{h}_{\text{mixture}} = \sum_i y_i\overline{h}_{i,\text{pure}}$$

FIGURE 13–20

The specific volume and enthalpy of individual components do not change during mixing if they form an ideal solution (this is not the case for entropy).
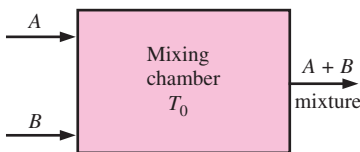
entropy generation during an adiabatic mixing process that forms an ideal solution becomes

$$S_{\text{gen}} = S_{\text{out}} - S_{\text{in}} = \Delta S_{\text{mixing}} = -R_u \sum_i N_i \ln y_i \qquad \text{(ideal solution)} \quad \textbf{(13–51}a\textbf{)}$$

or

$$\bar{s}_{\text{gen}} = \bar{s}_{\text{out}} - \bar{s}_{\text{in}} = \Delta \bar{s}_{\text{mixing}} = -R_u \sum_i y_i \ln y_i \qquad \text{(per unit mole of mixture)}$$

$$\textbf{(13–51}b\textbf{)}$$

Also noting that $X_{\text{destroyed}} = T_0 S_{\text{gen}}$, the exergy destroyed during this (and any other) process is obtained by multiplying the entropy generation by the temperature of the environment T_0. It gives

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} = -R_u T_0 \sum_i N_i \ln y_i \qquad \text{(ideal soluton)} \quad \textbf{(13–52}a\textbf{)}$$

or

$$\bar{x}_{\text{destroyed}} = T_0 \bar{s}_{\text{gen}} = -R_u T_0 \sum_i y_i \ln y_i \qquad \text{(per unit mole of mixture)} \quad \textbf{(13–52}b\textbf{)}$$

Exergy destroyed represents the wasted work potential—the work that would be produced if the mixing process occurred reversibly. For a reversible or "thermodynamically perfect" process, the entropy generation and thus the exergy destroyed is zero. Also, for reversible processes, the work output is a maximum (or, the work input is a minimum if the process does not occur naturally and requires input). The difference between the reversible work and the actual useful work is due to irreversibilities and is equal to the exergy destruction. Therefore, $X_{\text{destroyed}} = W_{\text{rev}} - W_{\text{actual}}$. Then it follows that for a naturally occurring process during which no work is produced, the reversible work is equal to the exergy destruction (Fig. 13–21). Therefore, for the adiabatic mixing process that forms an ideal solution, the reversible work (total and per unit mole of mixture) is, from Eq. 13–52,

$$W_{\text{rev}} = -R_u T_0 \sum_i N_i \ln y_i \quad \text{and} \quad \bar{w}_{\text{rev}} = -R_u T_0 \sum_i y_i \ln y_i \quad \textbf{(13–53)}$$

A reversible process, by definition, is a process that can be reversed without leaving a net effect on the surroundings. This requires that the direction of all interactions be reversed while their magnitudes remain the same when the process is reversed. Therefore, the work input during a reversible separation process must be equal to the work output during the reverse process of mixing. A violation of this requirement will be a violation of the second law of thermodynamics. The required work input for a reversible separation process is the minimum work input required to accomplish that separation since the work input for reversible processes is always less than the work input of corresponding irreversible processes. Then the minimum work input required for the separation process can be expressed as

$$W_{\text{min,in}} = -R_u T_0 \sum_i N_i \ln y_i \quad \text{and} \quad \bar{w}_{\text{min,in}} = -R_u T_0 \sum_i y_i \ln y_i \quad \textbf{(13–54)}$$

$$W_{\text{rev}} = X_{\text{destruction}} = T_0 S_{\text{gen}}$$

FIGURE 13–21

For a naturally occurring process during which no work is produced or consumed, the reversible work is equal to the exergy destruction.

It can also be expressed in the rate form as

$$\dot{W}_{\text{min,in}} = -R_u T_0 \sum_i \dot{N}_i \ln y_i = -\dot{N}_m R_u T_0 \sum_i y_i \ln y_i \qquad (\text{kW}) \qquad \textbf{(13–55)}$$

where $\dot{W}_{\text{min,in}}$ is the minimum power input required to separate a solution that approaches at a rate of $\dot{N}_m$ kmol/s (or $\dot{m}_m = \dot{N}_m M_m$ kg/s) into its components. The work of separation per unit mass of mixture can be determined from $w_{\text{min,in}} = \bar{w}_{\text{min,in}}/M_m$, where M_m is the apparent molar mass of the mixture.

The minimum work relations above are for complete separation of the components in the mixture. The required work input will be less if the exiting streams are not pure. The reversible work for incomplete separation can be determined by calculating the minimum separation work for the incoming mixture and the minimum separation works for the outgoing mixtures, and then taking their difference.

Reversible Mixing Processes

The mixing processes that occur naturally are irreversible, and all the work potential is wasted during such processes. For example, when the fresh water from a river mixes with the saline water in an ocean, an opportunity to produce work is lost. If this mixing is done reversibly (through the use of semipermeable membranes, for example) some work can be produced. The maximum amount of work that can be produced during a mixing process is equal to the minimum amount of work input needed for the corresponding separation process (Fig. 13–22). That is,

$$W_{\text{max,out,mixing}} = W_{\text{min,in,separation}} \qquad \textbf{(13–56)}$$

Therefore, the minimum work input relations given above for separation can also be used to determine the maximum work output for mixing.
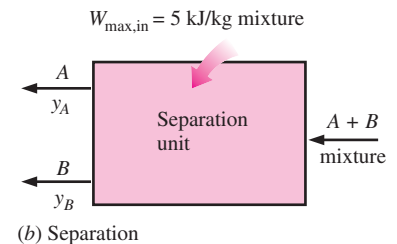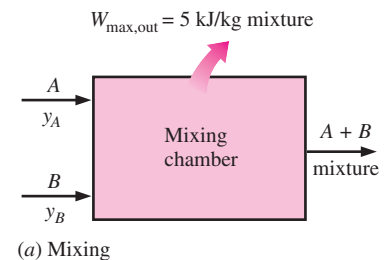
The minimum work input relations are independent of any hardware or process. Therefore, the relations developed above are applicable to any separation process regardless of actual hardware, system, or process, and can be used for a wide range of separation processes including the desalination of sea or brackish water.

