Chapter 13
GAS MIXTURES
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.
• Perform energy and exergy analysis of mixing processes.
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

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

\[ m_m = \sum_{i=1}^{k} m_i \]

\[ N_m = \sum_{i=1}^{k} N_i \]

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

\[ mf_i = \frac{m_i}{m_m} \]

\[ y_i = \frac{N_i}{N_m} \]
Apparent (or average) molar mass

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

\[ m = NM \]

Gas constant

\[ R_m = \frac{R_u}{M_m} \]

The molar mass of a mixture

\[ M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i / M_i} = \frac{1}{\sum m_i / (m_m M_i)} = \frac{1}{\sum_{i=1}^{k} \frac{m_f_i}{M_i}} \]

Mass and mole fractions of a mixture are related by

\[ m_f_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m} \]

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

\[ \sum_{i=1}^{k} m_f_i = 1 \quad \text{and} \quad \sum_{i=1}^{k} y_i = 1 \]

\[
\begin{align*}
H_2 + O_2 \\
y_{H_2} &= 0.75 \\
y_{O_2} &= 0.25 \\
&= 1.00
\end{align*}
\]

The sum of the mole fractions of a mixture is equal to 1.
**P-v-T BEHAVIOR OF GAS MIXTURES: IDEAL AND REAL 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.
Dalton’s law:

\[ P_m = \sum_{i=1}^{k} P_i(T_m, V_m) \]

exact for ideal gases, approximate for real gases

Amagat’s law:

\[ V_m = \sum_{i=1}^{k} V_i(T_m, P_m) \]

\[ P_i \] 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.

\[ \begin{align*}
O_2 + N_2 & \\
100 \text{ kPa} & \\
400 \text{ K} & \\
1 \text{ m}^3 & \\
\end{align*} \]

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

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)
Real-Gas Mixtures

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

Compressibility factor

$P V = Z N R_u T$

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

$Z_i$ 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.

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.

Kay’s rule

Pseudopure substance

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

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

$Z_m$ is determined by using these pseudocritical properties.

The result by Kay’s rule is accurate to within about 10% over a wide range of temperatures and pressures.
PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

Extensive properties of a gas mixture

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

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

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

Changes in properties of a gas mixture

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

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

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

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

\[ u_m = \sum_{i=1}^{k} m_{i} u_i \text{ (kJ/kg)} \quad \text{and} \quad \bar{u}_m = \sum_{i=1}^{k} y_i \bar{u}_i \text{ (kJ/kmol)} \]

\[ h_m = \sum_{i=1}^{k} m_{i} h_i \text{ (kJ/kg)} \quad \text{and} \quad \bar{h}_m = \sum_{i=1}^{k} y_i \bar{h}_i \text{ (kJ/kmol)} \]

\[ s_m = \sum_{i=1}^{k} m_{i} s_i \text{ (kJ/kg \cdot K)} \quad \text{and} \quad \bar{s}_m = \sum_{i=1}^{k} y_i \bar{s}_i \text{ (kJ/kmol \cdot K)} \]

Properties per unit mass involve mass fractions \((m_f)\) and properties per unit mole involve mole fractions \((y_i)\).

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

<table>
<thead>
<tr>
<th>[2 \text{ kmol A}]</th>
<th>[3 \text{ kmol B}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\ddot{u}_A = 500 \text{ kJ/kmol}]</td>
<td>[\ddot{u}_B = 600 \text{ kJ/kmol}]</td>
</tr>
<tr>
<td>[\ddot{u}_m = 560 \text{ kJ/kmol}]</td>
<td></td>
</tr>
</tbody>
</table>
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.

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

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

\[
P_{i,2} = y_{i,2}P_{m,2} \quad P_{i,1} = y_{i,1}P_{m,1}
\]

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

\[ dh_m = T_m ds_m + \nu_m dP_m \]

\[ d\left( \sum mf_i h_i \right) = T_m d\left( \sum mf_i s_i \right) + \left( \sum mf_i \nu_i \right) dP_m \]

\[ \sum mf_i (dh_i - T_m ds_i - \nu_i dP_m) = 0 \]

\[ dh_i = T_m ds_i + \nu_i dP_m \]

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.

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

• Composition of a gas mixture: Mass and mole fractions
• $P-v-T$ behavior of gas mixtures
  ✓ Ideal-gas mixtures
  ✓ Real-gas mixtures
• Properties of gas mixtures
  ✓ Ideal-gas mixtures
  ✓ Real-gas mixtures