

Chapter One

Mixtures of ideal gases

* 1. Introduction

- Any equation that relates
 - ✓ The pressure P
 - ✓ The temperature T , and
 - ✓ The specific volume v of a substance is called an equation of state
- An ideal or perfect gas is one which strictly obeys all the gas laws under given conditions of temperature and pressure.

1.1 The characteristic gas equation

- The physical properties of a gas is governed by
 - ✓ The pressure P exerted by the gas
 - ✓ The volume v occupied by the gas, and
 - ✓ The temperature T
- The behavior of an ideal gas undergoing any change in the above conditions is governed by such laws as:
 1. Boyles law, and
 2. Charles law

- Boyles law states that:

- The volume of a given mass of a gas varies inversely as its absolute pressure provided that the temperature remains constant. That is when T is constant

$$v \sim 1/P \quad \dots\dots\dots (1.1)$$

OR

- The pressure of the gas is inversely proportional to the volume

- Charles law which states that:

- The volume of a given mass of a gas varies directly as its absolute temperature provided the pressure is kept constant. i.e. when P is constant

$$v \sim T \quad \dots\dots\dots (1.2)$$

- However, in engineering practice, volume, pressure and temperature of a system all vary simultaneously.
- Thus, by combining these two laws (i.e. Boles and Charles law) a more general equation for a mass of gas undergoing changes in volume, pressure & temperature Can be obtained.
- When both temperature T & pressure P varies, the volume of a gas varies directly with temperature & inversely with pressure. i.e.

$$v \sim T/P \dots\dots\dots (1.3)$$

*Introducing the proportionality constant R equation (1.3) can be written as:

$$v = RT/P \dots\dots\dots (1.4)$$

- The constant of proportionality R is called the characteristic gas constant or simply the gas constant

Equation 1.4 can be written as:

$$Pv = RT \dots\dots\dots (1.5)$$

- Where
- P is the absolute pressure of gas in N/m²
 - T is the absolute temperature of gas in K
 - v is the specific volume in m³/kg

*Note that: Equation (1.5) is called the characteristics gas equation or the ideal gas equation of state or simply the ideal gas relation and a gas that obeys this relation is called an ideal gas.

- * For a given mass m of a particular gas equation (1.5) can also be written as:

$$PV = mRT \dots\dots\dots(1.6)$$

How?

1.2 The universal gas constant, R_u

- * The product of the **gas constant R** and the **molecular weight M** (also called the molar mass) of the gas is constant known as the **universal gas constant**. i.e

$$R_u = MR \dots\dots\dots(1.7)$$

Thus, R_u is the same for all substances & its value is $8.314 \text{ kJ/kmol}^\circ\text{K}$

- * Thus, the gas constant R for any gas can therefore be determined from equation (1.7)

$$R = R_u/M \dots\dots\dots(1.8)$$

- * Note that: The gas constant is d/t for each gas

* 1.3 Avogadro's Law

* Avogadro's law states that **equal volume** of all gases contain the **same number of moles** at the same **pressure** and **temperature**.

➤ From this it follows that **proportions by number of moles** are also **proportional by volume**. **How?**

* Consider two gases A and B with $P_a = P_b = P$ and $T_a = T_b = T$ from the characteristic gas equation (1.6)

$$PV_a = m_a R_a T \text{ and } PV_b = m_b R_b T$$

If $V_a = V_b = V$, then

$$PV = m_a R_a T \quad \& \quad PV = m_b R_b T, \text{ combining them}$$

$$m_a R_a = m_b R_b \dots\dots\dots (a)$$

But from the number of moles relation, i.e.

$$n_a = m_a / M_a$$

$$m_a = n_a M_a, \text{ similarly } m_b = n_b M_b \dots\dots\dots (b)$$

*Thus, substituting equation (b) in to (a), we obtain

$$n_a M_a R_a = n_b M_b R_b \dots\dots\dots (c)$$

But $M_a R_a = M_b R_b = R_u$

Thus equation (c) becomes

$$n_a R_u = n_b R_u$$

$$n_a = n_b$$

Hence, $n_a/n_b = v_a/v_b$ How? Assignment

*Therefore, we can say that, if there are twice the number of moles present for gas A as there are for gas B, then gas A will have twice the volume of gas B at the same pressure and temperature

