CHAPTER 13

# GAS MIXTURES

1. **Composition of a Gas Mixture**

   **- Mass and Mole Fractions**

2. **P-v-T Behavior of Gas Mixtures**

   **- Ideal and Real Gases**

3. **Properties of Gas Mixtures ($u_m$, $h_m$, $s_m$, etc)**

   **- Ideal and Real Gases**

# Objectives

- 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.

# 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:

**Molar analysis:** specifying the number of moles of each component

**Gravimetric analysis:** specifying the mass of each component

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

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

Mass fraction

Mole fraction

# 13.1 COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

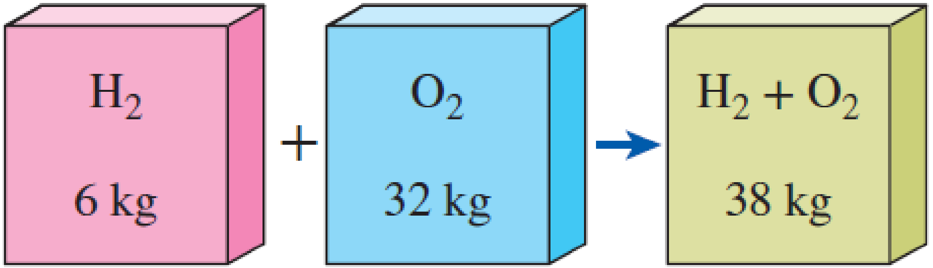


**FIGURE 13–1**
The mass of a mixture is equal to the sum of the masses of its components.

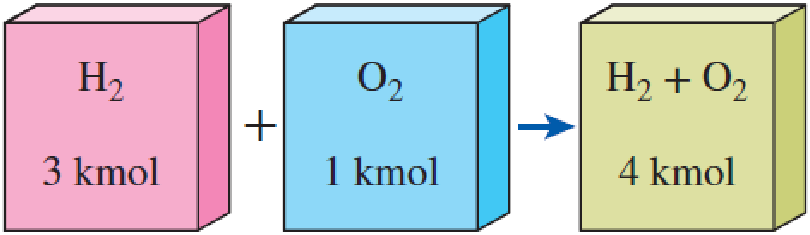


**FIGURE 13–2**
The number of moles of a nonreacting mixture is equal to the sum of the number of moles of its components.

# 13.1 COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

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

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

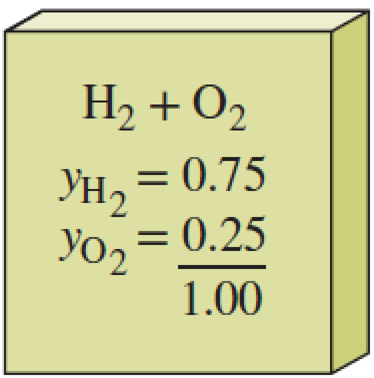


**FIGURE 13–3**
The sum of the mole fractions of a mixture is equal to 1.

# 13.1 COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_{i=1}^{k} y_i M_i$$

Apparent (or average) molar mass

$$m = NM$$

$$R_m = \frac{R_u}{M_m}$$

Gas constant (13-3a, b)

$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i / M_i} = \frac{1}{\sum m_i / (m_m M_i)} = \frac{1}{\sum_{i=1}^{k} \frac{\mathrm{mf}_i}{M_i}}$$

The molar mass of a mixture

$$\mathrm{mf}_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m}$$

Relation between mass and mole fractions of a mixture (13-5)

