Chapter 6

Nonreactive gas mixture

6.1 Introduction:

The thermodynamic behavior of a mixture of gases depends upon the individual properties and the amounts of its constituent gases. Because substances in the gaseous phase are so miscible with each other, there is no limit to the number of different gaseous mixture that can be formed. From a given set of components, and a wide variation is therefore possible in the properties of gaseous mixtures.

A homogenous mixture is frequently treated as if it considered a single component rather than many. Properties of the individual constitutes of an inert gas tend to be submerged so that the gas behaves, in certain way, as though it were a single pure substance.

6.2 Mixture of ideal gases:

Consider a mixture of ideal gases a, b, c, …… , existing in equilibrium at a pressure $p$, and occupying a volume $V$, as shown in figure 1. Each constituent occupies the same volume $V$ that the entire mixture occupies, and each constituent is at the same temperature as the mixture. The total mass of the mixture is equal to the masses of the individual gases, or

$m = m_a + m_b + m_c + \cdots = \sum_i m_i$

Similarly, the number of moles of the mixture is the sum of the moles of the individual components:
According to Dalton’s model, the total pressure of the mixture of ideal gases is equal to the sum of the partial pressures of the constituents. The partial pressure of a gas in the mixture is the pressure that would exert if it alone occupied the whole volume of the mixture at the same temperature. Dalton models can be written as:

\[ p = p_a + p_b + p_c + \cdots = \sum_i (p_i)_{v,T} \]  

Suppose it were possible to separate a gases a, b, c, ..., and to have each constituent at the pressure and temperature of the mixture, as shown in figure 1(b). According to Amagat’s model, the sum of the partial volumes of the constituents would be equal to the total volume, or

\[ V = V_a + V_b + V_c + \cdots = \sum_i (V_i)_{p,T} \]  

<table>
<thead>
<tr>
<th>Constituent s</th>
<th>Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>a: ( m_a, p_a, V, T )</td>
<td>( m, p, V, T )</td>
</tr>
<tr>
<td>b: ( m_b, p_b, V, T )</td>
<td></td>
</tr>
<tr>
<td>c: ( m_c, p_c, V, T )</td>
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<table>
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<tr>
<th>Gas a</th>
<th>Gas b</th>
<th>Gas c</th>
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<tbody>
<tr>
<td>( m_a )</td>
<td>( m_b )</td>
<td>( m_c )</td>
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<tr>
<td>( p )</td>
<td>( p )</td>
<td>( p )</td>
</tr>
<tr>
<td>( V_a )</td>
<td>( V_b )</td>
<td>( V_c )</td>
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<td>( T )</td>
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Figure 1 (a) Dalton’s law (b) Amaga’s law
These models assume that no intermolecular forces exist in a mixture of gases and that each constituent act as if no other constituents were present. Both models are exact for ideal gases but approximate for real gases.

When the mixture is analyzed from the standpoint of Dalton’s model, the ideal gas equation can be applied individually to each constituent:

\[ p_a V = n_a \tilde{R}T \]
\[ p_b V = n_b \tilde{R}T \]
\[ p_c V = n_c \tilde{R}T \]

And so on adding the preceding equation gives

\[ (p_a + p_b + p_c + \cdots) V = (n_a + n_b + n_c + \cdots) \tilde{R}T \]

or \( pV = n\tilde{R}T \)

This equation of state has the same form as the equation of state of a single component ideal gas so that a mixture of ideal gases also act like an ideal gas. When the equation of state of each constituent gas is divided by the mixture equation of state, the following expression of the partial pressure obtained:

\[ p_a = \frac{n_a}{n} p = x_ap \]
\[ p_b = \frac{n_b}{n} p = x_bp \]
\[ p_c = \frac{n_c}{n} p = x_cp \]

and so on. Therefore in general, for the \(i\)th component, the partial pressure \(p\) is

\[ p_i = x_ip \quad (3) \]
Where $x_i$ is the mole fraction or (molar concentration) of constituent $i$, and is defined as the ratio of the number of moles of that constituent to the total number of moles in the mixture:

$$x_i = \frac{n_i}{\sum_i n_i} = \frac{n_i}{n} \quad (4)$$

The mole fraction of all the components in the gas mixture then must added up to unity:

$$x_a + x_b + x_c + \cdots = \sum_i x_i = 1 \quad (5)$$

According to equation (3), the ratio of the partial pressure of any constituent to the total pressure is equal the mole fraction of that constituent. Since each constituent occupies the same volume and has the same temperature as the mixture if follows that:

$$\frac{p_a}{n_a} = \frac{p_b}{n_b} = \frac{p_c}{n_c} = \cdots = \frac{p_i}{n_i} = \frac{p}{n} \quad (6)$$

When the mixture is analyzed from the standpoint of Amagat’s model, the ideal gas law leads to

$$pV_a = n_a\bar{R}T$$

$$pV_b = n_b\bar{R}T$$

$$pV_c = n_c\bar{R}T$$

and so on adding the preceding equation gives

$$p(V_a + V_b + V_c + \cdots) = (n_a + n_b + n_c + \cdots)\bar{R}T$$
by dividing the ideal gas equation for each constituent by the equation for the entire mixture obtained:

\[ \frac{V_a}{V} = \frac{n_a}{n} \text{ or } V_a = x_a V \]

and in general for the \( i \)th component, the partial volume \( V_i \) is

\[ V_{ai} = x_i V \quad (7) \]

