

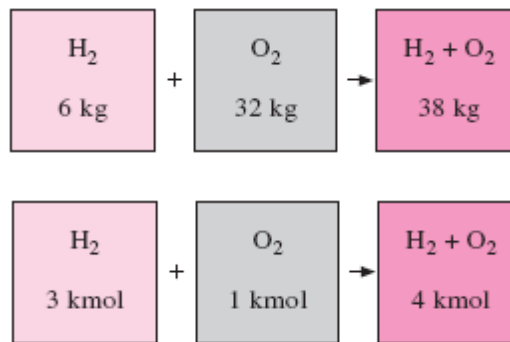
7. Gas Mixtures

A pure substance is defined as a substance having a constant and uniform chemical composition, and this definition can be extended to include a homogeneous mixture of gases when there is no chemical reaction taking place. The thermodynamic properties of a mixture of gases can be determined in the same way as for a single gas.

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:



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

The ratio of the mass of a component to the mass of the mixture is called the mass fraction mf :

$$mf_i = \frac{m_i}{m_m} \dots\dots\dots (7.1)$$

The ratio of the mole number of a component to the mole number of the mixture is called the mole fraction y :

$$y_i = \frac{N_i}{N_m} \dots\dots\dots (7.2)$$

Divide equations (8.1) by m_m and divide equation (8.2) and N_m respectively. It can easily show that the sum of the mass fractions or mole fractions for a mixture is equal to 1.

| |
|---------------------------------|
| H ₂ + O ₂ |
| $y_{H_2} = 0.75$ |
| $y_{O_2} = \frac{0.25}{1.00}$ |

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

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** (**molecular weight**) of a mixture can be expressed as

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

$$\text{Or; } M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i / M_i} = \frac{1}{\sum_{i=1}^k \frac{mf_i}{M_i}}$$

And the **gas constant** of a mixture as

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

Mass and mole fractions of a mixture are related by;

$$mf_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \cdot \frac{M_i}{M_m}$$

Example (7.1) Consider a gas mixture that consists of 3 kg of O_2 , 5 kg of N_2 , and 12 kg of CH_4 . 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:

(a) The total mass of the mixture is:

$$m_m = m_{O_2} + m_{N_2} + m_{CH_4} = 3 + 5 + 12 = 20 \text{ kg}$$

Mass fraction of each component is:

$$mf_{O_2} = \frac{m_{O_2}}{m_m} = \frac{3}{20} = 0.15$$

$$mf_{N_2} = \frac{m_{N_2}}{m_m} = \frac{5}{20} = 0.25$$

$$mf_{CH_4} = \frac{m_{CH_4}}{m_m} = \frac{12}{20} = 0.6$$

3 kg O_2
5 kg N_2
12 kg CH_4

(b) To get the mole fractions, we need to determine the mole number of each component:

$$N_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{3 \text{ kg}}{32 \text{ kg/kmol}} = 0.094 \text{ kmol}$$

$$N_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{5 \text{ kg}}{28 \text{ kg/kmol}} = 0.179 \text{ kmol}$$

$$N_{CH_4} = \frac{m_{CH_4}}{M_{CH_4}} = \frac{12 \text{ kg}}{16 \text{ kg/kmol}} = 0.750 \text{ kmol}$$

$$\text{Thus, } N_m = N_{O_2} + N_{N_2} + N_{CH_4} = 0.094 + 0.179 + 0.750 = 1.023 \text{ kmol}$$

$$y_{O_2} = \frac{N_{O_2}}{N_m} = \frac{0.094}{1.023} = 0.092$$

$$y_{N_2} = \frac{N_{N_2}}{N_m} = \frac{0.179}{1.023} = 0.175$$

$$y_{CH_4} = \frac{N_{CH_4}}{N_m} = \frac{0.750}{1.023} = 0.733$$

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

$$M_m = \frac{m_m}{N_m} = \frac{20 \text{ kg}}{1.023 \text{ kmol}} = 19.6 \text{ kg/kmol}$$

$$\text{Or } M_m = \sum y_i M_i = y_{O_2} \cdot M_{O_2} + y_{N_2} \cdot M_{N_2} + y_{CH_4} \cdot M_{CH_4} =$$

$$M_m = 0.092 \times 32 + 0.175 \times 28 + 0.733 \times 16 = 19.6 \text{ kg/kmol}$$

$$R_m = \frac{R_0}{M_m} = \frac{8.314 \text{ kJ/kmol.K}}{19.6 \text{ kg/kmol}} = 0.424 \text{ kJ/kg.K}$$

(Ideal and, Real) Gas Mixtures

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.