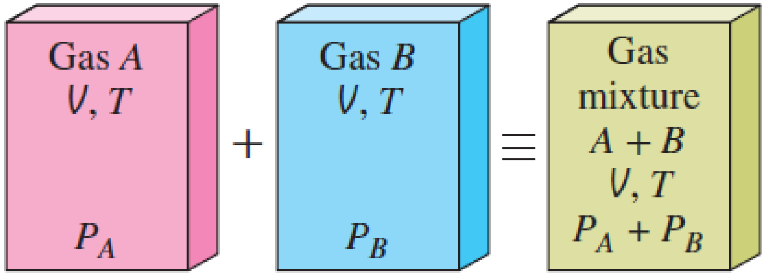


**FIGURE 13–5**
Dalton's law of additive pressures for a mixture of two ideal gases.

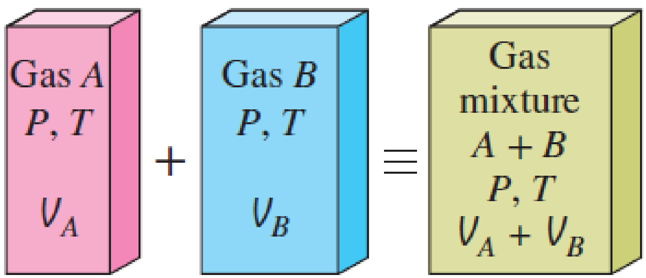


**FIGURE 13–6**
Amagat's law of additive volumes for a mixture of two ideal gases.

The prediction of the *P-v-T* behavior of gas mixtures is usually based on two models:

**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.

**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.

# 13.2 *P-v-T* BEHAVIOR OF GAS MIXTURES: IDEAL AND REAL GASES

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

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

exact for ideal gases, approximate for real gases

$P_i$ component pressure

$V_i$ component volume

$P_i / P_m$ pressure fraction

$V_i / V_m$ volume fraction

For ideal gases, Dalton's and Amagad's laws are identical and give identical results.

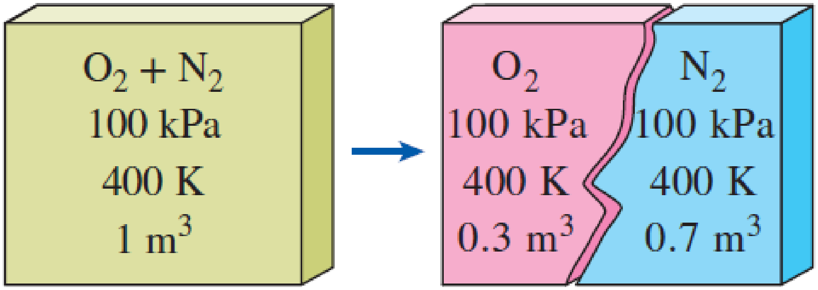


**FIGURE 13–7**
The volume a component would occupy if it existed alone at the mixture *T* and *P* is called the *component volume* (for ideal gases, it is equal to the partial volume $y_i V_m$).

## Ideal-Gas Mixtures

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

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

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

This equation is only valid for ideal-gas mixtures as 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 (Orsat Analysis).

# 13.2 *P-v-T* BEHAVIOR OF GAS MIXTURES: IDEAL AND REAL GASES

## Real-Gas Mixtures

$$PV = ZNR_uT$$

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

Compressibility factor

$Z_i$ 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.

Using Dalton's law gives more accurate results.