Second-Law Efficiency

The second-law efficiency is a measure of how closely a process approximates a corresponding reversible process, and it indicates the range available for potential improvements. Noting that the second-law efficiency ranges from 0 for a totally irreversible process to 100 percent for a totally reversible process, the second-law efficiency for separation and mixing processes can be defined as

$$\eta_{\text{II,separation}} = \frac{\dot{W}_{\text{min,in}}}{\dot{W}_{\text{act,in}}} = \frac{w_{\text{min,in}}}{w_{\text{act,in}}} \quad \text{and} \quad \eta_{\text{II,mixing}} = \frac{\dot{W}_{\text{act,out}}}{\dot{W}_{\text{max,out}}} = \frac{w_{\text{act,out}}}{w_{\text{max,out}}} \qquad \textbf{(13–57)}$$

where $\dot{W}_{\text{act,in}}$ is the actual power input (or exergy consumption) of the separation plant and $\dot{W}_{\text{act,out}}$ is the actual power produced during mixing. Note that

$W_{\text{max,out}} = 5$ kJ/kg mixture

A
y_A

B
y_B

Mixing chamber

$A + B$
mixture

(a) Mixing

$W_{\text{max,in}} = 5$ kJ/kg mixture

A
y_A

B
y_B

Separation unit

$A + B$
mixture

(b) Separation

FIGURE 13–22

Under reversible conditions, the work consumed during separation is equal to the work produced during the reverse process of mixing.

the second-law efficiency is always less than 1 since the actual separation process requires a greater amount of work input because of irreversibilities. Therefore, the minimum work input and the second-law efficiency provide a basis for comparison of actual separation processes to the "idealized" ones and for assessing the thermodynamic performance of separation plants.

A second-law efficiency for mixing processes can also be defined as the actual work produced during mixing divided by the maximum work potential available. This definition does not have much practical value, however, since no effort is done to produce work during most mixing processes and thus the second-law efficiency is zero.

Special Case: Separation of a Two Component Mixture

Consider a mixture of two components A and B whose mole fractions are y_A and y_B. Noting that $y_B = 1 - y_A$, the minimum work input required to separate 1 kmol of this mixture at temperature T_0 completely into pure A and pure B is, from Eq. 13–54,

$$\bar{w}_{min,in} = -R_u T_0 (y_A \ln y_A + y_B \ln y_B) \quad \text{(kJ/kmol mixture)} \quad \textbf{(13–58a)}$$

or

$$W_{min,in} = -R_u T_0 (N_A \ln y_A + N_B \ln y_B) \quad \text{(kJ)} \quad \textbf{(13–58b)}$$

or, from Eq. 13–55,

$$\dot{W}_{min,in} = -\dot{N}_m R_u T_0 (y_A \ln y_A + y_B \ln y_B)$$
$$= -\dot{m}_m R_m T_0 (y_A \ln y_A + y_B \ln y_B) \quad \text{(kW)} \quad \textbf{(13–58c)}$$

Some separation processes involve the extraction of just one of the components from a large amount of mixture so that the composition of the remaining mixture remains practically the same. Consider a mixture of two components A and B whose mole fractions are y_A and y_B, respectively. The minimum work required to separate 1 kmol of pure component A from the mixture of $N_m = N_A + N_B$ kmol (with $N_A \gg 1$) is determined by subtracting the minimum work required to separate the remaining mixture $-R_u T_0[(N_A - 1)\ln y_A + N_B \ln y_B]$ from the minimum work required to separate the initial mixture $W_{min,in} = -R_u T_0 (N_A \ln y_A + N_B \ln y_B)$. It gives (Fig. 13–23)

$$\bar{w}_{min,in} = -R_u T_0 \ln y_A = R_u T_0 \ln(1/y_A) \quad \text{(kJ/kmol } A) \quad \textbf{(13–59)}$$

The minimum work needed to separate a unit mass (1 kg) of component A is determined from the above relation by replacing R_u by R_A (or by dividing the relation above by the molar mass of component A) since $R_A = R_u/M_A$. Eq. 13–59 also gives the maximum amount of work that can be done as one unit of pure component A mixes with a large amount of $A + B$ mixture.

An Application: Desalination Processes

The potable water needs of the world is increasing steadily due to population growth, rising living standards, industrialization, and irrigation in agriculture. There are over 10,000 desalination plants in the world, with a total desalted

$\bar{w}_{min,in} = -R_u T_0 \ln y_A$ (kJ/kmol A)
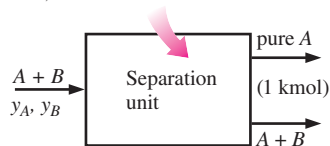
(a) Separating 1 kmol of A from a large body of mixture

$\bar{w}_{min,in} = -R_u T_0 (y_A \ln y_A + y_B \ln y_B)$ (kJ/kmol mixture)
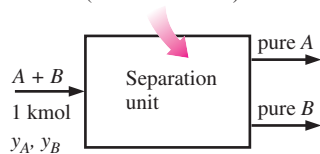
(b) Complete separation of 1 kmol mixture into its components A and B

FIGURE 13–23

The minimum work required to separate a two-component mixture for the two limiting cases.

water capacity of over 5 billion gallons a day. Saudi Arabia is the largest user of desalination with about 25 percent of the world capacity, and the United States is the second largest user with 10 percent. The major desalination methods are distillation and reverse osmosis. The relations can be used directly for desalination processes, by taking the water (the solvent) to be component A and the dissolved salts (the solute) to be component B. Then the minimum work needed to produce 1 kg of pure water from a large reservoir of brackish or seawater at temperature T_0 in an environment at T_0 is, from Eq. 13–59,

Desalination: $w_{min,in} = -R_w T_0 \ln(1/y_w)$ (kJ/kg pure water)   **(13–60)**

where $R_w = 0.4615$ kJ/kg $\cdot$ K is the gas constant of water and y_w is the mole fraction of water in brackish or seawater. The relation above also gives the maximum amount of work that can be produced as 1 kg of fresh water (from a river, for example) mixes with seawater whose water mole fraction is y_w.

   The reversible work associated with liquid flow can also be expressed in terms of pressure difference ΔP and elevation difference Δz (potential energy) as $w_{min,in} = \Delta P/\rho = g\,\Delta z$ where ρ is the density of the liquid. Combining these relations with Eq. 13–60 gives

$$\Delta P_{min} = \rho w_{min,in} = \rho R_w T_0 \ln(1/y_w)   \text{(kPa)}   \textbf{(13–61)}$$

and

$$\Delta z_{min} = w_{min,in}/g = R_w T_0 \ln(1/y_w)/g   \text{(m)}   \textbf{(13–62)}$$

where ΔP_{min} is the **osmotic pressure,** which represents the pressure difference across a semipermeable membrane that separates fresh water from the saline water under equilibrium conditions, ρ is the density of saline water, and Δz_{min} is the **osmotic rise,** which represents the vertical distance the saline water would rise when separated from the fresh water by a membrane that is permeable to water molecules alone (again at equilibrium). For desalination processes, ΔP_{min} represents the minimum pressure that the saline water must be compressed in order to force the water molecules in saline water through the membrane to the fresh water side during a reverse osmosis desalination process. Alternately, Δz_{min} represents the minimum height above the fresh water level that the saline water must be raised to produce the required osmotic pressure difference across the membrane to produce fresh water. The Δz_{min} also represents the height that the water with dissolved organic matter inside the roots will rise through a tree when the roots are surrounded by fresh water with the roots acting as semipermeable membranes. The reverse osmosis process with semipermeable membranes is also used in dialysis machines to purify the blood of patients with failed kidneys.

EXAMPLE 13–6   Obtaining Fresh Water from Seawater

Fresh water is to be obtained from seawater at 15°C with a salinity of 3.48 percent on mass basis (or TDS = 34,800 ppm). Determine (*a*) the mole fractions of the water and the salts in the seawater, (*b*) the minimum work input required to separate 1 kg of seawater completely into pure water and pure salts, (*c*) the minimum work input required to obtain 1 kg of fresh

water from the sea, and (d) the minimum gauge pressure that the seawater must be raised if fresh water is to be obtained by reverse osmosis using semipermeable membranes.