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**. Moreover, the real gases approximate this behavior closely when they are at a low pressure or high temperature relative to their critical-point values. The P - v - T behavior of real gases is expressed by more complex equations of state or by $Pv = ZRT$, where Z is the **compressibility factor**.

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 non-reacting 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. When a gas mixture consists of real (non-ideal) gases, however, the prediction of the P - v - T behavior of the mixture becomes rather involved. 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: The pressure of a mixture gases is equal o the sum of the partial pressures of the constituents.

Or: The partial pressure of each constituent is that the pressure which the gas would exert if it occupied alone that volume occupied by the mixture at the same temperature.

Consider Dalton model for the special case in which both mixture and the separated components can be considered an ideal gas.

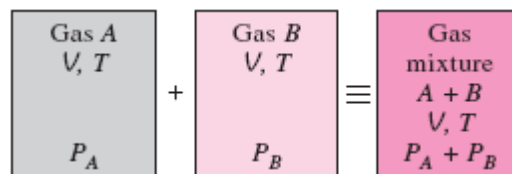
For the mixture: $pv = nR_oT$ where $n = n_A + n_B$

For the components: $p_A v = n_A R_o T$ and, $p_B v = n_B R_o T$

On substituting we have $n = n_A + n_B \rightarrow \frac{pv}{R_o T} = \frac{p_A v}{R_o T} + \frac{p_B v}{R_o T}$

Thus, $p = p_A + p_B$

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



Amagat's (Leduc's) law: 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.

Consider Dalton model for the special case in which both mixture and the separated components can be considered an ideal gas.

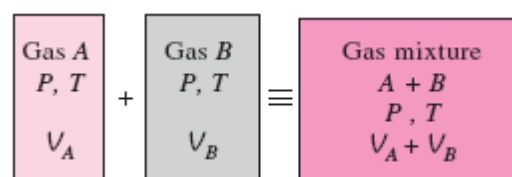
For the mixture: $pv = nR_oT$ where $n = n_A + n_B$

For the components: $p v_A = n_A R_o T$ and, $p v_B = n_B R_o T$

On substituting we have $n = n_A + n_B \rightarrow \frac{pv}{R_o T} = \frac{p v_A}{R_o T} + \frac{p v_B}{R_o T}$

Thus, $v = v_A + v_B$

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



Where: P_i is called the **component pressure**.
and V_i is called the **component volume**.

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. For ideal gases, these two laws are identical and give identical results.

Ideal-Gas Mixture: 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: $PV = NR_oT$

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

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

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

Example (7.2) A vessel of volume 0.4 m^3 contains 0.45 kg of Carbone monoxide (28) and 1 kg of air at 15°C . Calculate the partial pressure of each constituent and the total pressure in the vessel. The gravimetric analysis of air is to be taken as 23.3 % oxygen (32), and 76.7 % nitrogen (28).

