Chapter 12:

GAS MIXTURES

Introduction: Gas Mixtures

Up 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 non-reacting 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.

Introduction: Gas Mixtures

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 possible (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.

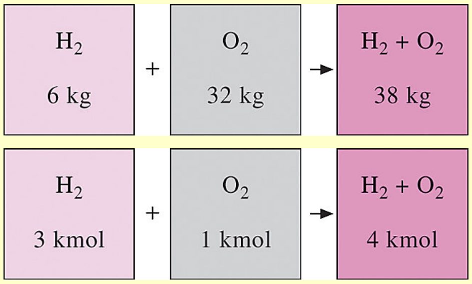
The basic principles involved are also applicable to liquid or solid mixtures, called *solutions*.

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. That is,



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

COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

*Note that: throughout this chapter, the subscript *m* denotes the gas mixture and the subscript *i* denotes any single component of the mixture.

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*:

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

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

$H_2 + O_2$

$y_{H_2} = 0.75$

$y_{O_2} = 0.25$

1.00

The mass and mole number for a given component are related through the molar mass (or molecular weight).

$$m_i = N_i M_i$$

COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

Similarly, we can find the average molar mass for the mixture M_m as:

$$m_m = N_m M_m$$

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

Solving for the average or **apparent molar mass** M_m

$$M_m = \frac{m_m}{N_m} = \sum_{i=1}^{k} \frac{N_i}{N_m} M_i = \sum_{i=1}^{k} y_i M_i \qquad (kg/kmol)$$

The **apparent** (or average) **gas constant** of a mixture is expressed as

$$\boxed{R_m = \frac{R_u}{M_m} \qquad (kJ/kg \cdot K)} \qquad R_u = 8.314 \qquad (kJ/kmol \cdot K)$$

COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

Can you show that R_m is given as

$$R_m = \sum_{i=1}^{k} mf_i R_i$$

To change from a mole fraction analysis to a mass fraction analysis, we can show that

$$mf_i = \frac{y_i M_i}{\sum_{i=1}^{k} y_i M_i}$$

To change from a mass fraction analysis to a mole fraction analysis, we can show that

$$y_i = \frac{mf_i / M_i}{\sum_{i=1}^{k} mf_i / M_i}$$

Example 12-1
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. 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.

	O2	*N2*	*CH4*	*mix*
m				
mf				
M				
N				
y				

3 kg O_2

5 kg N_2

12 kg CH_4

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.

We also mentioned that real gases approximate this behavior closely when they are at a low pressure and 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*.

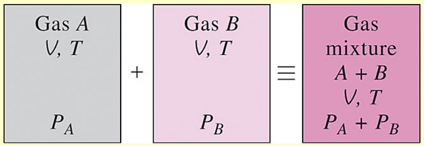
When two or more ideal gases are mixed, the behavior of a molecule normally is not influenced by the presence of other similar or dissimilar molecules, and therefore a nonreacting mixture of ideal gases also behaves as an ideal gas.

Air, for example, is conveniently treated as an ideal gas in the range where nitrogen and oxygen behave as ideal gases.

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

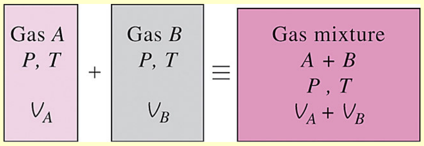
The prediction of the *P-v-T* behavior of gas mixtures is usually based on two models: *Dalton's law of additive pressures* and *Amagat's law of additive volumes*.

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.*



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

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.*



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

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

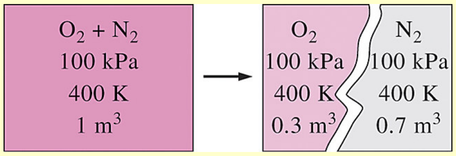
In these relations, P_i is called the **component pressure** and V_i is called the **component volume**.

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

Note that for an ideal-gas mixture, the mole fraction, the pressure fraction, and the volume fraction of a component are identical.

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

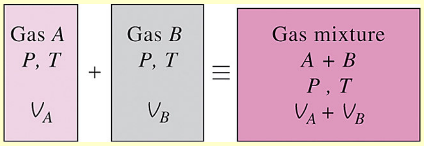
This equation is strictly valid for ideal-gas mixtures since it is derived by assuming ideal-gas behavior for the gas mixture and each of its components.

The quantity y_iP_m is called the **partial pressure** (identical to the *component pressure* for ideal gases), and the quantity y_iV_m is called the **partial volume** (identical to the *component volume* for ideal gases).

Problem 12-30

P-v-T BEHAVIOR OF GAS MIXTURES

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.



