Thermodynamics: An Engineering Approach, 6th Edition
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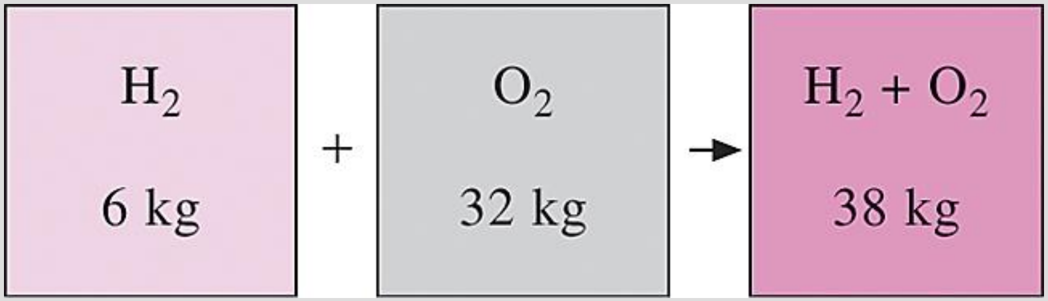
Chapter 13
GAS MIXTURES

Objectives

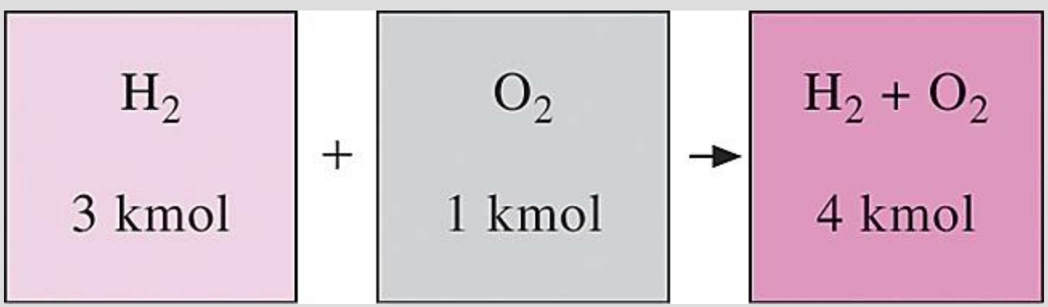
- Develop rules for determining nonreacting gas mixture properties from knowledge of mixture composition and the properties of the individual components.
- Define the quantities used to describe the composition of a mixture, such as mass fraction, mole fraction, and volume fraction.
- Apply the rules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



