

# Topic 1: Gas Mixtures



# Further Reading

## Chapter 13 Gas Mixtures



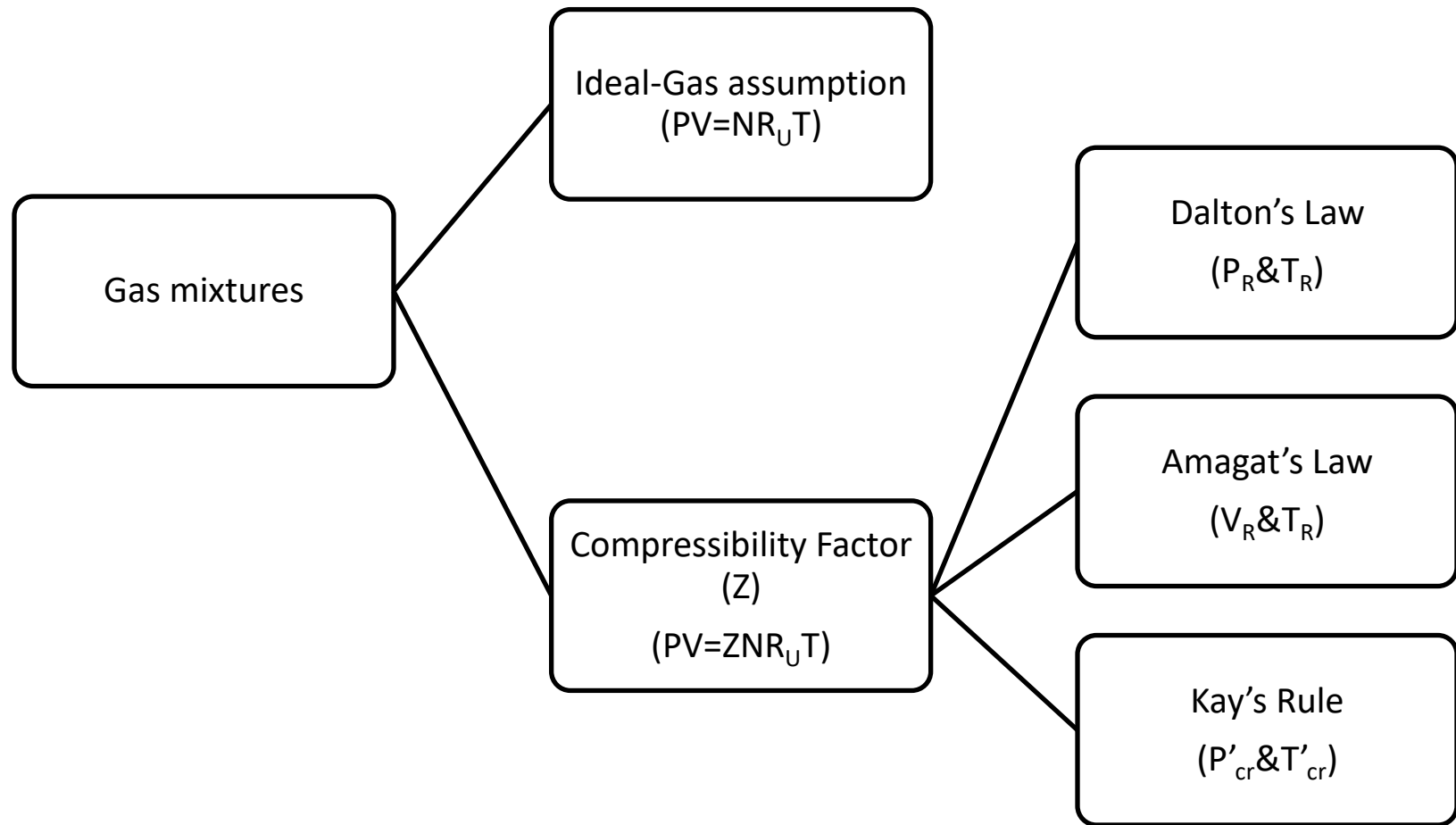
# Content

- Composition of a gas mixture: Mass and mole fractions
- $P$ - $v$ - $T$  behaviour of gas mixtures: Ideal and Real Gases
- Properties of gas mixtures: 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  $P$ - $v$ - $T$  behaviour of gas mixtures based on Dalton's law of additive pressures and Amagat's law of additive volumes.

# Gas Mixtures: Ideal And Real Gases <sup>5</sup>



# 13–1 Composition of a Gas Mixture: Mass and Mole Fractions <sub>1</sub>

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

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

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**  $y$ :

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

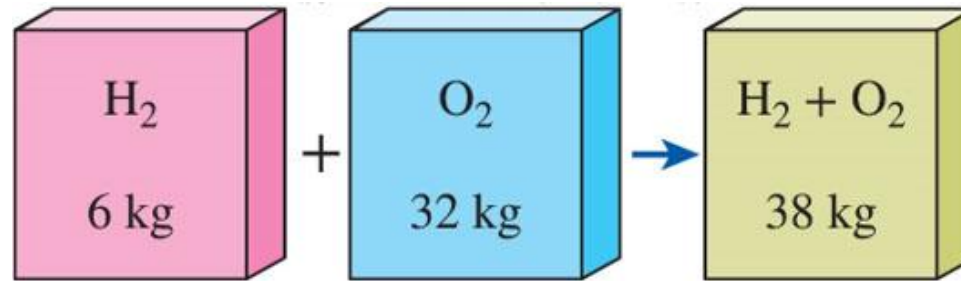
Mass fraction

Mole fraction

# 13–1 Composition of a Gas Mixture: Mass and Mole Fractions <sub>2</sub>

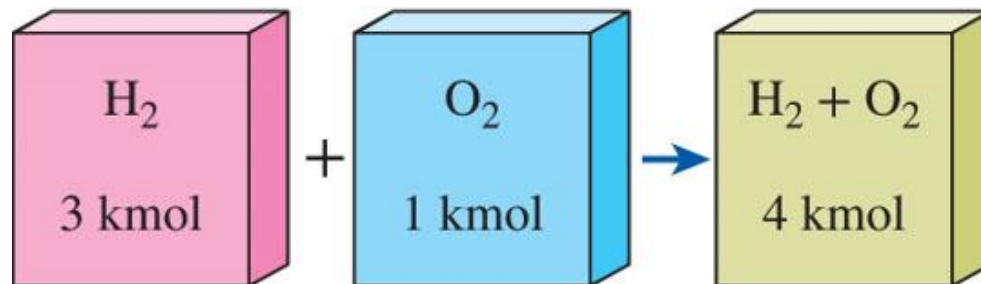
**Figure 13–1**

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.