Solution Fresh water is to be obtained from seawater. The mole fractions of seawater, the minimum works of separation needed for two limiting cases, and the required pressurization of seawater for reverse osmosis are to be determined.

Assumptions **1** The seawater is an ideal solution since it is dilute. **2** The total dissolved solids in water can be treated as table salt (NaCl). **3** The environment temperature is also 15°C.

Properties The molar masses of water and salt are $M_w = 18.0$ kg/kmol and $M_s = 58.44$ kg/kmol. The gas constant of pure water is $R_w = 0.4615$ kJ/kg · K (Table A–1). The density of seawater is 1028 kg/m^3.

Analysis (a) Noting that the mass fractions of salts and water in seawater are $mf_s = 0.0348$ and $mf_w = 1 - mf_s = 0.9652$, the mole fractions are determined from Eqs. 13–4 and 13–5 to be

$$M_m = \frac{1}{\sum \dfrac{mf_i}{M_i}} = \frac{1}{\dfrac{mf_s}{M_s} + \dfrac{mf_w}{M_w}} = \frac{1}{\dfrac{0.0348}{58.44} + \dfrac{0.9652}{18.0}} = 18.44 \text{ kg/kmol}$$

$$y_w = mf_w \frac{M_m}{M_w} = 0.9652 \frac{18.44 \text{ kg/kmol}}{18.0 \text{ kg/kmol}} = 0.9888$$

$$y_s = 1 - y_w = 1 - 0.9888 = 0.0112 = 1.12\%$$

(b) The minimum work input required to separate 1 kg of seawater completely into pure water and pure salts is

$$\bar{w}_{\text{min,in}} = -R_u T_0 (y_A \ln y_A + y_B \ln y_B) = -R_u T_0 (y_w \ln y_w + y_s \ln y_s)$$

$$= -(8.314 \text{ kJ/kmol} \cdot \text{K})(288.15 \text{ K})(0.9888 \ln 0.9888 + 0.0112 \ln 0.0112)$$

$$= 147.2 \text{ kJ/kmol}$$

$$w_{\text{min,in}} = \frac{\bar{w}_{\text{min,in}}}{M_m} = \frac{147.2 \text{ kJ/kmol}}{18.44 \text{ kg/kmol}} = \textbf{7.98 kJ/kg seawater}$$

Therefore, it takes a minimum of 7.98 kJ of work input to separate 1 kg of seawater into 0.0348 kg of salt and 0.9652 kg (nearly 1 kg) of fresh water.

(c) The minimum work input required to produce 1 kg of fresh water from seawater is

$$w_{\text{min,in}} = R_w T_0 \ln(1/y_w)$$

$$= (0.4615 \text{ kJ/kg} \cdot \text{K})(288.15 \text{ K})\ln(1/0.9888)$$

$$= \textbf{1.50 kJ/kg fresh water}$$

Note that it takes about 5 times more work to separate 1 kg of seawater completely into fresh water and salt than it does to produce 1 kg of fresh water from a large amount of seawater.

(d) The osmotic pressure in this case is

$$\Delta P_{min} = \rho_m R_w T_0 \ln(1/y_w)$$

$$= (1028 \text{ kg/m}^3)(0.4615 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(288.15 \text{ K})\ln(1/0.9888)$$

$$= \textbf{1540 kPa}$$

which is equal to the minimum gauge pressure to which seawater must be compressed if the fresh water is to be discharged at the local atmospheric pressure. As an alternative to pressurizing, the minimum height above the fresh water level that the seawater must be raised to produce fresh water is (Fig. 13–24)

$$\Delta z_{min} = \frac{w_{min,in}}{g} = \frac{1.50 \text{ kJ/kg}}{9.81 \text{ m/s}^2}\left(\frac{1 \text{ kg} \cdot \text{m/s}^2}{1 \text{ N}}\right)\left(\frac{1000 \text{ N} \cdot \text{m}}{1 \text{ kJ}}\right) = 153 \text{ m}$$

Discussion The minimum separation works determined above also represent the maximum works that can be produced during the reverse process of mixing. Therefore, 7.98 kJ of work can be produced when 0.0348 kg of salt is mixed with 0.9652 kg of water reversibly to produce 1 kg of saline water, and 1.50 kJ of work can be produced as 1 kg of fresh water is mixed with seawater reversibly. Therefore, the power that can be generated as a river with a flow rate of 10^6 m^3/s mixes reversibly with seawater through semipermeable membranes is (Fig. 13–25)

$$\dot{W}_{max,out} = \rho\dot{V}w_{max,out} = (1000 \text{ kg/m}^3)(10^6 \text{ m}^3/\text{s})(1.50 \text{ kJ/kg})\left(\frac{1 \text{ MW}}{10^3 \text{ kJ/s}}\right)$$

$$= 1.5 \times 10^6 \text{ MW}$$

which shows the tremendous amount of power potential wasted as the rivers discharge into the seas.

$$\Delta P = P_2 - P_1$$
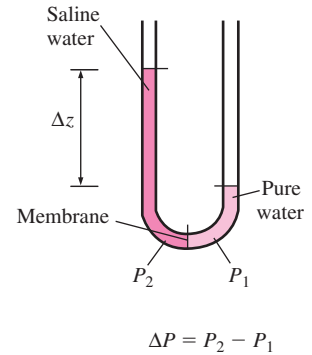
FIGURE 13–24

The osmotic pressure and the osmotic rise of saline water.
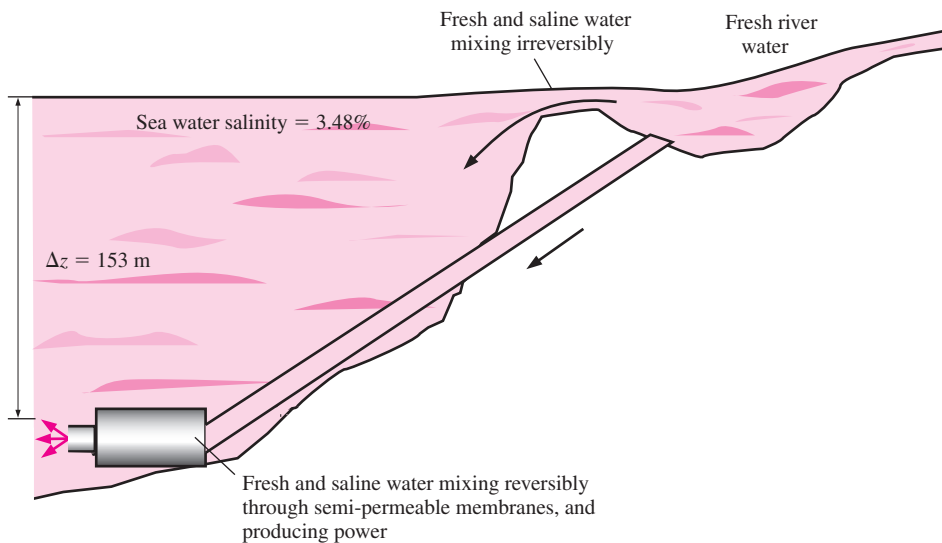
FIGURE 13–25

Power can be produced by mixing solutions of different concentrations reversibly.