* 1.4 Gravimetric analysis

1.4.1 Composition of a gas mixture: Mass & mole fraction

- * To determine the properties of a mixture, we need to know
 - * The composition of a 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** or **mass analysis**
- * Gravimetric analysis ξ (epsilon) of a mixture of gas gives the **percentage or fraction** by **mass** of each constituent in the mixture.
- * The gravimetric or mass analysis of a mixture of gases A, B & C, with masses m_a , m_b & m_c , respectively are given by:

$$\xi_a = m_a / (m_a + m_b + m_c) = m_a / m_m$$

$$\xi_b = m_b / (m_a + m_b + m_c) = m_b / m_m$$

$$\xi_c = m_c / (m_a + m_b + m_c) = m_c / m_m \dots\dots\dots(1.9)$$

Where m_m is the mass of the mixture = $m_a + m_b + m_c$

- * In a more general form, 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 (Figs. 1 and 2). That is,

$$m_m = \sum_{i=1}^k m_i \quad \text{and} \quad N_m = \sum_{i=1}^k N_i \quad \text{..... (1.10a and b)}$$

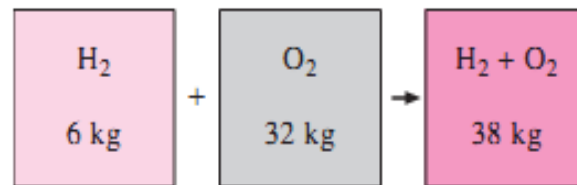


FIGURE 1: The mass of a mixture is equal to the sum of the masses of its components.

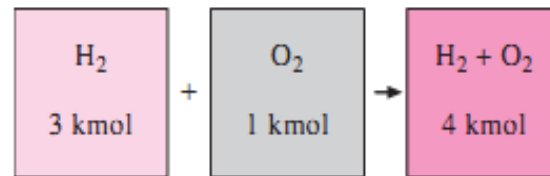


FIGURE 2: The number of moles of a non reacting mixture is equal to the sum of the number of moles of its components.

Where 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

* 1

$$mf_i = \frac{m_i}{m_m} \quad \text{and} \quad y_i = \frac{N_i}{N_m} \quad \dots\dots\dots (1.11a, b)$$

* Thus we can say that the sum of the mass fractions or mole fractions

for $\sum_{i=1}^k mf_i = 1$ and $\sum_{i=1}^k y_i = 1$.e.

How?

- Just dividing equation (1.10a) by m_m or equation (1.10b) by N_m would give us unity

* The mass of a substance can be expressed in terms of

- * The mole number N and
- * The molar mass M of the substance as:

$$m = NM \quad \dots\dots\dots(1.12)$$

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

$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_{i=1}^k y_i M_i \quad \text{and} \quad R_m = \frac{R_u}{M_m} \quad \dots\dots\dots(1.13a, b)$$

$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i / M_i} = \frac{1}{\sum m_i / (m_m M_i)} = \frac{1}{\sum_{i=1}^k \frac{mf_i}{M_i}} \quad \dots\dots\dots(1.14)$$

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

$$mf_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m} \quad \dots\dots\dots(1.15)$$

* These three quantities are related by

* 1.5 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.
- * Amagat's leduc law states that:
 - * 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 (as shown in figure 3).

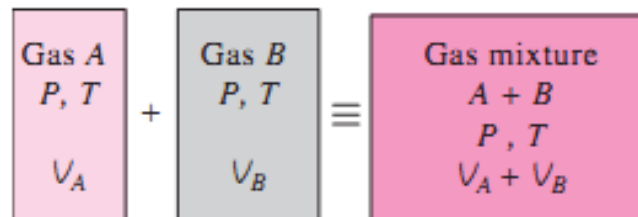


FIGURE 3: Amagat's law of additive volumes for a mixture of two ideal gases

- * Dalton's law of additive pressures: states that
 - * 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. 4).

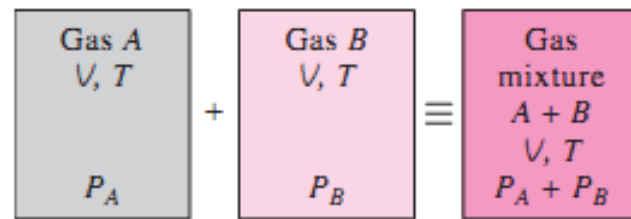


FIGURE 4: Dalton's law of additive pressures for a mixture of two ideal gases

- * Dalton's and Amagat's laws hold exactly for ideal-gas mixtures, but only approximately for real-gas mixtures.
- * This is due to intermolecular forces that may be significant for real gases at high densities.

* *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

.....1.16a,
b

In these relations:

P_i is called the component pressure and

V_i is called the component volume (see figure 5 below).

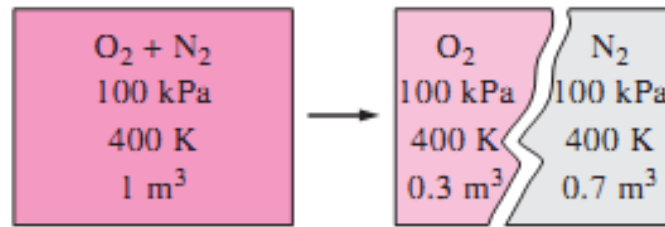


FIGURE 5: The volume a component would occupy if it existed alone at the mixture T and P is called the component volume (for ideal gases, it is equal to the partial volume $y_i V_m$).