Solution:

$$m_{O_2} = \frac{23.3}{100} \times 1 = 0.233 \text{ kg}$$

$$m_{N_2} = \frac{76.7}{100} \times 1 = 0.767 \text{ kg}$$

$$p_{O_2} \times v = n_{O_2} \times R_o \times T \quad \text{and,} \quad M_{O_2} = \frac{m_{O_2}}{n_{O_2}}$$

$$\text{Thus, } p_{N_2} = \frac{m_{N_2} \times R_o \times T}{M_{N_2} \times V} = \frac{0.767 \times 8314 \times 288}{28 \times 0.4} = 1.64 \times 10^5 \text{ N/m}^2 = 1.64 \text{ bar}$$

$$p_{O_2} = \frac{m_{O_2} \times R_o \times T}{M_{O_2} \times V} = \frac{0.233 \times 8314 \times 288}{32 \times 0.4} = 4.359 \times 10^4 \text{ N/m}^2 = 0.4359 \text{ bar}$$

$$p_{CO} = \frac{m_{CO} \times R_o \times T}{M_{CO} \times V} = \frac{0.45 \times 8314 \times 288}{28 \times 0.4} = 9.62 \times 10^4 \text{ N/m}^2 = 0.962 \text{ bar}$$

$$P_m = \sum_{i=1}^3 P_i = 0.4359 + 1.64 + 0.962 = 3.038 \text{ bar}$$

Real-Gas Mixture:

Dalton's law of additive pressures and Amagat's law of additive volumes can also be used for real gases, often with reasonable accuracy. One way of doing that is to use more exact equations of state (van der Waals, Beattie–Bridgeman, Benedict–Webb–Rubin, etc.) instead of the ideal-gas equation of state. Another way is to use the compressibility factor as:

$$pv = ZnR_oT$$

Z_m is the compressibility factor of the mixture can be expressed in terms of the compressibility factors of the individual gases.

$$Z_m = \sum_{i=1}^k Z_i(T_m, V_m) \quad \text{According to Dalton's law}$$

$$Z_m = \sum_{i=1}^k Z_i(T_m, P_m) \quad \text{According to Amagat's law}$$

Gas Constant of the Mixture R_m

To get the gas constant for the mixture in terms of the gas constant of the components, apply the equation of state for both mixture and component i .

$$P_m V = m_m R_m T \quad \text{and,} \quad P_i V = m_i R_i T$$

$$\text{Then } \sum P_i V = \sum m_i R_i T \rightarrow V \sum P_i = T \sum m_i R_i$$

$$\text{Also, } P_m = \sum P_i$$

$$\text{Therefore, } P_m V = T \sum m_i R_i \quad \text{or, } P_m V = m_m R_m T = T \sum m_i R_i$$

$$\text{i.e. } m_m R_m = \sum m_i R_i \quad \text{or, } R_m = \sum \frac{m_i}{m_m} R_i = \sum m f_i \times R_i$$

Example (7.3) The gravimetric analysis of air is 23.14 % oxygen, 75.53 % nitrogen, 1.28 % argon, 0.05 % carbon dioxide. Calculate the gas constant for the air and the apparent molecular weight. Take the molecular weights as follows: for oxygen equals 32, nitrogen equals 28, argon equals 40, carbon dioxide equals 44.

Solution:

$$R_{O_2} = \frac{8.314}{32} = 0.2598 \text{ kJ/kg.K}$$

$$R_{N_2} = \frac{8.314}{28} = 0.2968 \text{ kJ/kg.K}$$

$$R_{Ar} = \frac{8.314}{40} = 0.2081 \text{ kJ/kg.K}$$

$$R_{CO_2} = \frac{8.314}{44} = 0.1889 \text{ kJ/kg.K}$$

$$R_m = \sum \frac{m_i}{m_m} R_i$$

$$R_m = 0.2314 \times 0.2598 + 0.7553 \times 0.2968 + 0.0128 \times 0.2081 + 0.0005 \times 0.1889 = 0.2871 \text{ kJ/kg.K}$$

$$R_m = \frac{R_o}{M_m} \rightarrow M_m = \frac{R_o}{R_m} = \frac{8.314}{0.2871} = 28.96$$

apparent molecular weight = 28.96

Apparent Molecular Weight M_m

Another method to determine the molar mass (apparent molecular weight) is as follows. Applying the equation of state [$p v = m R T$] to each component and to the mixture to get:

For component: $m_i = p_i v / R_i T$

For mixture: $m_m = p_m v / R_m T$

We know previously that $m_m = \sum_{i=1}^k m_i$

Therefore: $\frac{p_m v}{R_m T} = \sum \frac{p_i v}{R_i T} \rightarrow \frac{p_m}{R_m} = \sum \frac{p_i}{R_i}$