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

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

$$\mathrm{mf}_i = \frac{m_i}{m_m}$$ Mass fraction

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

Apparent (or average) molar mass

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

$$m = NM$$

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

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

Gas constant

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

The molar mass of a mixture

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

Mass and mole fractions of a mixture are related by

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

$$H_2 + O_2$$

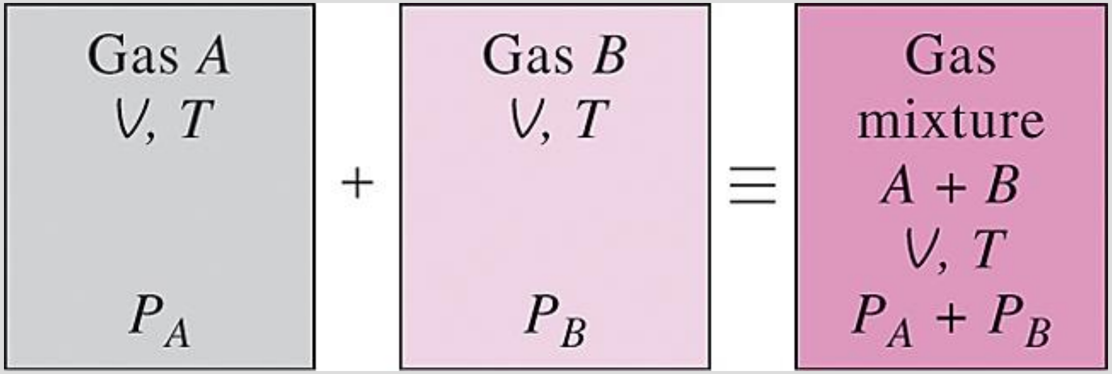
$$y_{H_2} = 0.75$$

$$y_{O_2} = 0.25$$

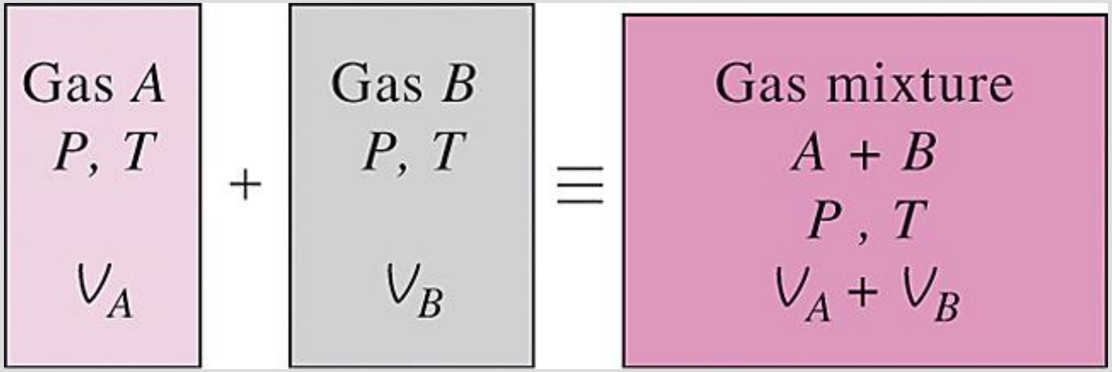
$$\overline{1.00}$$

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.

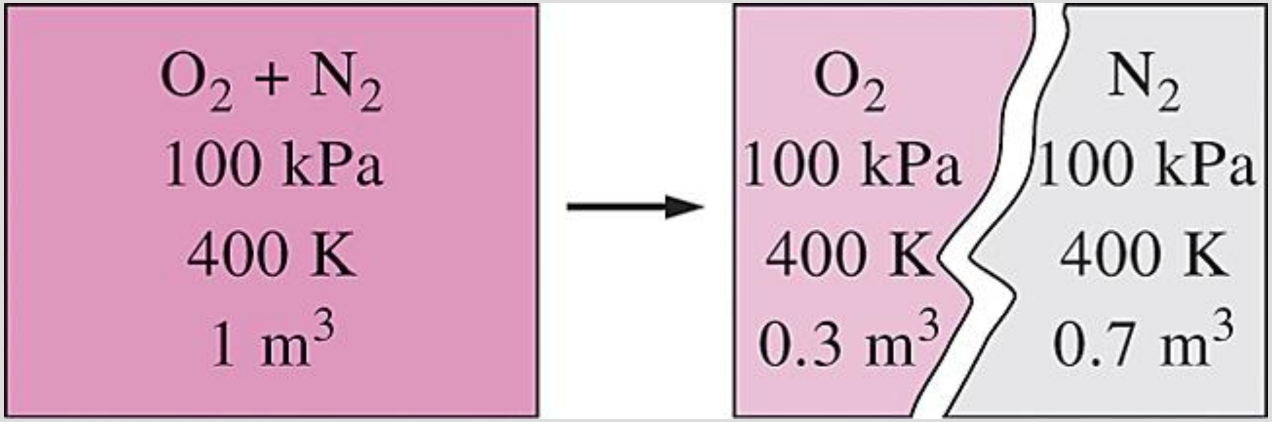
Dalton's law: $P_m = \sum_{i=1}^{k} P_i(T_m, V_m)$

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 Amagad'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

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

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

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

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)

Real-Gas Mixtures

Compressibility factor

$$PV = ZNR_uT$$

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

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.

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.

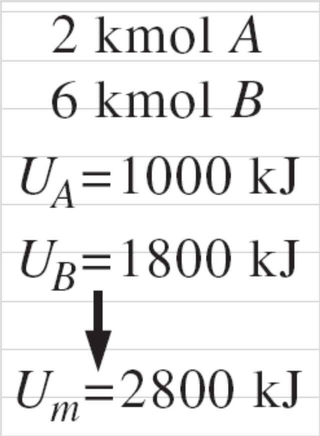
PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

Extensive properties of a gas mixture

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

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

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



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

Changes in properties of a gas mixture

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

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

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

Extensive properties of a gas mixture

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

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

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

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

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

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.