- * In addition, 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 .
- * For ideal gases P_i & V_i can be related to y_i by using the ideal-gas relation for both the components and the gas:

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

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

$$\frac{P_i}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i \quad \dots\dots\dots (1.17)$$

- * Therefore

- * Equation 1.17 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 $y_i \cdot P_m$ is called the partial pressure (identical to the component pressure for ideal gases), and
- * the quantity $y_i \cdot V_m$ 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.

Examples

1. Somebody claims that the mass and mole fractions for a mixture of CO_2 and N_2O gases are identical. Is this true? Why?

Solution

- * Yes, because both CO_2 and N_2O has the same molar mass, $M = 44 \text{ kg/kmol}$.
2. Consider a mixture of two gases A and B . Show that when the mass fractions mf_A and mf_B are known, the mole fractions can be determined from

$$y_A = \frac{M_B}{M_A(1/\text{mf}_A - 1) + M_B} \quad \text{and} \quad y_B = 1 - y_A$$

where M_A and M_B are the molar masses of A and B .

Solutions

*

Analysis The mass fractions of A and B are expressed as

$$\text{mf}_A = \frac{m_A}{m_m} = \frac{N_A M_A}{N_m M_m} = y_A \frac{M_A}{M_m} \quad \text{and} \quad \text{mf}_B = y_B \frac{M_B}{M_m}$$

Where m is mass, M is the molar mass, N is the number of moles, and y is the mole fraction. The apparent molar mass of the mixture is

$$M_m = \frac{m_m}{N_m} = \frac{N_A M_A + N_B M_B}{N_m} = y_A M_A + y_B M_B$$

Combining the two equations above and noting that $y_A + y_B = 1$ gives the following convenient relations for converting mass fractions to mole fractions,

$$y_A = \frac{M_B}{M_A (1 / \text{mf}_A - 1) + M_B} \quad \text{and} \quad y_B = 1 - y_A$$

which are the desired relations.

3. A gas mixture consists of 5 kg of O₂, 8 kg of N₂, and 10 kg of CO₂. 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.

Solution

* The molar masses of O₂, N₂, and CO₂ are 32.0, 28.0 and 44.0 kg/kmol, respectively (Table A-1)

(a) The total mass of the mixture is

$$m_m = m_{\text{O}_2} + m_{\text{N}_2} + m_{\text{CO}_2} = 5 \text{ kg} + 8 \text{ kg} + 10 \text{ kg} = 23 \text{ kg}$$

Then the mass fraction of each component becomes

$$\text{mf}_{\text{O}_2} = \frac{m_{\text{O}_2}}{m_m} = \frac{5 \text{ kg}}{23 \text{ kg}} = 0.217$$

$$\text{mf}_{\text{N}_2} = \frac{m_{\text{N}_2}}{m_m} = \frac{8 \text{ kg}}{23 \text{ kg}} = 0.348$$

$$\text{mf}_{\text{CO}_2} = \frac{m_{\text{CO}_2}}{m_m} = \frac{10 \text{ kg}}{23 \text{ kg}} = 0.435$$

5 kg O₂
8 kg N₂
10 kg CO₂

(b) To find the mole fractions, we need to determine the mole numbers of each component first,

$$N_{\text{O}_2} = \frac{m_{\text{O}_2}}{M_{\text{O}_2}} = \frac{5 \text{ kg}}{32 \text{ kg/kmol}} = 0.156 \text{ kmol}$$

$$N_{\text{N}_2} = \frac{m_{\text{N}_2}}{M_{\text{N}_2}} = \frac{8 \text{ kg}}{28 \text{ kg/kmol}} = 0.286 \text{ kmol}$$

$$N_{\text{CO}_2} = \frac{m_{\text{CO}_2}}{M_{\text{CO}_2}} = \frac{10 \text{ kg}}{44 \text{ kg/kmol}} = 0.227 \text{ kmol}$$

Thus

$$N_m = N_{\text{O}_2} + N_{\text{N}_2} + N_{\text{CO}_2} = 0.156 \text{ kmol} + 0.286 \text{ kmol} + 0.227 \text{ kmol} = 0.669 \text{ kmol}$$

$$y_{\text{O}_2} = \frac{N_{\text{O}_2}}{N_m} = \frac{0.156 \text{ kmol}}{0.669 \text{ kmol}} = \mathbf{0.233}$$

$$y_{\text{N}_2} = \frac{N_{\text{N}_2}}{N_m} = \frac{0.286 \text{ kmol}}{0.669 \text{ kmol}} = \mathbf{0.428}$$

$$y_{\text{CO}_2} = \frac{N_{\text{CO}_2}}{N_m} = \frac{0.227 \text{ kmol}}{0.669 \text{ kmol}} = \mathbf{0.339}$$