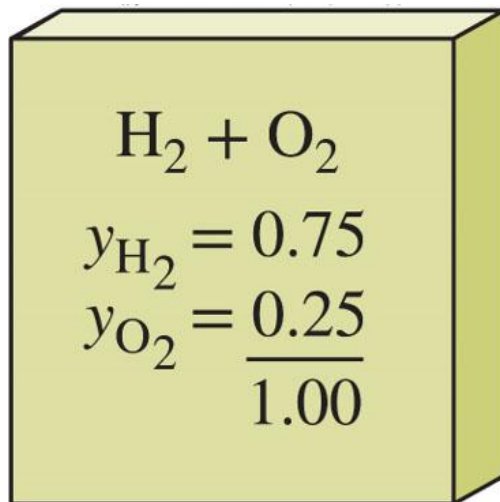
# 13–1 Composition of a Gas Mixture: Mass and Mole Fractions <sub>3</sub>

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

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 <sup>4</sup>

$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_{i=1}^k y_i M_i \quad \text{Apparent (or average) molar mass}$$

The mass of a substance can be expressed in terms of the mole number  $N$  and molar mass  $M$  of the substance as  $m = NM$

$$R_m = \frac{R_u}{M_m} \quad \text{Gas constant}$$

$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i / M_i} = \frac{1}{\sum m_i / (m_m M_i)} = \frac{1}{\sum_{i=1}^k \frac{mf_i}{M_i}} \quad \text{The molar mass of a mixture}$$

$$mf_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m} \quad \text{Relation between mass fractions (mf) and mole fractions (y) of a mixture}$$

# 13–1 Composition of a Gas Mixture: Mass and Mole Fractions <sub>5</sub>

**Example2:** Find the mass of 6 kmol of O<sub>2</sub>

**Solution:**  $m = M n = 32 \times 6 = 192 \text{ kg}$

**Example3:** If a system contains 1.8kg of CH<sub>3</sub>OH, find the associated molar mass.

**Solution:** Firstly, we need to find the molecular weight of CH<sub>3</sub>OH. To do this, we sum the molecular weights of its constituent components

$$(M_w)_{\text{CH}_3\text{OH}} = (1 \times 12) + (3 \times 1) + (1 \times 16) + (1 \times 1) = 32$$

Now,  $m = 1.8 \text{ kg}$  and so

$$\frac{m}{M} = n = \frac{1.8}{32} = 0.05625 \text{ kmol.}$$

**Example4:** Find the characteristic gas constant for methane (CH<sub>4</sub>).

**Solution:**

$$(M_w)_{\text{CH}_4} = (1 \times 12) + (4 \times 1) = 16$$

$$R_{\text{CH}_4} = \frac{\Re}{M_{\text{CH}_4}} = \frac{8314.5}{16} = 519.7 \text{ J/kgK}$$

# 13–1 Composition of a Gas Mixture: Mass and Mole Fractions <sub>5</sub>

**Example5:** Molar analysis of air indicates that is composed primarily of nitrogen (78%) and oxygen (22%). Determine the characteristic gas constant for the mixture along with mass fractions.

**Solution:** In this case mole fractions are  $y_1 = 0.78$  and  $y_2 = 0.22$ , and the molar masses are  $M_1 = 28$  kg/kmol and  $M_2 = 32$  kg/kmol (see table above). Thus

$M = y_1 M_1 + y_2 M_2 = 0.78 \times 28 + 0.22 \times 32 = 28.88$  kg/kmol and recall that  $\mathfrak{R} = 8.3145$  kJ/kmolK, so it follows that  $R = \mathfrak{R}/M = 8.3145/28.88 = 0.288$  kJ/kgK. Note that

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

$$\text{Mf}_1 = 0.78 \times \frac{28}{28.88} = 0.756 \quad \& \quad \text{Mf}_2 = 0.22 \times \frac{32}{28.88} = 0.244.$$

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

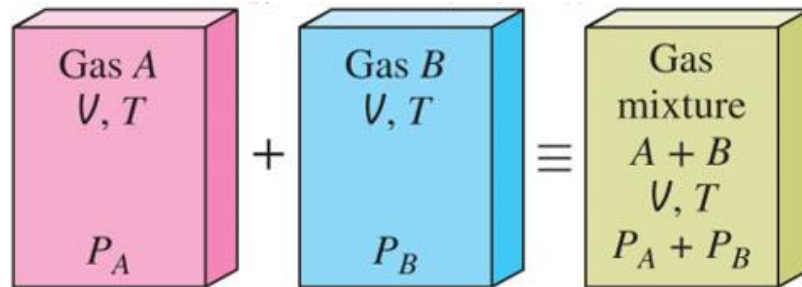
$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_{i=1}^k y_i M_i$$

# 13–2 $P$ - $v$ - $T$ Behaviour Of Gas Mixtures: Ideal And Real Gases <sub>1</sub>

An ideal gas is defined as a gas whose molecules are spaced far apart so that the behaviour of a molecule is not influenced by the presence of other molecules—a situation encountered at low densities.

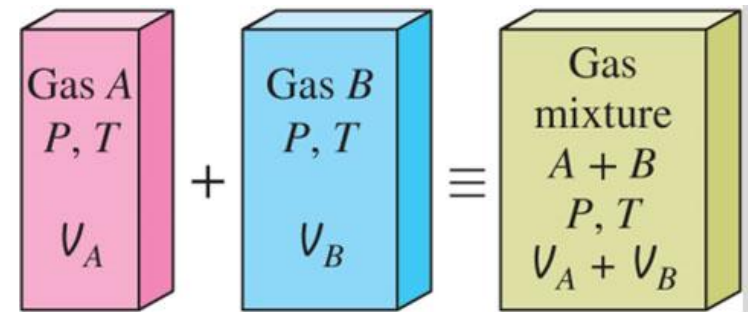
**Figure 13–5**

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  $P$ - $v$ - $T$  behaviour 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 $P$ - $v$ - $t$ Behaviour Of Gas Mixtures: Ideal And Real Gases <sub>2</sub>

Dalton's law:	$P_m = \sum_{i=1}^k P_i(T_m, V_m)$	$\left\{ \begin{array}{l} \text{exact for ideal gases,} \\ \text{approximate} \\ \text{for real gases} \end{array} \right.$	$P_i$ component pressure
Amagat's law:	$V_m = \sum_{i=1}^k V_i(T_m, P_m)$		$V_i$ component volume $P_i/P_m$ pressure fraction $V_i/V_m$ volume fraction

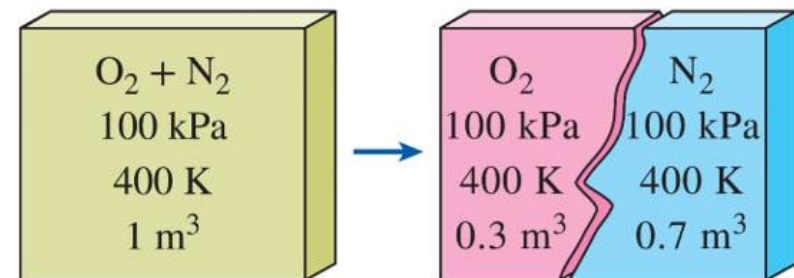
Dalton's and Amagat's laws hold exactly for ideal-gas mixtures, but only approximately for real-gas mixtures.