SUMMARY

A mixture of two or more gases of fixed chemical composition is called a *nonreacting gas mixture* The composition of a gas mixture is described by specifying either the *mole fraction* or the *mass fraction* of each component, defined as

$$\text{mf}_i = \frac{m_i}{m_m} \quad \text{and} \quad y_i = \frac{N_i}{N_m}$$

where

$$m_m = \sum_{i=1}^{k} m_i \quad \text{and} \quad N_m = \sum_{i=1}^{k} N_i$$

The *apparent* (or average) *molar mass* and *gas constant* of a mixture are expressed as

$$M_m = \frac{m_m}{N_m} = \sum_{i=1}^{k} y_i M_i \quad \text{and} \quad R_m = \frac{R_u}{M_m}$$

Also,

$$\text{mf}_i = y_i \frac{M_i}{M_m} \quad \text{and} \quad M_m = \frac{1}{\displaystyle\sum_{i=1}^{k} \frac{\text{mf}_i}{M_i}}$$

Dalton's law of additive pressures states that the pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at the mixture temperature and volume. *Amagat's law of additive volumes* states that the volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure. Dalton's and Amagat's laws hold exactly for ideal-gas mixtures, but only approximately for real-gas mixtures. They can be expressed as

Dalton's law: $\qquad P_m = \displaystyle\sum_{i=1}^{k} P_i(T_m, V_m)$

Amagat's law: $\qquad V_m = \displaystyle\sum_{i=1}^{k} V_i(T_m, P_m)$

Here P_i is called the *component pressure* and V_i is called the *component volume*. Also, the ratio P_i/P_m is called the *pressure fraction* and the ratio V_i/V_m is called the *volume fraction* of component i. For *ideal gases*, P_i and V_i can be related to y_i by

$$\frac{P_i}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$

The quantity $y_i P_m$ is called the *partial pressure* and the quantity $y_i V_m$ is called the *partial volume*. The *P-v-T* behavior of real-gas mixtures can be predicted by using generalized compressibility charts. The compressibility factor of the mixture can be expressed in terms of the compressibility factors of the individual gases as

$$Z_m = \sum_{i=1}^{k} y_i Z_i$$

where Z_i is determined either at T_m and V_m (Dalton's law) or at T_m and P_m (Amagat's law) for each individual gas. The *P-v-T* behavior of a gas mixture can also be predicted approximately by *Kay's rule*, which involves treating a gas mixture as a pure substance with pseudocritical properties determined from

$$P'_{\text{cr},m} = \sum_{i=1}^{k} y_i P_{\text{cr},i} \quad \text{and} \quad T'_{\text{cr},m} = \sum_{i=1}^{k} y_i T_{\text{cr},i}$$

The *extensive properties* of a gas mixture, in general, can be determined by summing the contributions of each component of the mixture. The evaluation of *intensive properties* of a gas mixture, however, involves averaging in terms of mass or mole fractions:

$$U_m = \sum_{i=1}^{k} U_i = \sum_{i=1}^{k} m_i u_i = \sum_{i=1}^{k} N_i \bar{u}_i$$

$$H_m = \sum_{i=1}^{k} H_i = \sum_{i=1}^{k} m_i h_i = \sum_{i=1}^{k} N_i \bar{h}_i$$

$$S_m = \sum_{i=1}^{k} S_i = \sum_{i=1}^{k} m_i s_i = \sum_{i=1}^{k} N_i \bar{s}_i$$

and

$$u_m = \sum_{i=1}^{k} \text{mf}_i u_i \quad \text{and} \quad \bar{u}_m = \sum_{i=1}^{k} y_i \bar{u}_i$$

$$h_m = \sum_{i=1}^{k} \text{mf}_i h_i \quad \text{and} \quad \bar{h}_m = \sum_{i=1}^{k} y_i \bar{h}_i$$

$$s_m = \sum_{i=1}^{k} \text{mf}_i s_i \quad \text{and} \quad \bar{s}_m = \sum_{i=1}^{k} y_i \bar{s}_i$$

$$c_{v,m} = \sum_{i=1}^{k} \text{mf}_i c_{v,i} \quad \text{and} \quad \bar{c}_{v,m} = \sum_{i=1}^{k} y_i \bar{c}_{v,i}$$

$$c_{p,m} = \sum_{i=1}^{k} \text{mf}_i c_{p,i} \quad \text{and} \quad \bar{c}_{p,m} = \sum_{i=1}^{k} y_i \bar{c}_{p,i}$$

These relations are exact for ideal-gas mixtures and approximate for real-gas mixtures. The properties or property changes of individual components can be determined by using ideal-gas or real-gas relations developed in earlier chapters.

REFERENCES AND SUGGESTED READING

1. A. Bejan. *Advanced Engineering Thermodynamics.* 2nd ed. New York: Wiley Interscience, 1997.

2. Y. A. Çengel, Y. Cerci, and B. Wood, "Second Law Analysis of Separation Processes of Mixtures," *ASME International Mechanical Engineering Congress and Exposition,* Nashville, Tennessee, 1999.

3. Y. Cerci, Y. A. Çengel, and B. Wood, "The Minimum Separation Work for Desalination Processes," *ASME*

International Mechanical Engineering Congress and Exposition, Nashville, Tennessee, 1999.

4. J. P. Holman. *Thermodynamics.* 3rd ed. New York: McGraw-Hill, 1980.

5. K. Wark, Jr. *Advanced Thermodynamics for Engineers.* New York: McGraw-Hill, 1995.

PROBLEMS*

Composition of Gas Mixtures

13–1C What is the *apparent gas constant* for a gas mixture? Can it be larger than the largest gas constant in the mixture?

13–2C Consider a mixture of two gases. Can the apparent molar mass of this mixture be determined by simply taking the arithmetic average of the molar masses of the individual gases? When will this be the case?

13–3C What is the *apparent molar mass* for a gas mixture? Does the mass of every molecule in the mixture equal the apparent molar mass?

13–4C Consider a mixture of several gases of identical masses. Will all the mass fractions be identical? How about the mole fractions?

13–5C The sum of the mole fractions for an ideal-gas mixture is equal to 1. Is this also true for a real-gas mixture?

13–6C What are mass and mole fractions?

13–7C Using the definitions of mass and mole fractions, derive a relation between them.

13–8C Somebody claims that the mass and mole fractions for a mixture of CO_2 and N_2O gases are identical. Is this true? Why?

13–9C Consider a mixture of two gases A and B. Show that when the mass fractions mf_A and mf_B are known, the mole fractions can be determined from

$$y_A = \frac{M_B}{M_A(1/mf_A - 1) + M_B} \quad \text{and} \quad y_B = 1 - y_A$$

where M_A and M_B are the molar masses of A and B.

13–10 The composition of moist air is given on a molar basis to be 78 percent N_2, 20 percent O_2, and 2 percent water vapor. Determine the mass fractions of the constituents of air.