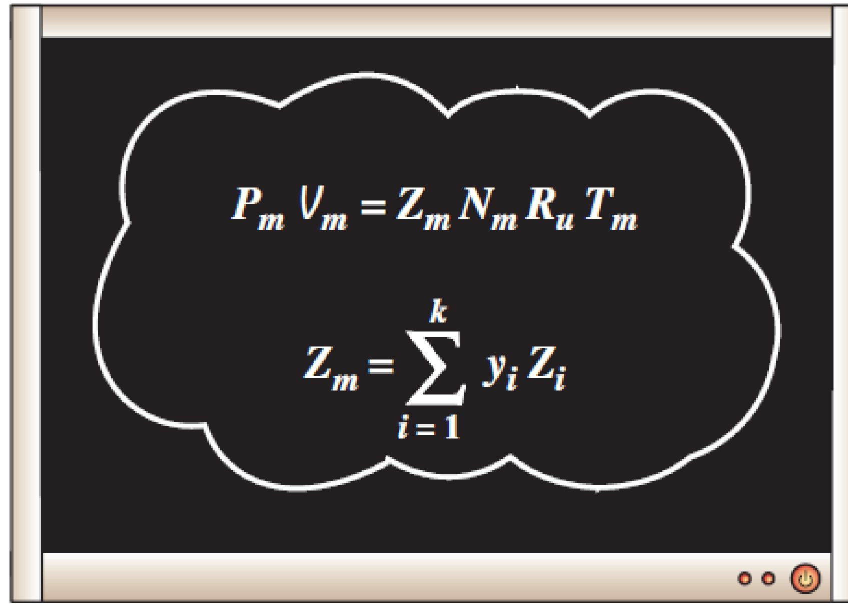


**FIGURE 13–8**
One way of predicting the *P-V-T* behavior of a real-gas mixture is to use the compressibility factor.

# *13.2 P-v-T* BEHAVIOR OF GAS MIXTURES: IDEAL AND REAL GASES

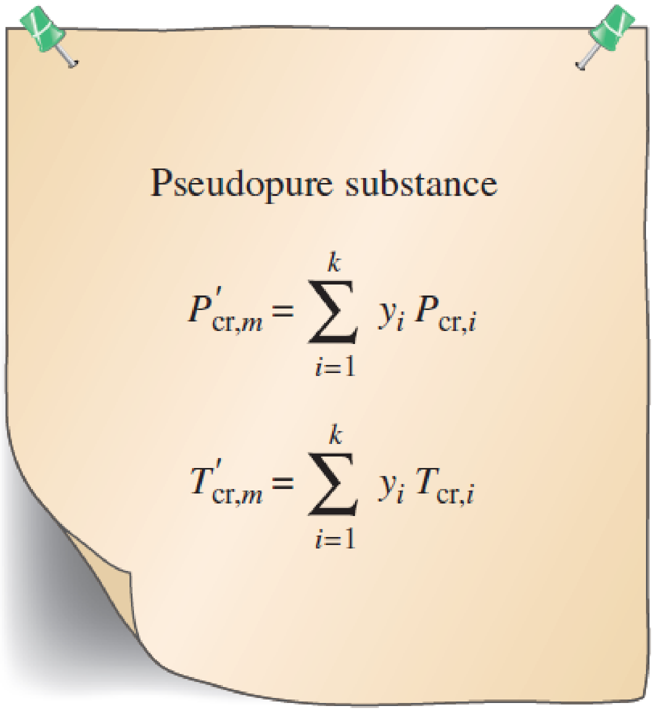


**FIGURE 13–9**
Another way of predicting the *P-υ-T* behavior of a real-gas mixture is to treat it as a pseudopure substance with critical properties $P'_{\mathrm{cr}}$ and $T'_{\mathrm{cr}}$.

## Kay's rule

$Z_m$ is determined by using these pseudocritical properties.

$$P'_{\mathrm{cr},m} = \sum_{i=1}^{k} y_i P_{\mathrm{cr},i}$$

$$T'_{\mathrm{cr},m} = \sum_{i=1}^{k} y_i T_{\mathrm{cr},i}$$

The result by Kay's rule is accurate to within about 10% over a wide range of temperatures and pressures.

# 13.3 PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

## Extensive properties of a gas mixture

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

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

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

Changes in properties of a gas mixture

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

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

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

# 13.3 PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

2 kmol $A$

6 kmol $B$

$U_A = 1000$ kJ

$U_B = 1800$ kJ

↓

$U_m = 2800$ kJ

**FIGURE 13–11**

The extensive properties of a mixture are determined by simply adding the properties of the components.

**Intensive properties** of a gas mixture

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

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

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

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

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

Properties per **unit mass** involve **mass fractions ($\mathrm{mf}_i$)** and properties per **unit mole** involve **mole fractions ($y_i$).**

The relations are exact for ideal-gas mixtures, and approximate for real-gas mixtures.