In addition, $R_m = \frac{R_o}{M_m}$ and $R_i = \frac{R_o}{M_i}$

Substitute into above equation $\frac{p_m M_m}{R_o} = \sum \frac{p_i M_i}{R_o}$ or, $p_m M_m = \sum p_i M_i$

Then $M_m = \sum \frac{p_i}{p_m} M_i$

Moreover it can be re-write $M_m = \sum \frac{v_i}{v_m} M_i$

And $M_m = \sum \frac{n_i}{n_m} M_i$

Example (7.4) The gravimetric analysis of air is 23.14 % oxygen, 75.53 % nitrogen, 1.28 % argon, and 0.05 % carbon dioxide. Calculate the analysis by volume and partial pressure of each constituent when the total pressure is 1 bar.

Solution:

| <i>constituent</i> | m_i | M_i | $n_i = \frac{m_i}{M_i}$ | $\frac{n_i}{n} \times 100\%$ $= \frac{V_i}{V} \times 100\%$ |
|-----------------------|--------|-------|--------------------------|--|
| <i>oxygen</i> | 0.2314 | 32 | 0.00723 | $\frac{0.00723 \times 100}{0.03452} = 20.95 \%$ |
| <i>nitrogen</i> | 0.7553 | 28 | 0.02696 | $\frac{0.02696 \times 100}{0.03452} = 78.09 \%$ |
| <i>argon</i> | 0.0128 | 40 | 0.00032 | $\frac{0.00032 \times 100}{0.03452} = 0.093 \%$ |
| <i>carbon dioxide</i> | 0.0005 | 44 | 0.00001 | $\frac{0.00001 \times 100}{0.03452} = 0.03 \%$ |
| | | | $n = \sum n_i = 0.03452$ | |

$$\frac{n_i}{n} = \frac{p_i}{p} = \frac{v_i}{v} \rightarrow p_i = \frac{n_i}{n} \times p$$

| | |
|-----------------------|---|
| <i>oxygen</i> | $P_{O_2} = 0.2095 \times 1 = 0.2095 \text{ bar}$ |
| <i>nitrogen</i> | $P_{N_2} = 0.7809 \times 1 = 0.7809 \text{ bar}$ |
| <i>argon</i> | $P_{Ar} = 0.0093 \times 1 = 0.0093 \text{ bar}$ |
| <i>carbon dioxide</i> | $P_{CO_2} = 0.0003 \times 1 = 0.0003 \text{ bar}$ |

Properties of Gas Mixtures

Consider a gas mixture that consists of m_i ($i=1$ to k) kg. The total mass (an extensive property) of this mixture is m_m kg [$m_m = \sum_i^k m_i$]. It can be simply added the mass of each component. This example suggests a simple way of evaluating the **extensive properties** of a non-reacting 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

$$U_m = \sum_{i=1}^k U_i = \sum_{i=1}^k m_i u_i = \sum_{i=1}^k N_i \bar{u}_i$$

$$H_m = \sum_{i=1}^k H_i = \sum_{i=1}^k m_i h_i = \sum_{i=1}^k N_i \bar{h}_i$$

$$S_m = \sum_{i=1}^k S_i = \sum_{i=1}^k m_i s_i = \sum_{i=1}^k N_i \bar{s}_i$$

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

$$\Delta U_m = \sum_{i=1}^k \Delta U_i = \sum_{i=1}^k m_i \Delta u_i = \sum_{i=1}^k N_i \Delta \bar{u}_i$$

$$\Delta H_m = \sum_{i=1}^k \Delta H_i = \sum_{i=1}^k m_i \Delta h_i = \sum_{i=1}^k N_i \Delta \bar{h}_i$$

$$\Delta S_m = \sum_{i=1}^k \Delta S_i = \sum_{i=1}^k m_i \Delta s_i = \sum_{i=1}^k N_i \Delta \bar{s}_i$$