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.

**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  $y_i V_m$ ).



# 13–2 *P-v-t* Behaviour Of Gas Mixtures: Ideal And Real Gases <sub>3</sub>

When two or more ideal gases are mixed, the behaviour 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*.

## Ideal-Gas Mixtures

For ideal gases, component pressure ( $P_i$ ) and component volume ( $V_i$ ) can be related to mole fraction ( $y_i$ ) by using the ideal-gas relation for both the components and the gas mixture:

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

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

This equation is only valid for ideal-gas mixtures as it is derived by assuming ideal-gas behaviour 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.

# 13–2 $P$ - $v$ - $T$ Behaviour Of Gas Mixtures: Ideal And Real Gases <sup>4</sup>

## 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 ( $P_i$ ) or component volumes ( $V_i$ ) should be evaluated from relations that take into account the deviation of each component from ideal-gas behaviour.

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 as



$$P_m V_m = Z_m N_m R_u T_m$$

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

$$PV = ZNR_u T$$

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

**Figure 13–8**

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

# 13–2 $P$ - $v$ - $t$ Behaviour Of Gas Mixtures: Ideal And Real Gases <sup>4</sup>

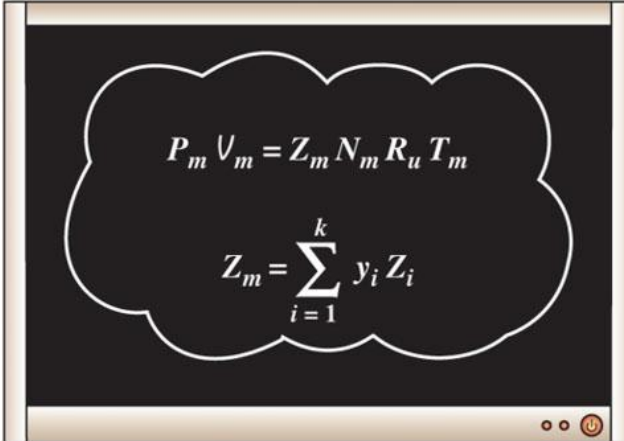
## Compressibility factor

$Z_i$  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.

The compressibility-factor approach, in general, gives more accurate results when the  $Z_i$ 's 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 (see next slide).

Dalton's law disregards the influence of dissimilar molecules in a mixture on each other, so it tends to underpredict the pressure of a gas mixture for a given  $T_m$  and  $V_m$ .

Therefore, Dalton's law is more appropriate for gas mixtures at low pressures, while Amagat's law is more appropriate at high pressures.

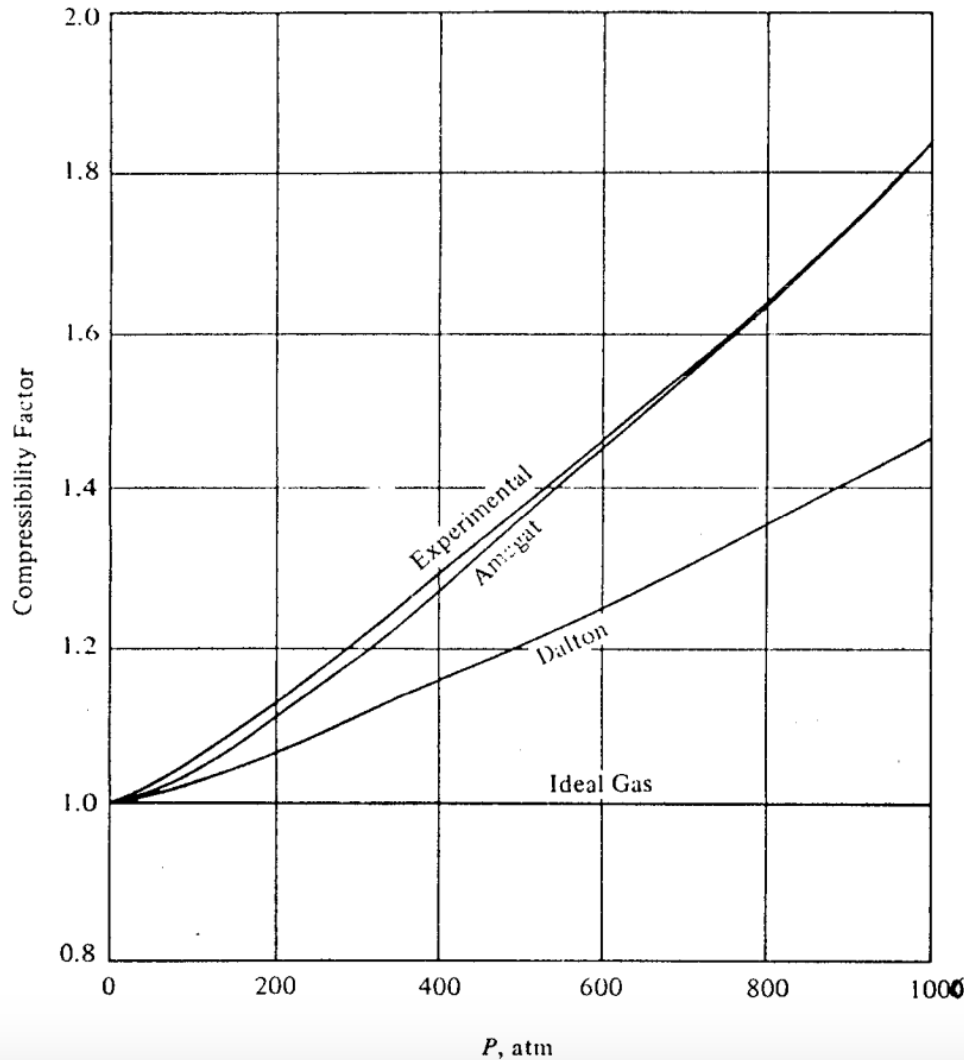


$$P_m V_m = Z_m N_m R_u T_m$$

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



# 13–2 $P$ - $v$ - $t$ Behaviour Of Gas Mixtures: Ideal And Real Gases <sup>4</sup>



Both laws for ideal mixtures are based on an additive approximation for  $Z_{\text{mix}}(P, T)$ . According to Dalton's law, the component compressibility factors are evaluated at the respective partial pressures - hence  $Z_i(P_i, T)$  - whereas, according to Amagat's law, the component compressibility factors are evaluated at the total pressure of the mixture - hence  $Z_i(P, T)$ .

