

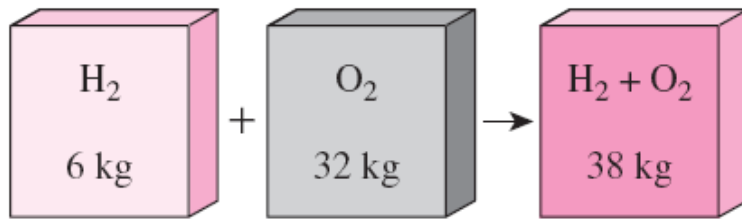
GAS MIXTURES

- 1. A Little Math – Partial Derivatives**
- 2. The Maxwell Relations**
- 3. The Clapeyron Equation**
- 4. General Relations for du , dh , ds , C_v and C_p**
- 5. The Joule-Thomson Coefficient**
- 6. The Δh , Δu and Δs of Real Gases**

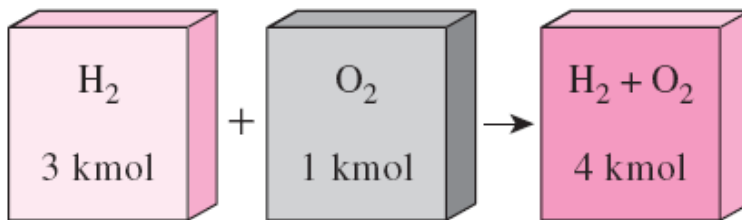
- Develop rules for determining nonreacting gas mixture properties from knowledge of mixture composition and the properties of the individual components.
- Define the quantities used to describe the composition of a mixture, such as mass fraction, mole fraction, and volume fraction.
- Apply the rules 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:



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



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

Molar analysis: specifying the number of moles of each component

Gravimetric analysis: specifying the mass of each component

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

$$mf_i = \frac{m_i}{m_m} \quad \text{Mass fraction}$$

$$y_i = \frac{N_i}{N_m} \quad \text{Mole fraction}$$

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

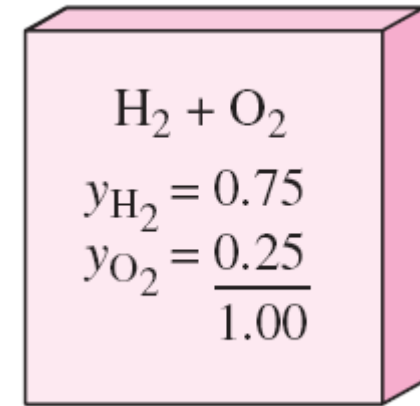
$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i / M_i} = \frac{1}{\sum m_i / (m_m M_i)} = \frac{1}{\sum_{i=1}^k \frac{mf_i}{M_i}}$$

Mass and mole fractions of a mixture are related by

$$mf_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m}$$

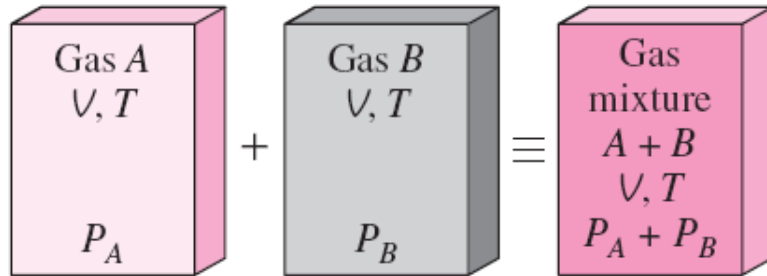
The sum of the mass and mole fractions of a mixture is equal to 1.

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

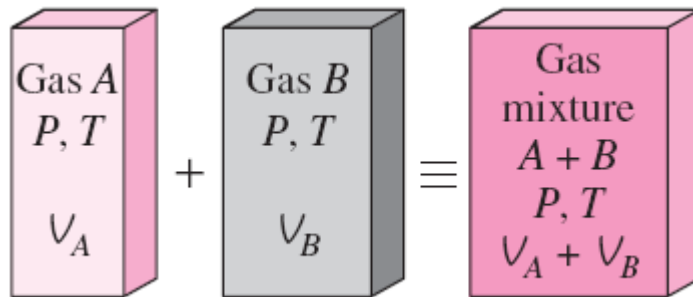


The sum of the mole fractions of a mixture is equal to 1.