Specific Heats of Gas Mixtures

Also for a perfect gas [$u = C_v T$]. Hence substituting we have

$$[m_m C_v T = \sum m_i C_{vi} T \rightarrow m_m C_v = \sum m_i C_{vi}]$$

$$C_v = \sum \frac{m_i}{m_m} C_{vi}$$

In the same manner it can be write

$$C_p = \sum \frac{m_i}{m_m} C_{pi}$$

$$R = \sum \frac{m_i}{m_m} R_i$$

And the adiabatic index γ can be established as:

$$\gamma = \frac{C_p}{C_v}; \quad C_v = \frac{R}{\gamma-1}; \quad C_p = \frac{\gamma R}{\gamma-1}$$

Example (7.5) The gas in an engine cylinder has a volumetric analysis of 12% CO_2 , 11.5 % O_2 , and 76.5 % N_2 . The temperature at the beginning of expansion is 1000°C and the gas mixture expands reversibly through a volume ration of 7 to 1 according to

the law $[pv^{1.25} = \text{constant}]$. Calculate the work done and heat flow per kg of gas. The values of C_p for constituents are as follows:

| | | |
|-----------------|----------------|------------------|
| CO ₂ | O ₂ | N ₂ . |
| 1.235 kJ/kg.K | 1.088 kJ/kg.K | 1.172 kJ/kg.K |

Solution:

$$m_i = n_i M_i$$

| Constituent | n _i | M _i | $m_i = n_i M_i$ | m_i/m_m |
|------------------|----------------|----------------|-------------------|-----------------------------|
| CO ₂ | 0.12 | 44 | 528 | $\frac{528}{3036} = 0.174$ |
| O ₂ | 0.115 | 32 | 368 | $\frac{368}{3036} = 0.121$ |
| N ₂ . | 0.765 | 28 | 2140 | $\frac{2140}{3036} = 0.705$ |
| | | | $\sum m_i = 3036$ | |

$$C_p = \sum \frac{m_i}{m_m} C_{pi}$$

$$C_p = 0.174 \times 1.235 + 0.121 \times 1.088 + 0.705 \times 1.172 = 1.173 \text{ kJ/kg.K}$$

$$R = \sum \frac{m_i}{m_m} R_i \quad \text{and,} \quad R_i = \frac{R_o}{M_i}$$

Therefore,

$$R = 0.174 \times \frac{8.314}{44} + 0.121 \times \frac{8.314}{32} + 0.705 \times \frac{8.314}{28} = 0.2739 \text{ kJ/kg.K}$$

$$C_v = C_p - R = 1.173 - 0.2739 = 0.899 \text{ kJ/kg.K}$$

The work done per kg of gas can be obtained as follows:

$$W = \frac{R(T_1 - T_2)}{n-1}$$

$$\text{To evaluate the final temperature; } \left(\frac{T_2}{T_1}\right) = \left(\frac{v_1}{v_2}\right)^{n-1} \rightarrow \frac{T_2}{1000+273} = \left(\frac{1}{7}\right)^{0.25}$$

$$T_2 = 783.2 \text{ K}$$

$$W = \frac{0.2739(1273-783.2)}{1.25-1} = 536.3 \text{ kJ/kg}$$

$$Q + u_1 = W + u_2$$

$$u_2 - u_1 = C_v(T_2 - T_1) = 0.899(783.2 - 1273) = -440.3 \text{ kJ/kg}$$

$$Q = -440.3 + 536.3 = 96 \text{ kJ/kg} \quad (\text{heat supplied})$$

Note: To calculate the entropy change through the process in the above example. The polytropic process is replaced by two processes, as follows;