**Figure 13–9:** Experimental and Calculated Compressibility Factors for the System  $3/4 \text{ H}_2 + 1/4 \text{ N}_2$  at  $0^\circ\text{C}$ . The experimental isotherm is based on the data of Bartlett, Cupples, and Tremearne, 1928, J. Am. Chem. Soc., 50, 1275.

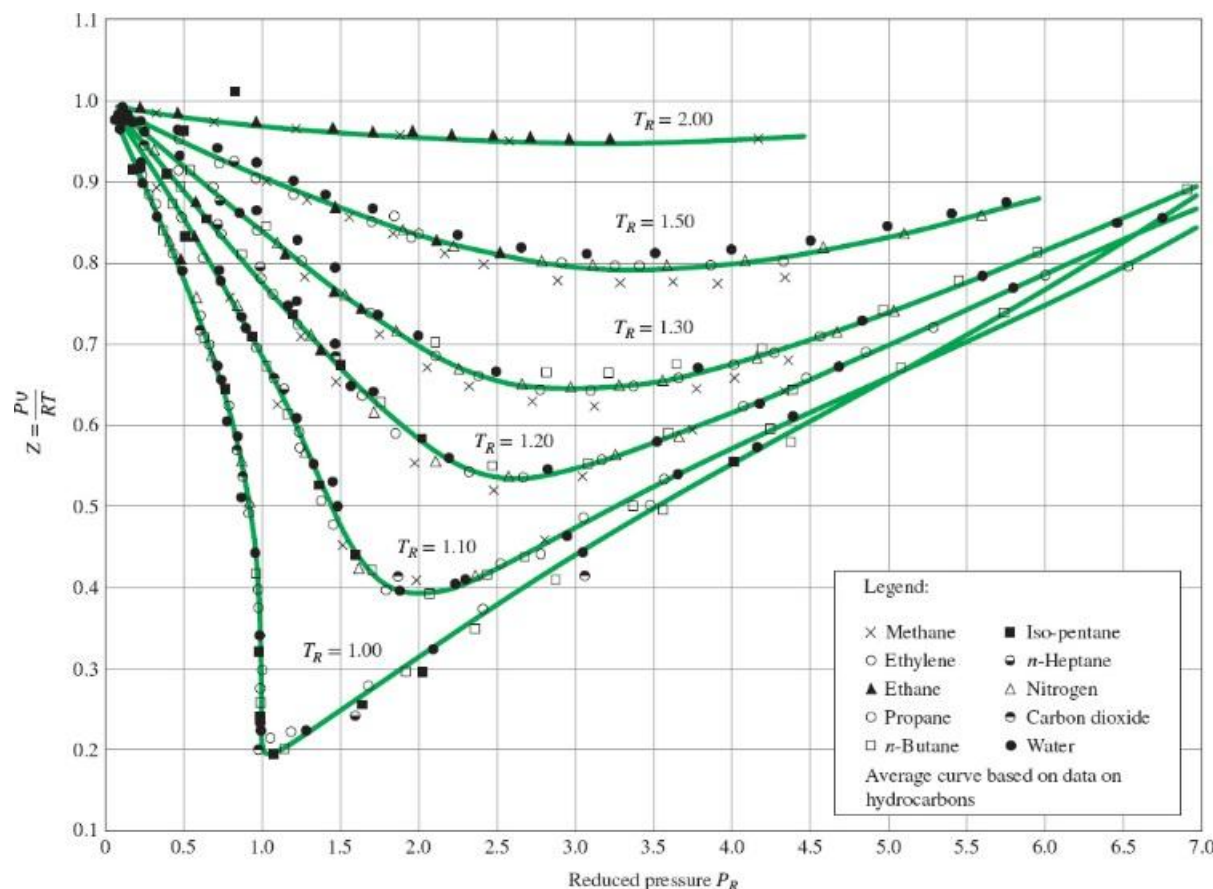
# Compressibility Factor—a Measure of Deviation from Ideal-Gas Behaviour

$$P_R = \frac{P}{P_{cr}} \quad \text{Reduced pressure} \quad T_R = \frac{T}{T_{cr}} \quad \text{Reduced temperature} \quad v_R = \frac{v_{\text{actual}}}{RT_{cr} / P_{cr}} \quad \text{Pseudo-reduced specific volume}$$

**Figure 3–48**

Comparison of Z factors for various gases.

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 behaviour of single gases rather accurately, but not for mixtures of gases.