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



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



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.

Dalton's law:

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

Amagat's law:

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

exact for ideal gases,
approximate
for real gases

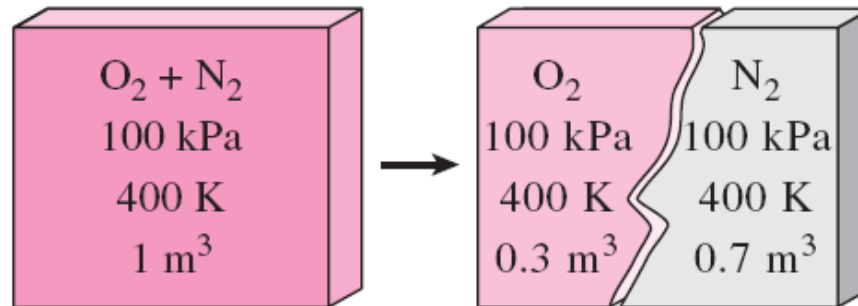
P_i component pressure

V_i component volume

P_i/P_m pressure fraction

V_i/V_m volume fraction

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



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

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

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

→

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

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**).

Compressibility factor

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

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.

$$P_m V_m = Z_m N_m R_u T_m$$

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

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

Kay's rule

Pseudopure substance

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

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

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} .

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

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

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

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

2 kmol A
6 kmol B
$U_A = 1000 \text{ kJ}$
$U_B = 1800 \text{ kJ}$
↓
$U_m = 2800 \text{ kJ}$

Changes in properties of a gas mixture

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

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

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

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

Extensive properties of a gas mixture

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

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

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

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

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

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

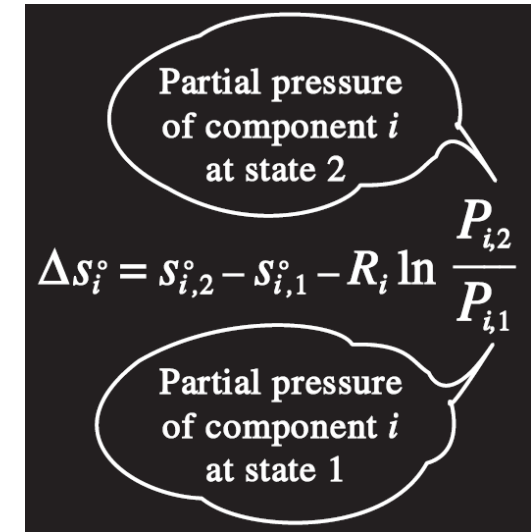
The relations are exact for ideal-gas mixtures, and approximate for real-gas mixtures.

$$\begin{array}{c} \hline 2 \text{ kmol } A \\ \hline 3 \text{ kmol } B \\ \hline \bar{u}_A = 500 \text{ kJ/kmol} \\ \hline \bar{u}_B = 600 \text{ kJ/kmol} \\ \hline \downarrow \\ \hline \bar{u}_m = 560 \text{ kJ/kmol} \\ \hline \end{array}$$

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

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.



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

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

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

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

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

$dh_m = T_m ds_m + v_m dP_m$ $T ds$ relation for a gas mixture

$$d\left(\sum mf_i h_i\right) = T_m d\left(\sum mf_i s_i\right) + \left(\sum mf_i v_i\right) dP_m$$