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

$$V_m = \frac{N_m R_u T_m}{P_m} = \frac{(18\ \text{kmol})(8.314\ \text{kPa}\cdot\text{m}^3/\text{kmol}\cdot\text{K})(290\ \text{K})}{150\ \text{kPa}} = \mathbf{289.3\ m^3}$$

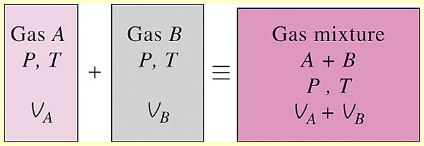
Answer: 289 m^3

Problem 12-32

P-v-T BEHAVIOR OF GAS MIXTURES

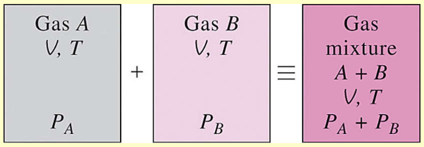
A rigid tank contains 0.5 kmol of Ar and 2 kmol of N_2 at 250 kPa and 280 K. The mixture is now heated to 400 K. Determine the volume of the tank and the final pressure of the mixture.

$$V_m = \frac{N_m R_u T_m}{P_m} = \frac{(2.5\ \text{kmol})(8.314\ \text{kPa}\cdot\text{m}^3/\text{kmol}\cdot\text{K})(280\ \text{K})}{250\ \text{kPa}} = \mathbf{23.3\ m^3}$$



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

$$\frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1} \longrightarrow P_2 = \frac{T_2}{T_1} P_1 = \frac{400\ \text{K}}{280\ \text{K}}(250\ \text{kPa}) = \mathbf{357.1\ kPa}$$



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

Real-Gas Mixtures

NOT CONSIDERED

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.
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*.

Then the total internal energy, enthalpy, and entropy of a gas mixture can be expressed, respectively, as:

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

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

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

PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

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

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

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

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

PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

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:

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

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

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

PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

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

$$C_{v,m} = \sum_{i=1}^{k} mf_i C_{v,i} \quad (\text{kJ/kg}\cdot{}^\circ\text{C}) \qquad \bar{C}_{v,m} = \sum_{i=1}^{k} y_i \bar{C}_{v,i} \quad (\text{kJ/kmol}\cdot{}^\circ\text{C})$$

$$C_{p,m} = \sum_{i=1}^{k} mf_i C_{p,i} \quad (\text{kJ/kg}\cdot{}^\circ\text{C}) \qquad \bar{C}_{p,m} = \sum_{i=1}^{k} y_i \bar{C}_{p,i} \quad (\text{kJ/kmol}\cdot{}^\circ\text{C})$$

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

Ratio of specific heats k is given as:

$$k_m = \frac{C_{p,m}}{C_{v,m}} = \frac{\bar{C}_{p,m}}{\bar{C}_{v,m}}$$

Ideal-Gas Mixtures

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 Pm is the mixture pressure.

Ideal-Gas Mixtures

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:

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

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

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 $P_{m.}$

Example 12-3
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

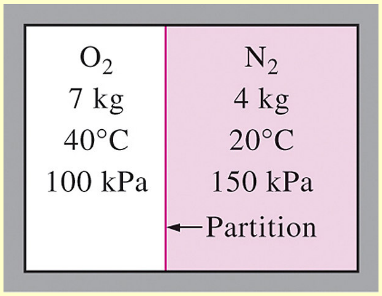
(b) the mixture pressure after equilibrium has been established.

$$P_m V_m = N_m R_u T_m$$

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

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

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



Problem 12-53

PROPERTY OF GAS MIXTURES

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.

$$w_{\text{out}} = h_1 - h_2$$

$$w_{\text{out}} = c_p\left(T_1 - T_2\right)$$

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{(k-1)/k}$$

$$c_{p,m} = \Sigma\, \text{mf}_i c_{p,i} = \frac{y_{\text{He}}M_{\text{He}}}{M_m}c_{p,\text{He}} + \frac{y_{\text{Ar}}M_{\text{Ar}}}{M_m}c_{p,\text{Ar}}$$

$$\text{mf}_i = \frac{m_i}{m_m} = \frac{N_iM_i}{N_mM_m} = \frac{y_iM_i}{M_m}$$

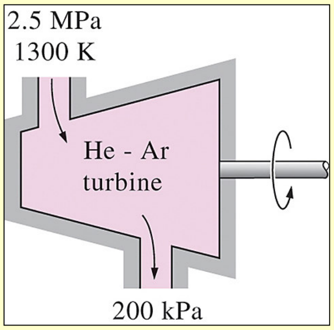
$$M_m = \Sigma\, y_iM_i = y_{\text{He}}M_{\text{He}} + y_{\text{Ar}}M_{\text{Ar}}$$

$k_m = 1.667$ since $k = 1.667$ for both gases.

$= 0.945$ kJ/kg · K

$= 473.2$ K

$=$ **781.3 kJ/kg**

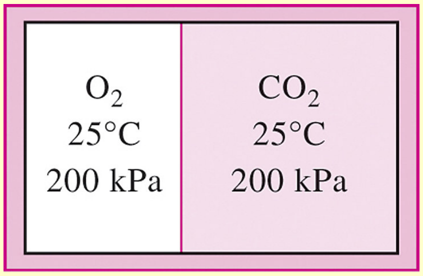


An equimolar mixture means $y_i = 0.5$

Example 12-4

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 O2, and the other compartment contains 5 kmol of CO2. 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.



Real-Gas Mixtures

NOT CONSIDERED