# 13–2 $P$ - $v$ - $T$ Behaviour Of Gas Mixtures: Ideal And Real Gases <sub>5</sub>

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

## Kay's rule

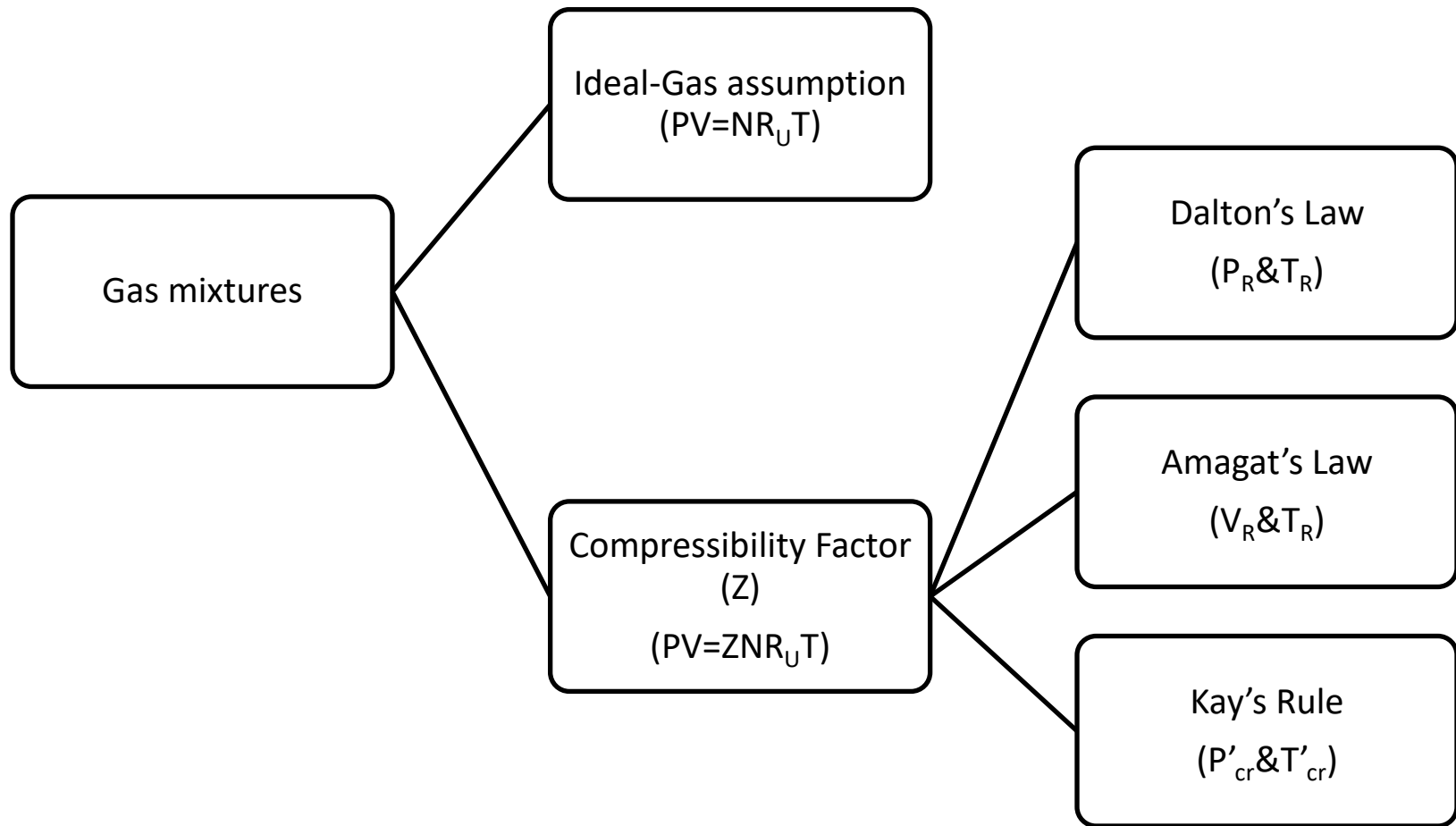
$Z_m$  is determined by using these pseudocritical properties.

$$P'_{cr,m} = \sum_{i=1}^k y_i P_{cr,i} \quad \text{pseudocritical pressure}$$

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

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

# 13–2 $P$ - $v$ - $t$ Behaviour Of Gas Mixtures: Ideal And Real Gases <sub>5</sub>



### 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:

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

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,

$$\left. \begin{aligned} T_R &= \frac{T_m}{T'_{cr,m}} = \frac{300 \text{ K}}{259.7 \text{ K}} = 1.16 \\ P_R &= \frac{P_m}{P'_{cr,m}} = \frac{15 \text{ MPa}}{6.39 \text{ MPa}} = 2.35 \end{aligned} \right\} Z_m = 0.49 \quad (\text{Fig. A-15b})$$

Thus,

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

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

(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:

$$PV = ZNR_u T$$

$$Z_m = \sum_{i=1}^k y_i Z_i \quad (\text{Fig. A-15b})$$

$$N_2: \quad \left. \begin{aligned} T_{R,N_2} &= \frac{T_m}{T_{cr,N_2}} = \frac{300 \text{ K}}{126.2 \text{ K}} = 2.38 \\ P_{R,N_2} &= \frac{P_m}{P_{cr,N_2}} = \frac{15 \text{ MPa}}{3.39 \text{ MPa}} = 4.42 \end{aligned} \right\} Z_{N_2} = 1.02$$

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

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

Thus,

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

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  $1.330 \text{ m}^3$ , 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 pseudo-reduced volume is determined from its definition in Chap. 3:

$$\begin{aligned} v_{R,N_2} &= \frac{\bar{v}_{N_2}}{R_u T_{cr,N_2} / P_{cr,N_2}} = \frac{V_m / N_{N_2}}{R_u T_{cr,N_2} / P_{cr,N_2}} \\ &= \frac{(1.33 \text{ m}^3) / (2 \text{ kmol})}{(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(126.2 \text{ K}) / (3390 \text{ kPa})} = 2.15 \end{aligned} \quad v_R = \frac{V_{actual}}{RT_{cr} / P_{cr}}$$

Similarly,

$$v_R = \frac{v_{\text{actual}}}{RT_{\text{cr}} / P_{\text{cr}}}$$

$$v_{R,\text{CO}_2} = \frac{(1.33 \text{ m}^3)/(6 \text{ kmol})}{(8.314 \text{ kPa}\cdot\text{m}^3/\text{kmol}\cdot\text{K})(304.2 \text{ K})/(7390 \text{ kPa})} = 0.648$$

From Fig. A-15, we read  $Z_{\text{N}_2} = 0.99$  and  $Z_{\text{CO}_2} = 0.56$ . Thus,

$$Z_m = y_{\text{N}_2}Z_{\text{N}_2} + y_{\text{CO}_2}Z_{\text{CO}_2} = (0.25)(0.99) + (0.75)(0.56) = 0.67$$

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 m<sup>3</sup> after the second iteration, 0.678 m<sup>3</sup> after the third iteration, and 0.648 m<sup>3</sup> after the fourth iteration. This value does not change with more iterations. Therefore,

$$v_m = 0.648 \text{ m}^3$$

**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 <sub>1</sub>

Consider a gas mixture that consists of 2 kg of N<sub>2</sub> and 3 kg of CO<sub>2</sub>. The total mass (an *extensive property*) of this mixture is 5 kg. This example suggests a simple way of evaluating the **extensive properties** of a non-reacting ideal- or real-gas mixture

Extensive properties of a gas mixture

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

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

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

Changes in properties of a gas mixture

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

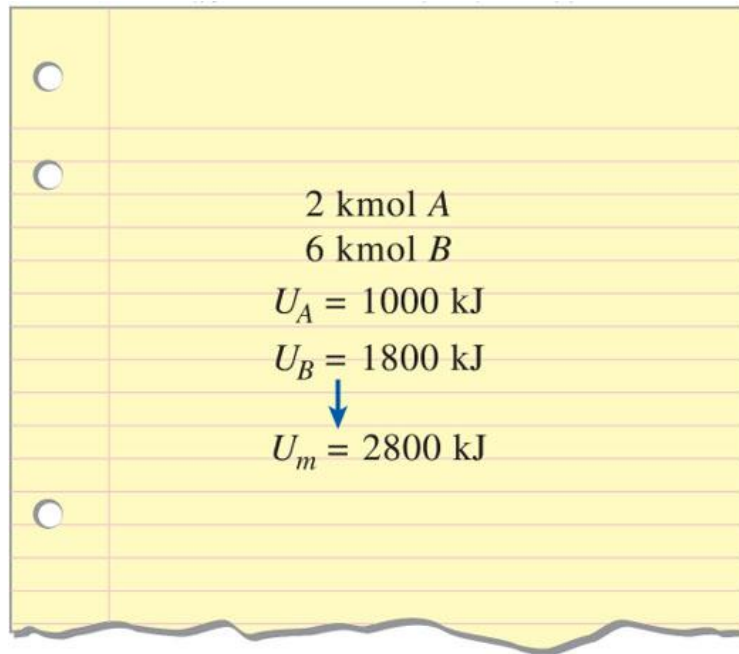
$$\Delta H_m = \sum_{i=1}^k \Delta H_i = \sum_{i=1}^k m_i \Delta h_i = \sum_{i=1}^k N_i \Delta \bar{h}_i \quad (\text{kJ})$$