13–11 A gas mixture has the following composition on a mole basis: 60 percent N_2 and 40 percent CO_2. Determine the gravimetric analysis of the mixture, its molar mass, and gas constant.

13–12 Repeat Prob. 13–11 by replacing N_2 by O_2.

13–13 A gas mixture consists of 5 kg of O_2, 8 kg of N_2, and 10 kg of CO_2. Determine (*a*) the mass fraction of each component, (*b*) the mole fraction of each component, and (*c*) the average molar mass and gas constant of the mixture.

13–14 Determine the mole fractions of a gas mixture that consists of 75 percent CH_4 and 25 percent CO_2 by mass. Also, determine the gas constant of the mixture.

13–15 A gas mixture consists of 8 kmol of H_2 and 2 kmol of N_2. Determine the mass of each gas and the apparent gas constant of the mixture. *Answers:* 16 kg, 56 kg, 1.155 kJ/kg · K

13–16E A gas mixture consists of 5 lbmol of H_2 and 4 lbmol of N_2. Determine the mass of each gas and the apparent gas constant of the mixture.

13–17 A gas mixture consists of 20 percent O_2, 30 percent N_2, and 50 percent CO_2 on mass basis. Determine the volumetric analysis of the mixture and the apparent gas constant.

P-v-T Behavior of Gas Mixtures

13–18C Is a mixture of ideal gases also an ideal gas? Give an example.

13–19C Express Dalton's law of additive pressures. Does this law hold exactly for ideal-gas mixtures? How about nonideal-gas mixtures?

13–20C Express Amagat's law of additive volumes. Does this law hold exactly for ideal-gas mixtures? How about nonideal-gas mixtures?

---

*Problems designated by a "C" are concept questions, and students are encouraged to answer them all. Problems designated by an "E" are in English units, and the SI users can ignore them. Problems with a CD-EES icon ⊚ are solved using EES, and complete solutions together with parametric studies are included on the enclosed DVD. Problems with a computer-EES icon ▣ are comprehensive in nature, and are intended to be solved with a computer, preferably using the EES software that accompanies this text.

13–21C How is the P-v-T behavior of a component in an ideal-gas mixture expressed? How is the P-v-T behavior of a component in a real-gas mixture expressed?

13–22C What is the difference between the *component pressure* and the *partial pressure*? When are these two equivalent?

13–23C What is the difference between the *component volume* and the *partial volume*? When are these two equivalent?

13–24C In a gas mixture, which component will have the higher partial pressure—the one with the higher mole number or the one with the larger molar mass?

13–25C Consider a rigid tank that contains a mixture of two ideal gases. A valve is opened and some gas escapes. As a result, the pressure in the tank drops. Will the partial pressure of each component change? How about the pressure fraction of each component?

13–26C Consider a rigid tank that contains a mixture of two ideal gases. The gas mixture is heated, and the pressure and temperature in the tank rise. Will the partial pressure of each component change? How about the pressure fraction of each component?

13–27C Is this statement correct? *The volume of an ideal-gas mixture is equal to the sum of the volumes of each individual gas in the mixture.* If not, how would you correct it?

13–28C Is this statement correct? *The temperature of an ideal-gas mixture is equal to the sum of the temperatures of each individual gas in the mixture.* If not, how would you correct it?

13–29C Is this statement correct? *The pressure of an ideal-gas mixture is equal to the sum of the partial pressures of each individual gas in the mixture.* If not, how would you correct it?

13–30C Explain how a real-gas mixture can be treated as a pseudopure substance using Kay's rule.

13–31 A rigid tank contains 8 kmol of O_2 and 10 kmol of CO_2 gases at 290 K and 150 kPa. Estimate the volume of the tank. *Answer: 289 m³*

13–32 Repeat Prob. 13–31 for a temperature of 400 K.

13–33 A rigid tank contains 0.5 kmol of Ar and 2 kmol of N_2 at 250 kPa and 280 K. The mixture is now heated to 400 K. Determine the volume of the tank and the final pressure of the mixture.

13–34 A gas mixture at 300 K and 200 kPa consists of 1 kg of CO_2 and 3 kg of CH_4. Determine the partial pressure of each gas and the apparent molar mass of the gas mixture.

13–35E A gas mixture at 600 R and 20 psia consists of 1 lbm of CO_2 and 3 lbm of CH_4. Determine the partial pressure of each gas and the apparent molar mass of the gas mixture.

13–36 A 0.3-m³ rigid tank contains 0.6 kg of N_2 and 0.4 kg of O_2 at 300 K. Determine the partial pressure of each gas and the total pressure of the mixture. *Answers: 178.1 kPa, 103.9 kPa, 282.0 kPa*

13–37 A gas mixture at 350 K and 300 kPa has the following volumetric analysis: 65 percent N_2, 20 percent O_2, and 15 percent CO_2. Determine the mass fraction and partial pressure of each gas.

13–38 A rigid tank that contains 1 kg of N_2 at 25°C and 300 kPa is connected to another rigid tank that contains 3 kg of O_2 at 25°C and 500 kPa. The valve connecting the two tanks is opened, and the two gases are allowed to mix. If the final mixture temperature is 25°C, determine the volume of each tank and the final mixture pressure. *Answers: 0.295 m³, 0.465 m³, 422 kPa*
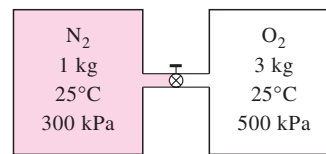

FIGURE P13–38

13–39 A volume of 0.3 m³ of O_2 at 200 K and 8 MPa is mixed with 0.5 m³ of N_2 at the same temperature and pressure, forming a mixture at 200 K and 8 MPa. Determine the volume of the mixture, using (*a*) the ideal-gas equation of state, (*b*) Kay's rule, and (*c*) the compressibility chart and Amagat's law. *Answers: (a) 0.8 m³, (b) 0.79 m³, (c) 0.80 m³*

13–40 A rigid tank contains 1 kmol of Ar gas at 220 K and 5 MPa. A valve is now opened, and 3 kmol of N_2 gas is allowed to enter the tank at 190 K and 8 MPa. The final mixture temperature is 200 K. Determine the pressure of the mixture, using (*a*) the ideal-gas equation of state and (*b*) the compressibility chart and Dalton's law.
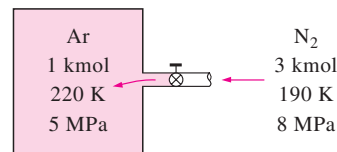

FIGURE P13–40

13–41 Reconsider Prob. 13–40. Using EES (or other) software, study the effect of varying the moles of nitrogen supplied to the tank over the range of 1 to 10 kmol of N_2. Plot the final pressure of the mixture as a function of the amount of nitrogen supplied using the ideal-gas equation of state and the compressibility chart with Dalton's law.