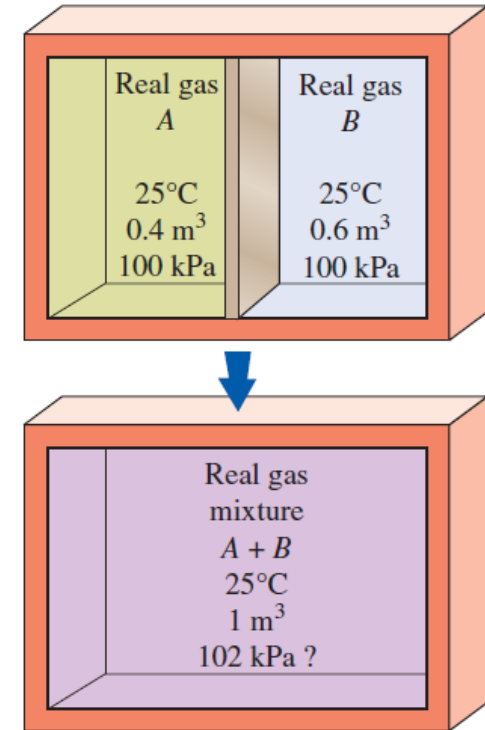
$$\sum mf_i (dh_i - T_m ds_i - v_i dP_m) = 0$$

$$dh_i = T_m ds_i + v_i dP_m$$

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.



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

Chung H. Jeon

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

A mixture of oxygen (O₂), carbon dioxide (CO₂), 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 and (b) the exergy destruction and the second-law efficiency of the turbine. Take the environment temperature to be $T_0 = 25^\circ\text{C}$.

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 $mf_{\text{O}_2} = 0.0625$, $mf_{\text{CO}_2} = 0.625$, and $mf_{\text{He}} = 0.3125$. 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

$$\begin{aligned}
 c_p &= mf_{\text{O}_2}c_{p,\text{O}_2} + mf_{\text{CO}_2}c_{p,\text{CO}_2} + mf_{\text{He}}c_{p,\text{He}} \\
 &= 0.0625 \times 0.918 + 0.625 \times 0.846 + 0.3125 \times 5.1926 \\
 &= 2.209 \text{ kJ/kg}\cdot\text{K}
 \end{aligned}$$

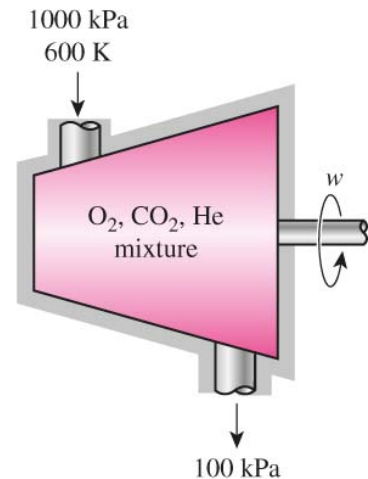


FIGURE 13–14
Schematic for Example 13–3.

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

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

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

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

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

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

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

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

(b) The entropy change of the gas mixture and the exergy destruction in the turbine are

$$s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} = (2.209 \text{ kJ/kg}\cdot\text{K}) \ln \frac{298.5 \text{ K}}{600 \text{ K}} \\ - (0.7836 \text{ kJ/kg}\cdot\text{K}) \ln \frac{100 \text{ kPa}}{1000 \text{ kPa}} = 0.2658 \text{ kJ/kg}\cdot\text{K}$$

$$x_{\text{dest}} = T_0 s_{\text{gen}} = T_0 (s_2 - s_1) = (298 \text{ K})(0.2658 \text{ kJ/kg}\cdot\text{K}) = \mathbf{79.2 \text{ kJ/kg}}$$

The expended exergy is the sum of the work output of turbine (exergy recovered) and the exergy destruction (exergy wasted),

$$x_{\text{expended}} = x_{\text{recovered}} + x_{\text{dest}} = w_{\text{out}} + x_{\text{dest}} = 666.0 + 79.2 = 745.2 \text{ kJ/kg}$$

The second-law efficiency is the ratio of the recovered to expended exergy,

$$\eta_{\text{II}} = \frac{x_{\text{recovered}}}{x_{\text{expended}}} = \frac{w_{\text{out}}}{x_{\text{expended}}} = \frac{666.0 \text{ kJ/kg}}{745.2 \text{ kJ/kg}} = \mathbf{0.894 \text{ or } 89.4 \text{ percent}}$$

Discussion The second-law efficiency is a measure of thermodynamic perfection. A process that generates no entropy and thus destroys no exergy always has a second-law efficiency of 100 percent.