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

# 13–3 Properties of Gas Mixtures: Ideal and Real Gases <sub>2</sub>

**Figure 13–11**

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



**Reminder:** Properties are considered to be either *intensive* or *extensive*:

- **Intensive properties** are those that are independent of the mass of a system, such as temperature, pressure, and density.
- **Extensive properties** are those whose values depend on the size (or extent) of the system.



# 13–3 Properties of Gas Mixtures: Ideal and Real Gases <sub>3</sub>

Intensive properties of a gas mixture

$$u_m = \sum_{i=1}^k mf_i u_i \quad (\text{kJ/kg}) \quad \text{and} \quad \bar{u}_m = \sum_{i=1}^k y_i \bar{u}_i \quad (\text{kJ/mol})$$

$$h_m = \sum_{i=1}^k mf_i h_i \quad (\text{kJ/kg}) \quad \text{and} \quad \bar{h}_m = \sum_{i=1}^k y_i \bar{h}_i \quad (\text{kJ/mol})$$

$$s_m = \sum_{i=1}^k mf_i s_i \quad (\text{kJ/kg} \cdot \text{K}) \quad \text{and} \quad \bar{s}_m = \sum_{i=1}^k y_i \bar{s}_i \quad (\text{kJ/mol} \cdot \text{K})$$

$$c_{v,m} = \sum_{i=1}^k mf_i c_{v,i} \quad (\text{kJ/kg} \cdot \text{K}) \quad \bar{c}_{v,m} = \sum_{i=1}^k y_i \bar{c}_{v,i} \quad (\text{kJ/kmol} \cdot \text{K})$$

$$c_{p,m} = \sum_{i=1}^k mf_i c_{p,i} \quad (\text{kJ/kg} \cdot \text{K}) \quad \bar{c}_{p,m} = \sum_{i=1}^k y_i \bar{c}_{p,i} \quad (\text{kJ/kmol} \cdot \text{K})$$

Properties per unit mass involve mass fractions ( $mf_i$ ) and properties per unit mole involve mole fractions ( $y_i$ ).

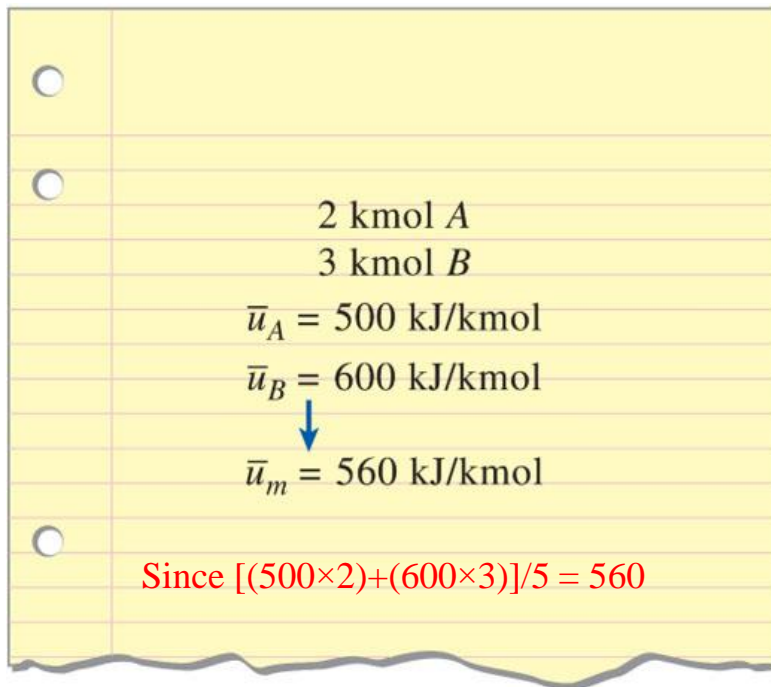
The relations are exact for ideal-gas mixtures, and approximate for real-gas mixtures.



# 13–3 Properties of Gas Mixtures: Ideal and Real Gases <sup>4</sup>

**Figure 13–12**

The intensive properties of a mixture are determined by weighted averaging.



# 13–3 Properties Of Gas Mixtures:

## Ideal and Real Gases <sup>5</sup>

### 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.

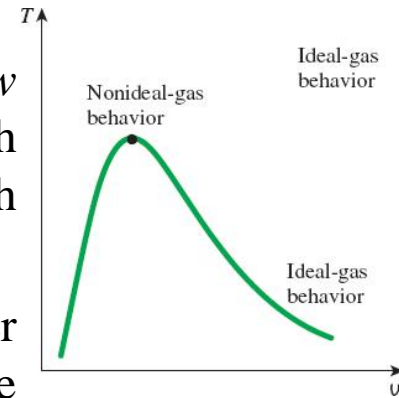
**Gibbs–Dalton law** (*extension of Dalton's law of additive pressures*): Under the ideal-gas approximation, the properties of a gas are not influenced by the presence of other gases, and each gas component in the mixture behaves as if it exists alone at the mixture temperature  $T_m$  and mixture volume  $V_m$ .