13–42E A rigid tank contains 1 lbmol of argon gas at 400 R and 750 psia. A valve is now opened, and 3 lbmol of N_2 gas is allowed to enter the tank at 340 R and 1200 psia. The final mixture temperature is 360 R. Determine the pressure of the mixture, using (*a*) the ideal-gas equation of state and (*b*) the compressibility chart and Dalton's law. *Answers:* (*a*) 2700 psia, (*b*) 2507 psia

Properties of Gas Mixtures

13–43C Is the total internal energy of an ideal-gas mixture equal to the sum of the internal energies of each individual gas in the mixture? Answer the same question for a real-gas mixture.

13–44C Is the specific internal energy of a gas mixture equal to the sum of the specific internal energies of each individual gas in the mixture?

13–45C Answer Prob. 13–43C and 13–44C for entropy.

13–46C Is the total internal energy change of an ideal-gas mixture equal to the sum of the internal energy changes of each individual gas in the mixture? Answer the same question for a real-gas mixture.

13–47C When evaluating the entropy change of the components of an ideal-gas mixture, do we have to use the partial pressure of each component or the total pressure of the mixture?

13–48C Suppose we want to determine the enthalpy change of a real-gas mixture undergoing a process. The enthalpy change of each individual gas is determined by using the generalized enthalpy chart, and the enthalpy change of the mixture is determined by summing them. Is this an exact approach? Explain.

13–49 A process requires a mixture that is 21 percent oxygen, 78 percent nitrogen, and 1 percent argon by volume. All three gases are supplied from separate tanks to an adiabatic, constant-pressure mixing chamber at 200 kPa but at different temperatures. The oxygen enters at 10°C, the nitrogen at 60°C, and the argon at 200°C. Determine the total entropy change for the mixing process per unit mass of mixture.

13–50 A mixture that is 15 percent carbon dioxide, 5 percent carbon monoxide, 10 percent oxygen, and 70 percent nitrogen by volume undergoes an adiabatic compression process having a compression ratio of 8:1. If the initial state of the mixture is 300 K and 100 kPa, determine the makeup of the mixture on a mass basis and the internal energy change per unit mass of mixture.

13–51 Propane and air are supplied to an internal combustion engine such that the air-fuel ratio is 16:1 when the pressure is 95 kPa and the temperature is 30°C. The compression ratio of the engine is 9.5:1. If the compression process is isentropic, determine the required work input for this compression process, in kJ/kg of mixture.

13–52 An insulated rigid tank is divided into two compartments by a partition. One compartment contains 2.5 kmol of CO_2 at 27°C and 200 kPa, and the other compartment contains 7.5 kmol of H_2 gas at 40°C and 400 kPa. Now the partition is removed, and the two gases are allowed to mix. Determine (*a*) the mixture temperature and (*b*) the mixture pressure after equilibrium has been established. Assume constant specific heats at room temperature for both gases.

CO_2	H_2
2.5 kmol	7.5 kmol
27°C	40°C
200 kPa	400 kPa

FIGURE P13–52

13–53 A 0.9-m³ rigid tank is divided into two equal compartments by a partition. One compartment contains Ne at 20°C and 100 kPa, and the other compartment contains Ar at 50°C and 200 kPa. Now the partition is removed, and the two gases are allowed to mix. Heat is lost to the surrounding air during this process in the amount of 15 kJ. Determine (*a*) the final mixture temperature and (*b*) the final mixture pressure. *Answers:* (*a*) 16.2°C, (*b*) 138.9 kPa

13–54 Repeat Prob. 13–53 for a heat loss of 8 kJ.

13–55 Ethane (C_2H_6) at 20°C and 200 kPa and methane (CH_4) at 45°C and 200 kPa enter an adiabatic mixing chamber. The mass flow rate of ethane is 9 kg/s, which is twice the mass flow rate of methane. Determine (*a*) the mixture temperature and (*b*) the rate of entropy generation during this process, in kW/K. Take $T_0 = 25$°C.

13–56 Reconsider Prob. 13–55. Using EES (or other) software, determine the effect of the mass fraction of methane in the mixture on the mixture temperature and the rate of exergy destruction. The total mass flow rate is maintained constant at 13.5 kg/s, and the mass fraction of methane is varied from 0 to 1. Plot the mixture temperature and the rate of exergy destruction against the mass fraction, and discuss the results.

13–57 An equimolar mixture of helium and argon gases is to be used as the working fluid in a closed-loop gas-turbine cycle.
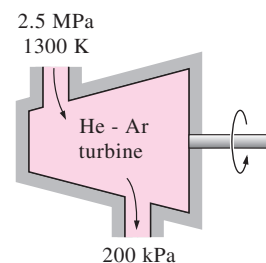
2.5 MPa
1300 K

He - Ar
turbine

200 kPa

FIGURE P13–57

The mixture enters the turbine at 2.5 MPa and 1300 K and expands isentropically to a pressure of 200 kPa. Determine the work output of the turbine per unit mass of the mixture.

13–58E A mixture of 80 percent N_2 and 20 percent CO_2 gases (on a mass basis) enters the nozzle of a turbojet engine at 90 psia and 1800 R with a low velocity, and it expands to a pressure of 12 psia. If the isentropic efficiency of the nozzle is 92 percent, determine (*a*) the exit temperature and (*b*) the exit velocity of the mixture. Assume constant specific heats at room temperature.

13–59E Reconsider Prob. 13–58E. Using EES (or other) software, first solve the stated problem and then, for all other conditions being the same, resolve the problem to determine the composition of the nitrogen and carbon dioxide that is required to have an exit velocity of 2600 ft/s at the nozzle exit.

13–60 A piston–cylinder device contains a mixture of 0.5 kg of H_2 and 1.6 kg of N_2 at 100 kPa and 300 K. Heat is now transferred to the mixture at constant pressure until the volume is doubled. Assuming constant specific heats at the average temperature, determine (*a*) the heat transfer and (*b*) the entropy change of the mixture.

13–61 An insulated tank that contains 1 kg of O_2 at 15°C and 300 kPa is connected to a 2-m^3 uninsulated tank that contains N_2 at 50°C and 500 kPa. The valve connecting the two tanks is opened, and the two gases form a homogeneous mixture at 25°C. Determine (*a*) the final pressure in the tank, (*b*) the heat transfer, and (*c*) the entropy generated during this process. Assume $T_0 = 25°C$.
Answers: (*a*) 444.6 kPa, (*b*) 187.2 kJ, (*c*) 0.962 kJ/K
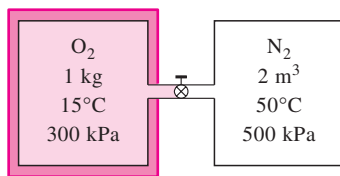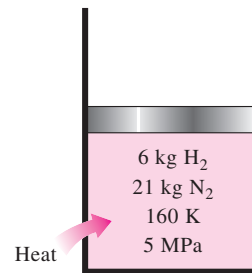

FIGURE P13–61

13–62 Reconsider Prob. 13–61. Using EES (or other) software, compare the results obtained assuming ideal-gas behavior with constant specific heats at the average temperature, and using real-gas data obtained from EES by assuming variable specific heats over the temperature range.