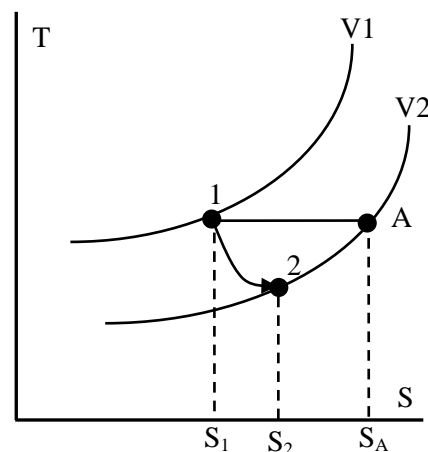
- Isothermal process from V_1 to V_2

$$[S_A - S_1 = R \ln \frac{v_2}{v_1} = 0.2739 \ln 7 = 0.533 \text{ kJ/kg.K}]$$

- Constant volume process from T_1 to T_2

$$[S_A - S_2 = C_v \ln \frac{T_1}{T_2} = 0.899 \ln \frac{1273}{783.2} = 0.436 \text{ kJ/kg.K}]$$

$$\text{Finally } [S_2 - S_1 = 0.533 - 0.436 = 0.097 \text{ kJ/kg.K}]$$



Exercises

Problem (7.1) Determine the mole fractions of a gas mixture that consists of 75 % CH₄ and 25 % CO₂ by mass. Also, determine the gas constant of the mixture. [reference: *Thermodynamics an Engineering Approach*, by Michael A. Boles, prob. 13-14,p-709]

Ans.: (89.2%, 10.8%, 0.437 kJ/kg.K)

Problem (7.2) A gas mixture consists of 8 kmol of H₂ and 2 kmol of N₂. Determine the mass of each gas and the apparent gas constant of the mixture. [reference: *Thermodynamics an Engineering Approach*, by Michael A. Boles, prob. 13-15,p-709]

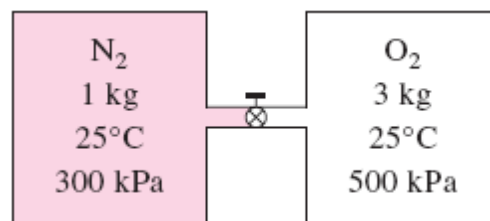
Ans.: (16 kg, 56 kg, 1.155 kJ/kg.K)

Problem (7.3) Is a mixture of ideal gases also an ideal gas? Give an example. [reference: *Thermodynamics an Engineering Approach*, by Michael A. Boles, prob. 13-18C,p-709]

Answer: Normally yes. Air, for example, behaves as an ideal gas in the range of temperatures and pressures at which oxygen and nitrogen behave as ideal gases.

Problem (7.4) A rigid tank that contains 1 kg of N₂ at 25°C and 300 kPa is connected to another rigid tank that contains 3 kg of O₂ at 25°C and 500 kPa. The valve connecting the two tanks is opened, and the two gases are allowed to mix. If the final mixture temperature is 25°C, determine the volume of each tank and the final mixture pressure. [reference: *Thermodynamics an Engineering Approach*, by Michael A. Boles, prob. 13-38,p-710]

Ans.: (0.295 m³, 0.465 m³, 422 kPa)



Problem (7.5) A gas mixture at 350 K and 300 kPa has the following volumetric analysis: 65 % N₂, 20 % O₂, and 15 % CO₂. Determine the mass fraction and partial pressure of each gas. [reference: *Thermodynamics an Engineering Approach*, by Michael A. Boles, prob. 13-37,p-710]

Ans.: (58.3 %, 20.5%, 21.2%, 195 kpa, 60 kpa, 45 kpa)

Problem (7.6) A rigid tank contains 0.5 kmol of Ar and 2 kmol of N₂ 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. [reference: *Thermodynamics an Engineering Approach*, by Michael A. Boles, prob. 13-33,p-710]

Ans.: (23.3 m³, 357.1 kpa)

Problem (7.7) A gas mixture at 300 K and 200 kPa consists of 1 kg of CO₂ and 3 kg of CH₄. Determine the partial pressure of each gas and the apparent molar mass of the gas mixture. [reference: *Thermodynamics an Engineering Approach*, by Michael A. Boles, prob. 13-34,p-710]

Ans.: (21.6 kpa, 178.4 kpa, 19.03 kg/kmol)