2 kmol A

3 kmol B

$\bar{u}_A = 500$ kJ/kmol

$\bar{u}_B = 600$ kJ/kmol

↓

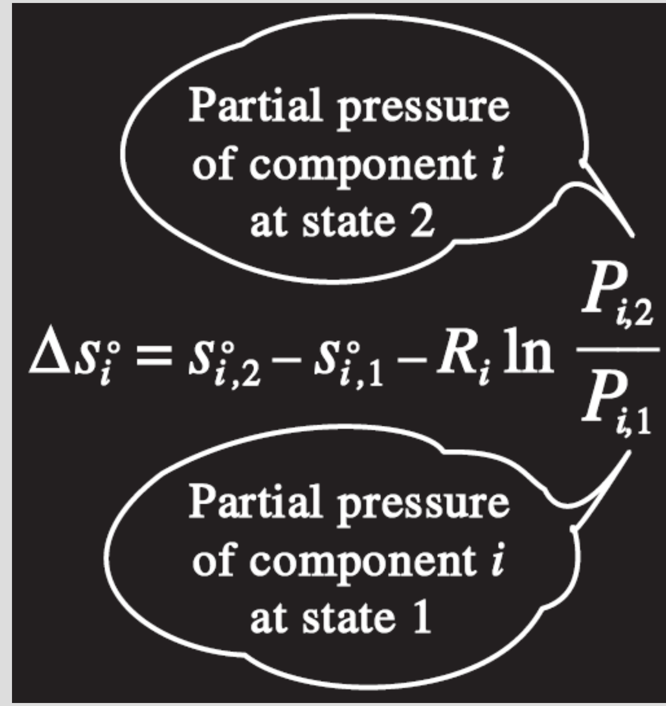
$\bar{u}_m = 560$ kJ/kmol

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

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.



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

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

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

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

Real-Gas Mixtures

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

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

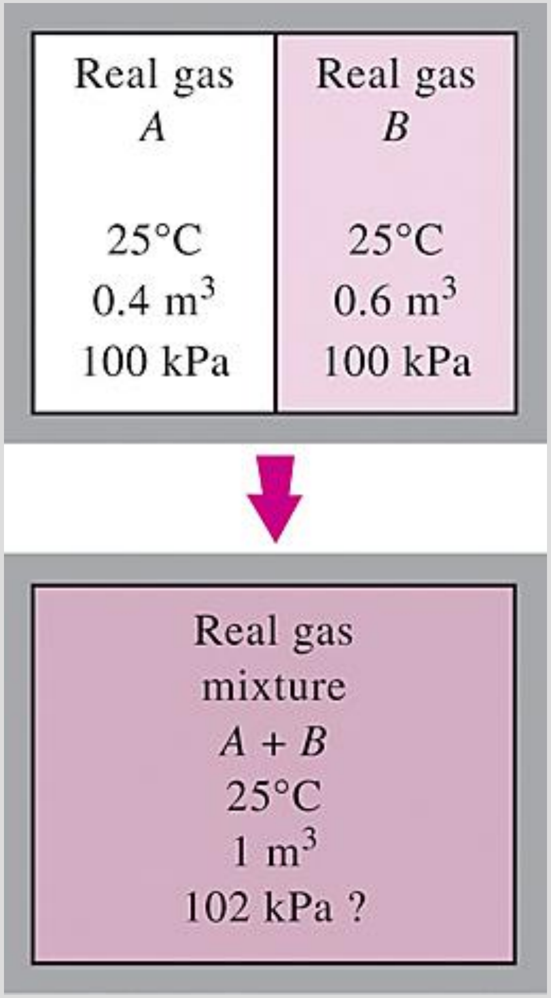
$$\sum \mathrm{mf}_i (dh_i - T_m\, ds_i - v_i\, dP_m) = 0$$

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

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.

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