# 13.3 PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

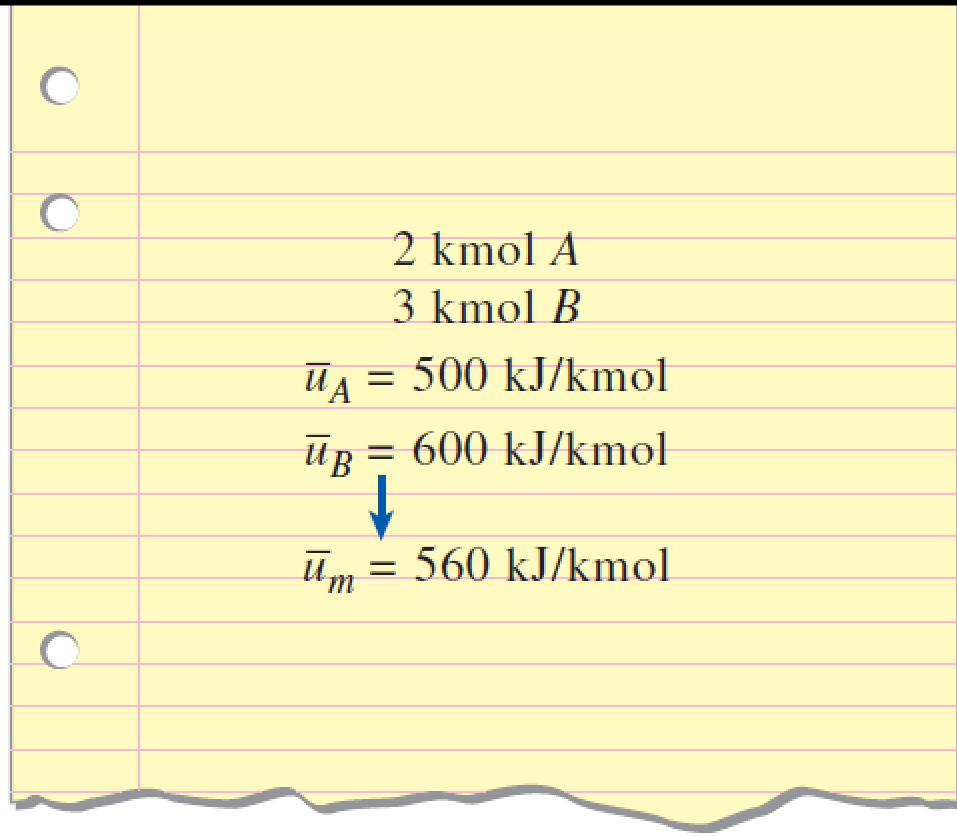


**FIGURE 13–12**
The intensive properties of a mixture are determined by weighted averaging.

# 13.3 PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

## Ideal-Gas Mixtures

**Gibbs–Dalton law:** 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 $V_m$.

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.

$$\Delta s_i = s^\circ_{i,2} - s^\circ_{i,1} - R_i \ln \frac{P_{i,2}}{P_{i,1}} \cong c_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_i \ln \frac{P_{i,2}}{P_{i,1}} \quad (13\text{-}24)$$

$$\Delta \bar{s}_i = \bar{s}^\circ_{i,2} - \bar{s}^\circ_{i,1} - R_u \ln \frac{P_{i,2}}{P_{i,1}} \cong \bar{c}_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_u \ln \frac{P_{i,2}}{P_{i,1}} \quad (13\text{-}25)$$