The ratio of partial volume of any constituent to the total volume, then, is equal to the mole fraction of that constituent. Since the partial volume of the constituents are at the same temperature and total pressure, it is follows that

\[ \frac{V_a}{n_a} = \frac{V_b}{n_b} = \frac{V_c}{n_c} = \ldots = \frac{V_i}{n_i} = \frac{V}{n} \quad (8) \]

It can be concluded, from (6) and (7), that the mole fraction of each constituent in a mixture of ideal gases is the same as it volume fraction and also the ratio of its partial pressure to its total pressure:

\[ x_i = \frac{n_i}{n} = \frac{V_i}{V} = \frac{p_i}{p} \quad (9) \]

In the equation of state of a gas mixture, the gas constant involving molar mass appears. The value of this constant is determined as follows:

The ideal gas law of the mixture is

\[ pV = nRT \quad (10) \]

Whereas for each constituent it is

\[ p_a V = m_a R_a T \]
\[ p_b V = m_b R_b T \]
\[ p_c V = m_c R_c T \]

Since \( p = p_a + p_b + p_c + \cdots \),
\[ pV = (m_a R_a + m_b R_b + m_c R_c + \cdots)T \]

By combining this equation with equation (10):
\[ R = \frac{m_a}{m} R_a + \frac{m_b}{m} R_b + \frac{m_c}{m} R_c + \cdots = \sum_i \frac{m_i R_i}{m} \]  \hspace{1cm} (11)

To determine the molar mass of the mixture, the total mass of the mixture is divided by the total number of moles present in the mixture
\[ M = \frac{\sum_i m_i}{\sum_i n_i} = \frac{\sum_i m_i}{\sum_i \frac{m_i}{M_i}} = \frac{\sum_i (nM)_i}{\sum_i n_i} \]  \hspace{1cm} (12)

The mass of the constituent is equal to the number of moles of that constituent multiplied by its molar mass. Therefore, the masses of the individual component of the mixture are
\[ m_a = n_a M_a \]
\[ m_b = n_b M_b \]
\[ m_c = n_c M_c \]

Adding the preceding equation yields
\[ m_a + m_b + m_c + \cdots = m = n_a M_a + n_b M_b + n_c M_c + \cdots \]

But the total mass of the mixture, \( m \) is equal to
\[ m = m_a + m_b + m_c + \cdots = nM \]
Where \( n \) and \( M \) are the total number of moles and the molar mass of the mixture.

The molar mass of the mixture is then obtained as:

\[
M = \frac{n_a}{n} M_a + \frac{n_b}{n} M_b + \frac{n_c}{n} M_c + \cdots
\]

or

\[
M = x_a M_a + x_b M_b + x_c M_c + \cdots = \sum_i x_i M_i
\]

Which express \( M \) in term of mole fraction.

### 6.3 Internal Energy, Enthalpy, Specific Heats, and Entropy

According to the Gibbs-Dalton law, an extensive property of a mixture of ideal gases is the sum of the contributions of the individual constituents. Properties of a mixture can be expressed on either a mass or a mole basis and refer to as per kg or per kg-mol, respectively. Expressions for some of the extensive properties are presented here on a mass basis. The internal energy per unit mass of a mixture is given by

\[
u = \frac{m_a}{\Sigma_i m_i} u_a + \frac{m_b}{\Sigma_i m_i} u_b + \frac{m_c}{\Sigma_i m_i} u_c + \cdots
\]

\[
= \frac{\Sigma_i m_i u_i}{\Sigma_i m_i}
\]

(14)

It was shown previously that

\[
pV = (m_a R_a + m_b R_b + m_c R_c + \cdots)T
\]

Dividing both sides by \( \Sigma_i m_i \) and substituting \( p_i v_i \) for \( R_i T \) gives
\[ pv = \frac{m_a}{\sum_i m_i} (p_a v_a) + \frac{m_b}{\sum_i m_i} (p_b v_b) + \frac{m_c}{\sum_i m_i} (p_c v_c) + \ldots \]

By adding the foregoing equation with equation (14), the expression of enthalpy per unit mass is obtained:

\[ h = \frac{m_a}{\sum_i m_i} h_a + \frac{m_b}{\sum_i m_i} h_b + \frac{m_c}{\sum_i m_i} h_c + \ldots \]

\[ = \frac{\sum_i m_i h_i}{\sum_i m_i} \quad (15) \]

By differentiating the internal energy, equation (14), and the enthalpy, equation (15), with respect to \( T \), the specific heat values are obtained for mixture :

\[ c_v = \frac{m_a}{\sum_i m_i} c_{v_a} + \frac{m_b}{\sum_i m_i} c_{v_b} + \frac{m_c}{\sum_i m_i} c_{v_c} + \ldots \]

\[ = \frac{\sum_i m_i c_{v_i}}{\sum_i m_i} \quad (16) \]

\[ c_p = \frac{m_a}{\sum_i m_i} c_{p_a} + \frac{m_b}{\sum_i m_i} c_{p_b} + \frac{m_c}{\sum_i m_i} c_{p_c} + \ldots \]

\[ = \frac{\sum_i m_i c_{p_i}}{\sum_i m_i} \quad (17) \]

Similarly the entropy of the mixture per unit mass is

\[ s = \frac{m_a}{\sum_i m_i} s_a + \frac{m_b}{\sum_i m_i} s_b + \frac{m_c}{\sum_i m_i} s_c + \ldots \]

\[ = \frac{\sum_i m_i s_i}{\sum_i m_i} \quad (18) \]