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. The entropy change of individual gases can be determined from:

$$\Delta s_i = s^\circ_{i,2} - s^\circ_{i,1} - R_i \ln \frac{P_{i,2}}{P_{i,1}} \cong c_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_i \ln \frac{P_{i,2}}{P_{i,1}}$$

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

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



We choose absolute zero as the reference temperature and define a function  $s^\circ$  as

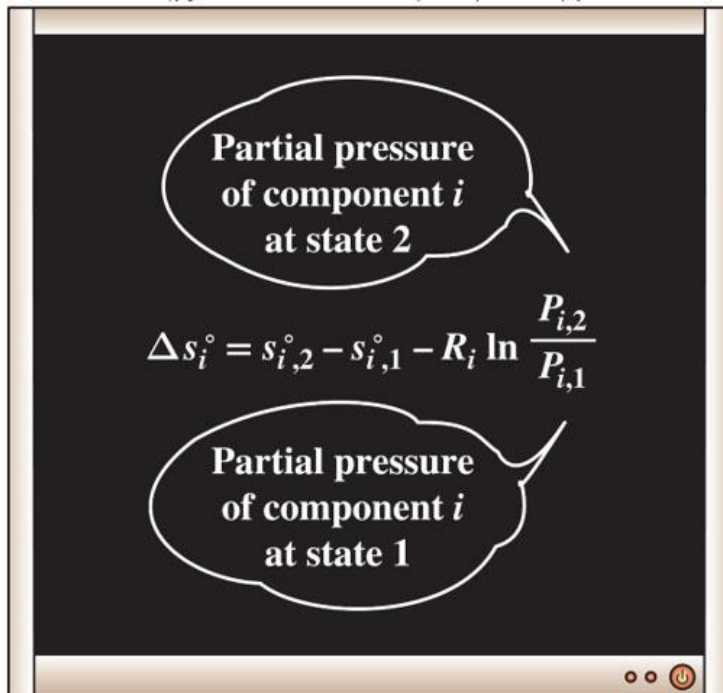
$$s^\circ = \int_0^T C_p(T) \frac{dT}{T}$$

The function  $s^\circ$  represents only the temperature-dependent part of entropy.

# 13–3 Properties Of Gas Mixtures: Ideal and Real Gases <sub>6</sub>

**Figure 13–13**

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



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

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

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

# 13–3 Properties Of Gas Mixtures: Ideal and Real Gases <sub>6</sub>

## EXAMPLE 13–3 Expansion of an Ideal Gas Mixture in a Turbine

A mixture of oxygen ( $O_2$ ), carbon dioxide ( $CO_2$ ), and helium ( $He$ ) gases with mass fractions of 0.0625, 0.625, and 0.3125, respectively, enter an adiabatic turbine at 1000 kPa and 600 K steadily and expand to 100 kPa pressure (Fig. 13–14). The isentropic efficiency of the turbine is 90 percent. For gas components assuming constant specific heats at room temperature, determine (a) the work output per unit mass of mixture.

**SOLUTION** The mass fractions of the components of a gas mixture that expands in an adiabatic turbine are given. The work output, the exergy destruction, and the second-law efficiency are to be determined.

**Assumptions** All gases will be modeled as ideal gases with constant specific heats.

**Analysis** (a) The mass fractions of mixture components are given to be  $mf_{CO_2} = 0.0625$ ,  $mf_{CO_2} = 0.625$ , and  $mf_{He} = 0.3125$ . The specific heats of these gases at room temperature are (Table A–2a):

	$c_v$ , kJ/kg·K	$c_p$ , kJ/kg·K
$O_2$ :	0.658	0.918
$CO_2$ :	0.657	0.846
$He$ :	3.1156	5.1926

Then, the constant-pressure and constant-volume specific heats of the mixture become

$$\begin{aligned} c_p &= mf_{O_2} c_{p,O_2} + mf_{CO_2} c_{p,CO_2} + mf_{He} c_{p,He} \\ &= 0.0625 \times 0.918 + 0.625 \times 0.846 + 0.3125 \times 5.1926 \\ &= 2.209 \text{ kJ/kg·K} \end{aligned}$$

$$\begin{aligned} c_v &= mf_{O_2} c_{v,O_2} + mf_{CO_2} c_{v,CO_2} + mf_{He} c_{v,He} \\ &= 0.0625 \times 0.658 + 0.625 \times 0.657 + 0.3125 \times 3.1156 \\ &= 1.425 \text{ kJ/kg·K} \end{aligned}$$

The apparent gas constant of the mixture and the specific heat ratio are

$$R = c_p - c_v = 2.209 - 1.425 = 0.7836 \text{ kJ/kg·K}$$

$$k = \frac{c_p}{c_v} = \frac{2.209 \text{ kJ/kg·K}}{1.425 \text{ kJ/kg·K}} = 1.550$$

The temperature at the end of the expansion for the isentropic process is

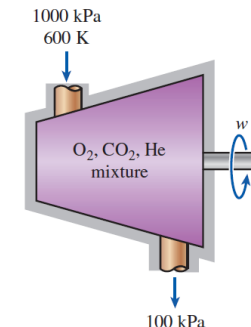
$$T_{2s} = T_1 \left( \frac{P_2}{P_1} \right)^{(k-1)/k} = (600 \text{ K}) \left( \frac{100 \text{ kPa}}{1000 \text{ kPa}} \right)^{0.55/1.55} = 265.0 \text{ K}$$

Using the definition of turbine isentropic efficiency, the actual outlet temperature is

$$T_2 = T_1 - \eta_T (T_1 - T_{2s}) = (600 \text{ K}) - (0.90)(600 - 265) \text{ K} = 298.5 \text{ K}$$

Noting that the turbine is adiabatic and thus there is no heat transfer, the actual work output is determined to be

$$\begin{aligned} w_{out} &= h_1 - h_2 = c_p (T_1 - T_2) = (2.209 \text{ kJ/kg·K})(600 - 298.5) \text{ K} \\ &= \mathbf{666.0 \text{ kJ/kg}} \end{aligned}$$

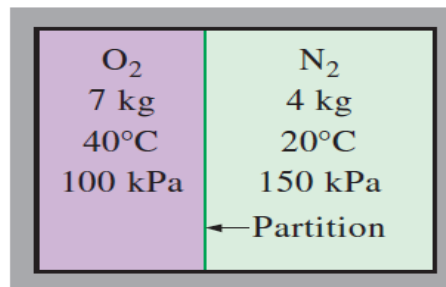


**FIGURE 13–14**  
Schematic for Example 13–3.

# Tutorial Questions

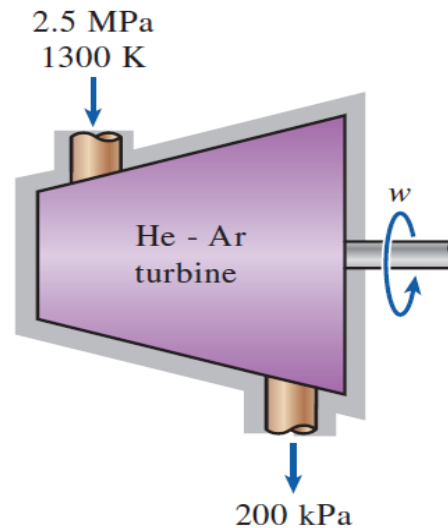
# Tutorial Questions

- 1) A gas mixture has the following composition on a mole basis: 60 percent  $\text{N}_2$  and 40 percent  $\text{CO}_2$ . Determine the gravimetric analysis of the mixture, its molar mass, and the gas constant.
- 2) A gas mixture at 300 K and 200 kPa consists of 1 kg of  $\text{CO}_2$  and 3 kg of  $\text{CH}_4$ . Determine the partial pressure of each gas and the apparent molar mass of the gas mixture.
- 3) An insulated rigid tank is divided into two compartments by a partition. One compartment contains 7 kg of oxygen gas at  $40^\circ\text{C}$  and 100 kPa, and the other compartment contains 4 kg of nitrogen gas at  $20^\circ\text{C}$  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.



