Chapter 13 GAS MIXTURES

13–1 COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

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.**

$$m_m = \sum_{i=1}^{k} m_i \quad \text{and} \quad N_m = \sum_{i=1}^{k} N_i \qquad \textbf{(13–1}\textit{a, b}\textbf{)}$$

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***:

$$\text{mf}_i = \frac{m_i}{m_m} \quad \text{and} \quad y_i = \frac{N_i}{N_m} \qquad \textbf{(13–2}\textit{a, b}\textbf{)}$$

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

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*. Then the **apparent** (or **average**) **molar mass** and the **gas constant** of a mixture can be expressed as

$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_{i=1}^{k} y_i M_i \quad \text{and} \quad R_m = \frac{R_u}{M_m} \qquad \textbf{(13–3a, b)}$$

$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i / M_i} = \frac{1}{\sum m_i / (m_m M_i)} = \frac{1}{\sum_{i=1}^{k} \frac{\mathrm{mf}_i}{M_i}} \qquad \textbf{(13–4)}$$

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

13–2 *P-v-T* BEHAVIOR OF GAS MIXTURES:

IDEAL AND REAL GASES

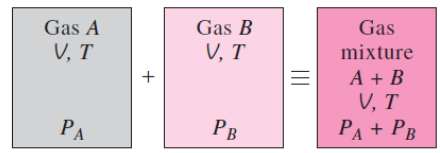

FIGURE 13–5
Dalton's law of additive pressures for a mixture of two ideal gases.

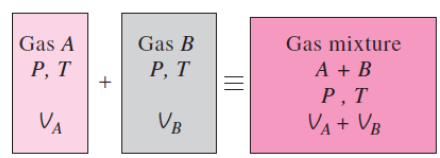

FIGURE 13–6
Amagat's law of additive volumes for a mixture of two ideal gases.

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 - a situation encountered at low densities. We also mentioned that real gases approximate this behavior closely when they are at a low pressure or high temperature relative to their critical-point values.

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*****.** Both models are described and discussed below.

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 (Fig. 13–5).

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 (Fig. 13–6).

Dalton's and Amagat's laws hold exactly for ideal-gas mixtures, but only approximately for real-gas mixtures. For ideal gases, these two laws are identical and give identical results.

Dalton's law:

$$P_m = \sum_{i=1}^{k} P_i(T_m, V_m) \qquad \text{(13–6)}$$

Amagat's law:

$$V_m = \sum_{i=1}^{k} V_i(T_m, P_m) \qquad \text{(13–7)}$$

exact for ideal gases, approximate for real gases

Ideal-Gas Mixtures

For ideal gases, P_i and V_i can be related to y_i by using the ideal-gas relation for both the components and the gas mixture:

$$\frac{P_i}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i \qquad \text{(13–8)}$$

Real-Gas Mixtures

Compressibility factor

$$PV = ZNR_uT \qquad (13\text{–}9)$$

$$Z_m = \sum_{i=1}^{k} y_i Z_i \qquad (13\text{–}10)$$

Where 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. It may seem that using either law gives the same result, but it does not.

The compressibility-factor approach, in general, gives more accurate results when the Z_i's in Eq. 13–10 are evaluated by using Amagat's law instead of Dalton's law. This is because Amagat's law involves the use of mixture pressure *Pm*, which accounts for the influence of intermolecular forces between the molecules of different gases. Dalton's law disregards the influence of dissimilar molecules in a mixture on each other. As a result, it tends to underpredict the pressure of a gas mixture for a given V_m and T_m. Therefore,

Dalton's law is more appropriate for gas mixtures at low pressures.

Amagat's law is more appropriate at high pressures.

Another approach for predicting the *P-v-T* behavior of a gas mixture is to treat the gas mixture as a pseudopure substance (Fig. 13–9). One such method, proposed by W. B. Kay in 1936 and called **Kay's rule,** involves the use of a *pseudocritical pressure* $P_{cr,m}$ and *pseudocritical temperature* $T_{cr,m}$ for the mixture, defined in terms of the critical pressures and temperatures of the mixture components as

$$P'_{cr,m} = \sum_{i=1}^{k} y_i P_{cr,i} \quad \text{and} \quad T'_{cr,m} = \sum_{i=1}^{k} y_i T_{cr,i} \qquad (13\text{–}11a, b)$$

$T_R = T_m / T'_{cr,m}$ $P_R = P_m / P'_{cr,m}$ Appendix D

Another way of treating a gas mixture as a pseudopure substance is to use a more accurate equation of state such as the van der Waals, Beattie–Bridgeman, or Benedict–Webb–Rubin equation for the mixture, and to determine the constant coefficients in terms of the coefficients of the components.

$$a_m = \left(\sum_{i=1}^{k} y_i a_i^{1/2} \right)^2 \quad \text{and} \quad b_m = \sum_{i=1}^{k} y_i b_i \qquad \textbf{(13–12a, b)}$$