13–63 A piston–cylinder device contains 6 kg of H_2 and 21 kg of N_2 at 160 K and 5 MPa. Heat is now transferred to the device, and the mixture expands at constant pressure until the temperature rises to 200 K. Determine the heat transfer

during this process by treating the mixture (*a*) as an ideal gas and (*b*) as a nonideal gas and using Amagat's law.
*Answers:* (*a*) 4273 kJ, (*b*) 4745 kJ

FIGURE P13–63

13–64 Determine the total entropy change and exergy destruction associated with the process described in Prob. 13–63 by treating the mixture (*a*) as an ideal gas and (*b*) as a nonideal gas and using Amagat's law. Assume constant specific heats at room temperature and take $T_0 = 30°C$.

13–65 Air, which may be considered as a mixture of 79 percent N_2 and 21 percent O_2 by mole numbers, is compressed isothermally at 200 K from 4 to 8 MPa in a steady-flow device. The compression process is internally reversible, and the mass flow rate of air is 2.9 kg/s. Determine the power input to the compressor and the rate of heat rejection by treating the mixture (*a*) as an ideal gas and (*b*) as a nonideal gas and using Amagat's law. *Answers:* (*a*) 115.3 kW, 115.3 kW, (*b*) 143.6 kW, 94.2 kW
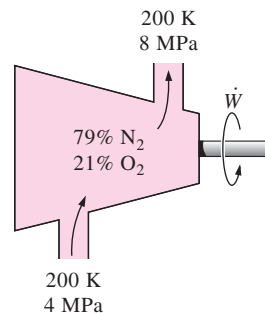
FIGURE P13–65

13–66 Reconsider Prob. 13–65. Using EES (or other) software, compare the results obtained by assuming ideal behavior, real gas behavior with Amagat's law, and real gas behavior with EES data.

13–67 The combustion of a hydrocarbon fuel with air results in a mixture of products of combustion having the composition on a volume basis as follows: 4.89 percent carbon dioxide,

6.50 percent water vapor, 12.20 percent oxygen, and 76.41 percent nitrogen. Determine the average molar mass of the mixture, the average specific heat at constant pressure of the mixture at 600 K, in kJ/kmol · K, and the partial pressure of the water vapor in the mixture for a mixture pressure of 200 kPa.

13–68 A mixture that is 20 percent carbon dioxide, 10 percent oxygen, and 70 percent nitrogen by volume undergoes a process from 300 K and 100 kPa to 500 K and 400 kPa. Determine the makeup of the mixture on a mass basis and the enthalpy change per unit mass of mixture.

Special Topic: Chemical Potential and the Separation Work of Mixtures

13–69C It is common experience that two gases brought into contact mix by themselves. In the future, could it be possible to invent a process that will enable a mixture to separate into its components by itself without any work (or exergy) input?

13–70C A 2-L liquid is mixed with 3 L of another liquid, forming a homogeneous liquid solution at the same temperature and pressure. Can the volume of the solution be more or less than the 5 L? Explain.

13–71C A 2-L liquid at 20°C is mixed with 3 L of another liquid at the same temperature and pressure in an adiabatic container, forming a homogeneous liquid solution. Someone claims that the temperature of the mixture rose to 22°C after mixing. Another person refutes the claim, saying that this would be a violation of the first law of thermodynamics. Who do you think is right?

13–72C What is an ideal solution? Comment on the volume change, enthalpy change, entropy change, and chemical potential change during the formation of ideal and nonideal solutions.

13–73 Brackish water at 12°C with total dissolved solid content of TDS = 780 ppm (a salinity of 0.078 percent on mass basis) is to be used to produce fresh water with negligible salt content at a rate of 280 L/s. Determine the minimum power input required. Also, determine the minimum height to which the brackish water must be pumped if fresh water is to be obtained by reverse osmosis using semipermeable membranes.

13–74 A river is discharging into the ocean at a rate of 400,000 m^3/s. Determine the amount of power that can be generated if the river water mixes with the ocean water reversibly. Take the salinity of the ocean to be 3.5 percent on mass basis, and assume both the river and the ocean are at 15°C.

13–75 Reconsider Prob. 13–74. Using EES (or other) software, investigate the effect of the salinity of the ocean on the maximum power generated. Let the salinity vary from 0 to 5 percent. Plot the power produced versus the salinity of the ocean, and discuss the results.

13–76E Fresh water is to be obtained from brackish water at 65°F with a salinity of 0.12 percent on mass basis (or TDS = 1200 ppm). Determine (a) the mole fractions of the water and the salts in the brackish water, (b) the minimum work input required to separate 1 lbm of brackish water completely into pure water and pure salts, and (c) the minimum work input required to obtain 1 lbm of fresh water.

13–77 A desalination plant produces fresh water from seawater at 10°C with a salinity of 3.2 percent on mass basis at a rate of 1.4 m^3/s while consuming 8.5 MW of power. The salt content of the fresh water is negligible, and the amount of fresh water produced is a small fraction of the seawater used. Determine the second-law efficiency of this plant.

13–78 Fresh water is obtained from seawater at a rate of 0.5 m^3/s by a desalination plant that consumes 3.3 MW of power and has a second-law efficiency of 18 percent. Determine the power that can be produced if the fresh water produced is mixed with the seawater reversibly.

Review Problems

13–79 Air has the following composition on a mole basis: 21 percent O_2, 78 percent N_2, and 1 percent Ar. Determine the gravimetric analysis of air and its molar mass. *Answers:* 23.2 percent O_2, 75.4 percent N_2, 1.4 percent Ar, 28.96 kg/kmol

13–80 Using Amagat's law, show that

$$Z_m = \sum_{i=1}^{k} y_i Z_i$$

for a real-gas mixture of k gases, where Z is the compressibility factor.

13–81 Using Dalton's law, show that

$$Z_m = \sum_{i=1}^{k} y_i Z_i$$

for a real-gas mixture of k gases, where Z is the compressibility factor.

13–82 A mixture of carbon dioxide and nitrogen flows through a converging nozzle. The mixture leaves the nozzle at a temperature of 500 K with a velocity of 360 m/s. If the velocity is equal to the speed of sound at the exit temperature, determine the required makeup of the mixture on a mass basis.

13–83 A piston–cylinder device contains products of combustion from the combustion of a hydrocarbon fuel with air. The combustion process results in a mixture that has the composition on a volume basis as follows: 4.89 percent carbon dioxide, 6.50 percent water vapor, 12.20 percent oxygen, and 76.41 percent nitrogen. This mixture is initially at 1800 K and 1 MPa and expands in an adiabatic, reversible process to 200 kPa. Determine the work done on the piston by the gas, in kJ/kg of mixture. Treat the water vapor as an ideal gas.

13–84 A rigid tank contains 2 kmol of N_2 and 6 kmol of CH_4 gases at 200 K and 12 MPa. Estimate the volume of the tank, using (*a*) the ideal-gas equation of state, (*b*) Kay's rule, and (*c*) the compressibility chart and Amagat's law.

13–85 A steady stream of equimolar N_2 and CO_2 mixture at 100 kPa and 18°C is to be separated into N_2 and CO_2 gases at 100 kPa and 18°C. Determine the minimum work required per unit mass of mixture to accomplish this separation process. Assume $T_0 = 18°C$.