(c) The average molar mass and gas constant of the mixture are determined from their definitions:

$$M_m = \frac{m_m}{N_m} = \frac{23 \text{ kg}}{0.669 \text{ kmol}} = 34.4 \text{ kg/kmol}$$

and

$$R_m = \frac{R_u}{M_m} = \frac{8.314 \text{ kJ/kmol} \cdot \text{K}}{34.4 \text{ kg/kmol}} = 0.242 \text{ kJ/kg} \cdot \text{K}$$

4. Determine the mole fractions of a gas mixture that consists of 75 percent CH₄ and 25 percent CO₂ by mass. Also, determine the gas constant of the mixture.

Solutions

* The molar masses of CH₄, and CO₂ are 16.0 and 44.0 kg/kmol, respectively (Table A-1)

* **Analysis** For convenience, consider 100 kg of the mixture. Then the number of moles of each component and the total number of moles are

$$m_{\text{CH}_4} = 75 \text{ kg} \longrightarrow N_{\text{CH}_4} = \frac{m_{\text{CH}_4}}{M_{\text{CH}_4}} = \frac{75 \text{ kg}}{16 \text{ kg/kmol}} = 4.688 \text{ kmol}$$

$$m_{\text{CO}_2} = 25 \text{ kg} \longrightarrow N_{\text{CO}_2} = \frac{m_{\text{CO}_2}}{M_{\text{CO}_2}} = \frac{25 \text{ kg}}{44 \text{ kg/kmol}} = 0.568 \text{ kmol}$$

$$N_m = N_{\text{CH}_4} + N_{\text{CO}_2} = 4.688 \text{ kmol} + 0.568 \text{ kmol} = 5.256 \text{ kmol}$$

- * The molar mass and the gas constant of the mixture are determined from their definitions,

5. A gas mixture consists of 8 kmol of H_2 and 2 kmol of N_2 . Determine the mass of each gas and the apparent gas constant of the mixture.

Solutions

Answers: 16 kg, 56 kg, 1.155 kJ/kg · K

*Cont..

Example 2 .A gas mixture at 300 K and 200 kPa consists of 1 kg of CO_2 and 3 kg of CH_4 Determine the partial pressure of each gas and the apparent molar mass of the gas mixture.

* ***Assumptions Under specified conditions both CO_2 and CH_4 can be treated as ideal gases, and the mixture as an ideal gas mixture.***

* ***Properties The molar masses of CO_2 and CH_4 are 44.0 and 16.0 kg/kmol, respectively (Table A-1)***

* ***Analysis The mole numbers of the constituents are***

$$m_{\text{CO}_2} = 1 \text{ kg} \longrightarrow N_{\text{CO}_2} = \frac{m_{\text{CO}_2}}{M_{\text{CO}_2}} = \frac{1 \text{ kg}}{44 \text{ kg/kmol}} = 0.0227 \text{ kmol}$$

$$m_{\text{CH}_4} = 3 \text{ kg} \longrightarrow N_{\text{CH}_4} = \frac{m_{\text{CH}_4}}{M_{\text{CH}_4}} = \frac{3 \text{ kg}}{16 \text{ kg/kmol}} = 0.1875 \text{ kmol}$$

$$N_m = N_{\text{CO}_2} + N_{\text{CH}_4} = 0.0227 \text{ kmol} + 0.1875 \text{ kmol} = 0.2102 \text{ kmol}$$

$$y_{\text{CO}_2} = \frac{N_{\text{CO}_2}}{N_m} = \frac{0.0227 \text{ kmol}}{0.2102 \text{ kmol}} = 0.108$$

$$y_{\text{CH}_4} = \frac{N_{\text{CH}_4}}{N_m} = \frac{0.1875 \text{ kmol}}{0.2102 \text{ kmol}} = 0.892$$

1 kg CO₂
3 kg CH₄

300 K
200 kPa

*Cont..

Then the partial pressures become

$$P_{\text{CO}_2} = y_{\text{CO}_2} P_m = (0.108)(200 \text{ kPa}) = \mathbf{21.6 \text{ kPa}}$$

$$P_{\text{CH}_4} = y_{\text{CH}_4} P_m = (0.892)(200 \text{ kPa}) = \mathbf{178.4 \text{ kPa}}$$

The apparent molar mass of the mixture is

$$M_m = \frac{m_m}{N_m} = \frac{4 \text{ kg}}{0.2102 \text{ kmol}} = \mathbf{19.03 \text{ kg / kmol}}$$