# Tutorial Questions

4) An equimolar mixture of helium and argon gases is to be used as the working fluid in a closed-loop gas-turbine cycle. 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.



5) A piston–cylinder device contains a mixture of 0.5 kg of  $H_2$  and 1.2 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.

# OPTIONAL READING



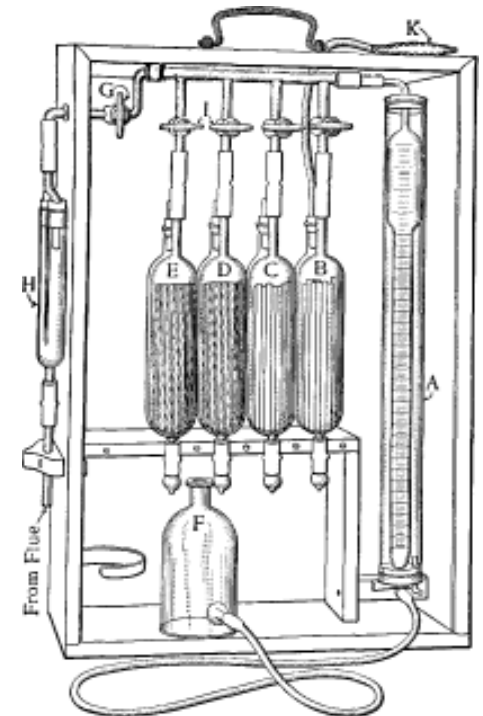
# 13–2 *P-v-t* Behaviour Of Gas Mixtures: Ideal And Real Gases <sub>3</sub>

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) and the following equation

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

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.

Orsat Analyzer which analyses a gas sample for its oxygen, carbon monoxide and carbon dioxide content



# 13–3 Properties Of Gas Mixtures: Ideal And Real Gases <sub>6</sub>

## 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  $25^\circ C$  and 200 kPa. Now the partition is removed, and the two gases are allowed to mix. Assuming the surroundings are at  $25^\circ C$  and both gases behave as ideal gases, determine the entropy change

### SOLUTION

**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.

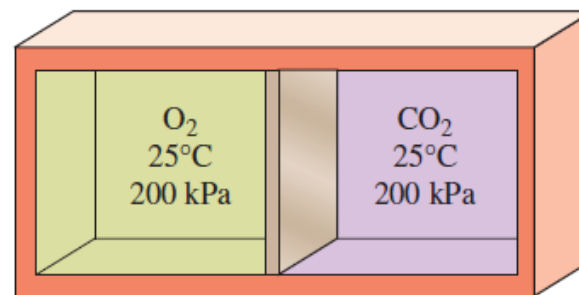
When two ideal gases initially at the same temperature and pressure are mixed by removing a partition between them, the mixture will also be at the same temperature and pressure. (Can you prove it? Will this be true for nonideal gases?) Therefore, the temperature and pressure in the tank will still be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

$$\begin{aligned}\Delta S_m &= \sum \Delta S_i = \sum N_i \Delta \bar{s}_i = \sum N_i \left( \bar{c}_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_u \ln \frac{P_{i,2}}{P_{i,1}} \right) \\ &= -R_u \sum N_i \ln \frac{y_{i,2} P_{m,2}}{P_{i,1}} = -R_u \sum N_i \ln y_{i,2}\end{aligned}$$

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 that it 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

$$\begin{aligned}N_m &= N_{O_2} + N_{CO_2} = (3 + 5) \text{ kmol} = 8 \text{ kmol} \\ y_{O_2} &= \frac{N_{O_2}}{N_m} = \frac{3 \text{ kmol}}{8 \text{ kmol}} = 0.375 \\ y_{CO_2} &= \frac{N_{CO_2}}{N_m} = \frac{5 \text{ kmol}}{8 \text{ kmol}} = 0.625 \\ \Delta S_m &= -R_u (N_{O_2} \ln y_{O_2} + N_{CO_2} \ln y_{CO_2}) \\ &= -(8.314 \text{ kJ/kmol}\cdot\text{K})[(3 \text{ kmol})(\ln 0.375) + (5 \text{ kmol})(\ln 0.625)] \\ &= \mathbf{44.0 \text{ kJ/K}}\end{aligned}$$



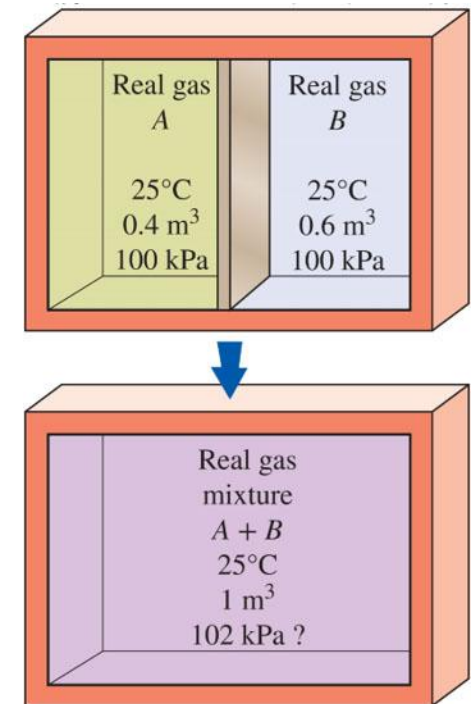
**FIGURE 13–15**  
Schematic for Example 13–4.

# 13–3 Properties Of Gas Mixtures: Ideal And Real Gases ,

## 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  $u$ ,  $h$ ,  $cv$ , and  $cp$  depend on the pressure (or specific volume) as well as on the temperature. In such cases, the effects of deviation from ideal-gas behaviour on the mixture properties should be accounted for.

When real-gas mixtures are involved, it may be necessary to account for the effect of nonideal behaviour on the mixture properties such as enthalpy and entropy.



**Figure 13–16**

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

# 13–3 Properties Of Gas Mixtures: Ideal And Real Gases <sub>8</sub>

$$dh_m = T_m ds_m + v_m dp_m \quad T ds \text{ relation for a gas mixture}$$

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

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

$$dh_i = T_m ds_i + v_i dP_m$$

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.