13–3 PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

Extensive properties

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

$$U_m = \sum_{i=1}^{k} U_i = \sum_{i=1}^{k} m_i u_i = \sum_{i=1}^{k} N_i \bar{u}_i \qquad (\text{kJ}) \qquad \textbf{(13–13)}$$

$$H_m = \sum_{i=1}^{k} H_i = \sum_{i=1}^{k} m_i h_i = \sum_{i=1}^{k} N_i \bar{h}_i \qquad (\text{kJ}) \qquad \textbf{(13–14)}$$

$$S_m = \sum_{i=1}^{k} S_i = \sum_{i=1}^{k} m_i s_i = \sum_{i=1}^{k} N_i \bar{s}_i \qquad (\text{kJ/K}) \qquad \textbf{(13–15)}$$

$$\Delta U_m = \sum_{i=1}^{k} \Delta U_i = \sum_{i=1}^{k} m_i \, \Delta u_i = \sum_{i=1}^{k} N_i \, \Delta \bar{u}_i \qquad (\text{kJ}) \qquad \textbf{(13–16)}$$

$$\Delta H_m = \sum_{i=1}^{k} \Delta H_i = \sum_{i=1}^{k} m_i \, \Delta h_i = \sum_{i=1}^{k} N_i \, \Delta \bar{h}_i \qquad (\text{kJ}) \qquad \textbf{(13–17)}$$

$$\Delta S_m = \sum_{i=1}^{k} \Delta S_i = \sum_{i=1}^{k} m_i \, \Delta s_i = \sum_{i=1}^{k} N_i \, \Delta \bar{s}_i \qquad (\text{kJ/K}) \qquad \textbf{(13–18)}$$

Intensive properties

$$u_m = \sum_{i=1}^{k} \text{mf}_i u_i \quad (\text{kJ/kg}) \quad \text{and} \quad \bar{u}_m = \sum_{i=1}^{k} y_i \bar{u}_i \quad (\text{kJ/kmol}) \qquad \textbf{(13–19)}$$

$$h_m = \sum_{i=1}^{k} \text{mf}_i h_i \quad (\text{kJ/kg}) \quad \text{and} \quad \bar{h}_m = \sum_{i=1}^{k} y_i \bar{h}_i \quad (\text{kJ/kmol}) \qquad \textbf{(13–20)}$$

$$s_m = \sum_{i=1}^{k} \text{mf}_i s_i \quad (\text{kJ/kg} \cdot \text{K}) \quad \text{and} \quad \bar{s}_m = \sum_{i=1}^{k} y_i \bar{s}_i \quad (\text{kJ/kmol} \cdot \text{K}) \qquad \textbf{(13–21)}$$

$$c_{v,m} = \sum_{i=1}^{k} \text{mf}_i c_{v,i} \quad (\text{kJ/kg} \cdot \text{K}) \quad \text{and} \quad \bar{c}_{v,m} = \sum_{i=1}^{k} y_i \bar{c}_{v,i} \quad (\text{kJ/kmol} \cdot \text{K}) \qquad \textbf{(13–22)}$$

$$c_{p,m} = \sum_{i=1}^{k} \text{mf}_i c_{p,i} \quad (\text{kJ/kg} \cdot \text{K}) \quad \text{and} \quad \bar{c}_{p,m} = \sum_{i=1}^{k} y_i \bar{c}_{p,i} \quad (\text{kJ/kmol} \cdot \text{K}) \qquad \textbf{(13–23)}$$

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

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. 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 P_m is the mixture pressure.

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

$$\Delta s_i = s^\circ_{i,2} - s^\circ_{i,1} - R_i \ln \frac{P_{i,2}}{P_{i,1}} \cong c_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_i \ln \frac{P_{i,2}}{P_{i,1}} \qquad \textbf{(13–24)}$$

or

$$\Delta \bar{s}_i = \bar{s}^\circ_{i,2} - \bar{s}^\circ_{i,1} - R_u \ln \frac{P_{i,2}}{P_{i,1}} \cong \bar{c}_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_u \ln \frac{P_{i,2}}{P_{i,1}} \qquad \textbf{(13–25)}$$

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.

Real-Gas Mixtures

$$dh_i = T_m \, ds_i + v_i \, dP_m \qquad \textbf{(13–26)}$$

This is an important result because Eq. 13–26 is the starting equation in the development of the generalized relations and charts for enthalpy and entropy.

It suggests that the generalized property relations and charts for real gases developed in Chapter 12 can also be used for the components of real-gas mixtures. But the reduced temperature T_R and reduced pressure P_R for each component should be evaluated by using the mixture temperature T_m and mixture pressure P_m. This is because Eq. 13–26 involves the mixture pressure Pm, not the component pressure P_i.

The approach described above is somewhat analogous to Amagat's law of additive volumes (evaluating mixture properties at the mixture pressure and temperature), which holds exactly for ideal-gas mixtures and approximately for real-gas mixtures. Therefore, the mixture properties determined with this approach are not exact, but they are sufficiently accurate.

What if the mixture volume and temperature are specified instead of the mixture pressure and temperature? Well, there is no need to panic. Just evaluate the mixture pressure, using Dalton's law of additive pressures, and then use this value (which is only approximate) as the mixture pressure.

Another way of evaluating the properties of a real-gas mixture 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. The approach is quite simple, and the accuracy is usually acceptable.