$$P_{i,2} = y_{i,2} P_{m,2} \text{ and } P_{i,1} = y_{i,1} P_{m,1}$$

# 13.3 PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

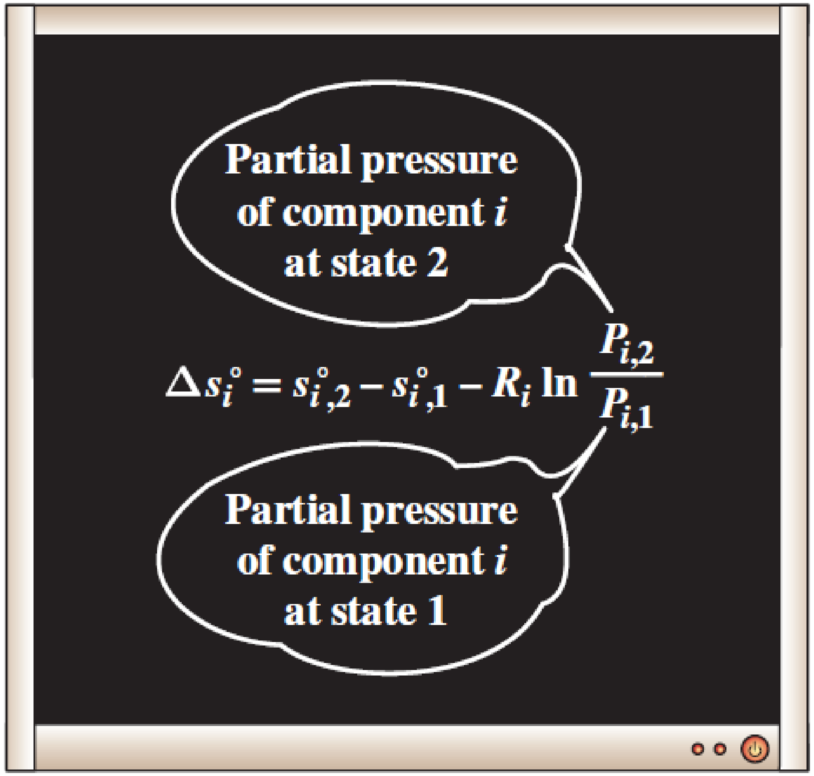


**FIGURE 13–13**
Partial pressures (not the mixture pressure) are used in the evaluation of entropy changes of ideal-gas mixtures.

## Real-Gas Mixtures

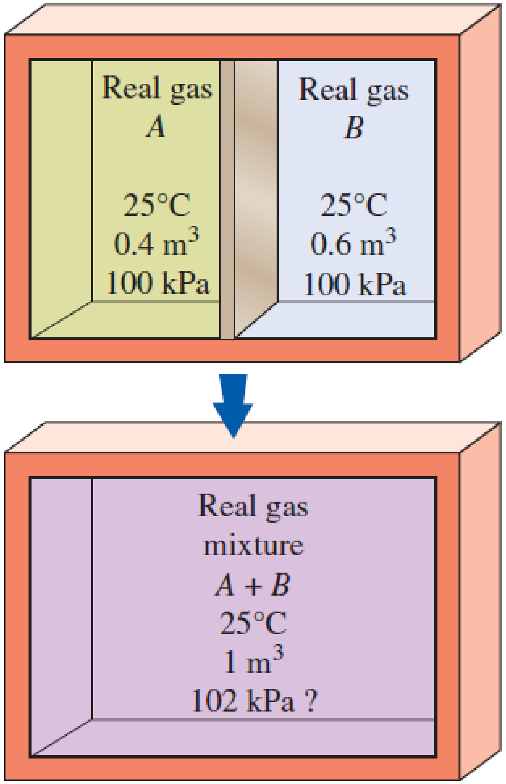


**FIGURE 13–16**
It is difficult to predict the behavior of nonideal-gas mixtures because of the influence of dissimilar molecules on each other.

# 13.3 PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

$$dh_m = T_m ds_m + \upsilon_m dP_m$$

*T ds* relation for a gas mixture

$$d(\sum \mathrm{mf}_i h_i) = T_m d(\sum \mathrm{mf}_i s_i) + (\sum \mathrm{mf}_i \upsilon_i) dP_m$$

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

$$dh_i = T_m ds_i + \upsilon_i \, dP_m$$

This equation suggests that the generalized property relations and charts for real gases developed in Chap. 12 can also be used for the components of real-gas mixtures. But $T_R$ and $P_R$ for each component should be evaluated using $T_m$ and $P_m$.

If the $V_m$ and $T_m$ are specified instead of $P_m$ and $T_m$, evaluate $P_m$ using Dalton's law of additive pressures.

Another way 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.

# Summary

- Composition of a gas mixture: Mass and mole fractions
- *P-v-T* behavior of gas mixtures: Ideal and Real Gases
- Properties of gas mixtures: Ideal and Real Gases