13–86 A gas mixture consists of O_2 and N_2. The ratio of the mole numbers of N_2 to O_2 is 3:1. This mixture is heated during a steady-flow process from 180 to 210 K at a constant pressure of 8 MPa. Determine the heat transfer during this process per mole of the mixture, using (*a*) the ideal-gas approximation and (*b*) Kay's rule.

13–87 Reconsider Prob. 13–86. Using EES (or other) software, investigate the effect of the mole fraction of oxygen in the mixture on heat transfer using real-gas behavior with EES data. Let the mole fraction of oxygen vary from 0 to 1. Plot the heat transfer against the mole fraction, and discuss the results.

13–88 Determine the total entropy change and exergy destruction associated with the process described in Prob. 13–86, using (*a*) the ideal-gas approximation and (*b*) Kay's rule. Assume constant specific heats and $T_0 = 30°C$.

13–89 A rigid tank contains a mixture of 4 kg of He and 8 kg of O_2 at 170 K and 7 MPa. Heat is now transferred to the tank, and the mixture temperature rises to 220 K. Treating the He as an ideal gas and the O_2 as a nonideal gas, determine (*a*) the final pressure of the mixture and (*b*) the heat transfer.

13–90 A mixture of 60 percent carbon dioxide and 40 percent methane on a mole basis expands through a turbine from 1600 K and 800 kPa to 100 kPa. The volume flow rate at the turbine entrance is 10 L/s. Determine the rate of work done by the mixture using (*a*) ideal-gas approximation and (*b*) Kay's rule.

13–91 A pipe fitted with a closed valve connects two tanks. One tank contains a 5-kg mixture of 62.5 percent CO_2 and 37.5 percent O_2 on a mole basis at 30°C and 125 kPa. The second tank contains 10 kg of N_2 at 15°C and 200 kPa. The valve in the pipe is opened and the gases are allowed to mix. During the mixing process 100 kJ of heat energy is supplied to the combined tanks. Determine the final pressure and temperature of the mixture and the total volume of the mixture.

13–92 Using EES (or other) software, write a program to determine the mole fractions of the components of a mixture of three gases with known molar masses when the mass fractions are given, and to determine the mass fractions of the components when the mole fractions are given. Run the program for a sample case, and give the results.

13–93 Using EES (or other) software, write a program to determine the apparent gas constant, constant volume specific heat, and internal energy of a mixture of three ideal gases when the mass fractions and other properties of the constituent gases are given. Run the program for a sample case, and give the results.

13–94 Using EES (or other) software, write a program to determine the entropy change of a mixture of three ideal gases when the mass fractions and other properties of the constituent gases are given. Run the program for a sample case, and give the results.

Fundamentals of Engineering (FE) Exam Problems

13–95 An ideal-gas mixture whose apparent molar mass is 36 kg/kmol consists of N_2 and three other gases. If the mole fraction of nitrogen is 0.30, its mass fraction is

(*a*) 0.15   (*b*) 0.23   (*c*) 0.30   (*d*) 0.39   (*e*) 0.70

13–96 An ideal-gas mixture consists of 2 kmol of N_2 and 6 kmol of CO_2. The mass fraction of CO_2 in the mixture is

(*a*) 0.175   (*b*) 0.250   (*c*) 0.500   (*d*) 0.750   (*e*) 0.875

13–97 An ideal-gas mixture consists of 2 kmol of N_2 and 4 kmol of CO_2. The apparent gas constant of the mixture is

(*a*) 0.215 kJ/kg · K   (*b*) 0.225 kJ/kg · K   (*c*) 0.243 kJ/kg · K
(*d*) 0.875 kJ/kg · K   (*e*) 1.24 kJ/kg · K

13–98 A rigid tank is divided into two compartments by a partition. One compartment contains 3 kmol of N_2 at 600 kPa and the other compartment contains 7 kmol of CO_2 at 200 kPa. Now the partition is removed, and the two gases form a homogeneous mixture at 300 kPa. The partial pressure of N_2 in the mixture is

(*a*) 75 kPa   (*b*) 90 kPa   (*c*) 150 kPa   (*d*) 175 kPa   (*e*) 225 kPa

13–99 An 80-L rigid tank contains an ideal-gas mixture of 5 g of N_2 and 5 g of CO_2 at a specified pressure and temperature. If N_2 were separated from the mixture and stored at mixture temperature and pressure, its volume would be

(*a*) 32 L   (*b*) 36 L   (*c*) 40 L   (*d*) 49 L   (*e*) 80 L

13–100 An ideal-gas mixture consists of 3 kg of Ar and 6 kg of CO_2 gases. The mixture is now heated at constant volume from 250 K to 350 K. The amount of heat transfer is

(*a*) 374 kJ   (*b*) 436 kJ   (*c*) 488 kJ
(*d*) 525 kJ   (*e*) 664 kJ

13–101 An ideal-gas mixture consists of 30 percent helium and 70 percent argon gases by mass. The mixture is now expanded isentropically in a turbine from 400°C and 1.2 MPa to a pressure of 200 kPa. The mixture temperature at turbine exit is

(*a*) 195°C   (*b*) 56°C   (*c*) 112°C
(*d*) 130°C   (*e*) 400°C

13–102 One compartment of an insulated rigid tank contains 2 kmol of CO_2 at 20°C and 150 kPa while the other compartment contains 5 kmol of H_2 gas at 35°C and 300 kPa. Now the partition between the two gases is removed, and the two gases form a homogeneous ideal-gas mixture. The temperature of the mixture is

(*a*) 25°C   (*b*) 29°C   (*c*) 22°C   (*d*) 32°C   (*e*) 34°C

13–103 A piston–cylinder device contains an ideal-gas mixture of 3 kmol of He gas and 7 kmol of Ar gas at 50°C and 400 kPa. Now the gas expands at constant pressure until its volume doubles. The amount of heat transfer to the gas mixture is

(*a*) 6.2 MJ   (*b*) 4.2 MJ   (*c*) 27 MJ
(*d*) 10 MJ   (*e*) 67 MJ

13–104 An ideal-gas mixture of helium and argon gases with identical mass fractions enters a turbine at 1200 K and 1 MPa at a rate of 0.3 kg/s, and expands isentropically to 100 kPa. The power output of the turbine is

(*a*) 478 kW   (*b*) 619 kW   (*c*) 926 KW
(*d*) 729 kW   (*e*) 564 kW

Design and Essay Problem

13–105 Prolonged exposure to mercury even at relatively low but toxic concentrations in the air is known to cause permanent mental disorders, insomnia, and pain and numbness in the hands and the feet, among other things. Therefore, the maximum allowable concentration of mercury vapor in the air at work places is regulated by federal agencies. These regulations require that the average level of mercury concentration in the air does not exceed 0.1 mg/m³.

Consider a mercury spill that occurs in an airtight storage room at 20°C in San Francisco during an earthquake. Calculate the highest level of mercury concentration in the air that can occur in the storage room, in mg/m³, and determine if it is within the safe level. The vapor pressure of mercury at 20°C is 0.173 Pa. Propose some guidelines to safeguard against the formation of toxic concentrations of mercury vapor in air in storage rooms and laboratories.