Gas Mixture

Content:
- Composition of gas mixture
- P-v-T behavior of gas mixture
- Properties of gas mixture: Ideal and real gases

### Composition of gas mixture

**Gravimetric analysis**

- Conservation of mass: \( m_n = \sum_{i=1}^{k} m_i \)
- Mass fraction: \( m_f = \frac{m_i}{m_n} \)
- Therefore, \( \sum m_f = 1 \)

**Molar analysis**

- Conservation of mass: \( N_n = \sum_{i=1}^{k} N_i \)
- Mole fraction: \( y_i = \frac{N_i}{N_n} \)
- Therefore, \( \sum y_i = 1 \)

\[
M_n = \frac{m_n}{N_n} = \frac{\sum m_i}{N_n} = \frac{\sum N_i M_i}{N_n} = \frac{\sum y_i M_i}{N_n}
\]

- \( N = \) mole number, \( M = \) molar mass
- \( R_n = \frac{R_s}{M_n} \)
- \( R_u = \) Universal gas const. = 8.313 kJ/kmolK

<table>
<thead>
<tr>
<th>H₂</th>
<th>O₂</th>
<th>H₂ + O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>6kg</td>
<td>32kg</td>
<td>38 kg</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H₂</th>
<th>O₂</th>
<th>H₂ + O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 kmol</td>
<td>1 kmol</td>
<td>4 kmol</td>
</tr>
</tbody>
</table>
Example 1 Consider a gas mixture which consists of 3 kg of O₂, 5 kg of N₂, and 12 kg of CH₄. 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

\[ m_m = m_{O_2} + m_{N_2} + m_{CH_4} = 3 + 5 + 12 \text{ kg} \]

The mass fraction of each component becomes:

\[ mf_{O_2} = \frac{m_{O_2}}{m_m} = \frac{3\text{ kg}}{20\text{ kg}} = 0.15, \quad mf_{N_2} = 0.25 \quad \text{and} \quad mf_{CH_4} = 0.60 \]

b) To find the mole fractions,

\[ N_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{3\text{ kg}}{32\text{ kg/kmol}} = 0.094\text{ kmol}, \quad N_{N_2} = 0.179\text{ kmol} \quad \text{and} \quad N_{CH_4} = 0.750\text{ kmol} \]

(b) To find the mole fractions,

\[ N_m = N_{O_2} + N_{N_2} + N_{CH_4} = 1.023\text{ kmol} \]

\[ y_{O_2} = \frac{N_{O_2}}{N_m} = \frac{0.094\text{ kmol}}{1.023\text{ kmol}} = 0.092, \quad y_{N_2} = 0.175 \quad \text{and} \quad y_{CH_4} = 0.733 \]

(c) The average molar mass and gas constant of the mixture

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

then

\[ R_m = \frac{R_u}{M_m} = \frac{8.314\text{ kJ/kmolK}}{19.6\text{ kg/kmol}} = 0.424\text{ kJ/kgK} \]
**Dalton’s law of additive pressure:**
The pressure of a gas mixture \( P_m \) is equal to the sum of the pressures each gas would exert if it existed alone at the mixture temperature and volume.

\[
P_m = \sum_{i=1}^{k} P_i(T_m, V_m)
\]

where \( P_i \) is component pressure of gas \( i \)

\[
\frac{P_i}{P_m}
\]

is pressure fraction of gas \( i \)

**Amagat’s law of additive volumes:**
The volume of a gas mixture \( V_m \) is equal to the sum of the volume each gas would occupy if it existed alone at the mixture temperature and pressure.

\[
V_m = \sum_{i=1}^{k} V_i(T_m, P_m)
\]

where \( V_i \) is component volume of gas \( i \)

\[
\frac{V_i}{V_m}
\]

is volume fraction of gas \( i \)
**Ideal Gas Mixtures**

Ideal Gas Eqn. of State  \( PV = NR_uT \)

for the mixture; \( P_m V_m = N_u R_u T_m \) \( \quad \text{(a)} \)

for gas i (Dalton's law); \( P_i V_i = N_i R_u T_m \) \( \quad \text{(b)} \)

Then  \( \frac{P_i}{P_m} = \frac{N_i}{N_m} = y_i \) (mole fraction)

for gas i (Amagat's law); \( P_i V_i = N_i R_u T_m \) \( \quad \text{(c)} \)

Then  \( \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i \) (mole fraction)

Therefore,  \( \frac{P_i}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i \) \( \quad (12.8) \)

Then partial pressure of gas i (\( P_i \), Component pressure) = \( y_i P_m \)

partial volume of gas i (\( V_i \), Component volume) = \( y_i V_m \)

---

**Ideal Gas and Compressibility Factor**

(Background from Thermo. 1)

The deviation of actual gas from ideal-gas behavior can be corrected by the **compressibility factor**, \( Z \)

\[ Z = \frac{PV}{RT} \quad \text{or} \quad PV = ZRT \]

where  \( Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}} \) and \( v_{\text{ideal}} = RT / P \)

The \( Z \) factor for all gases is approximate the same at the same reduced pressure, \( P_R \) and reduced temperature, \( T_R \)

\[ P_R = \frac{P}{P_{cr}} \quad \text{and} \quad T_R = \frac{T}{T_{cr}} \]

\( Z, P_R \) and \( T_R \) can be found in Table A-15 and \( T_{cr} \) and \( P_{cr} \) from Table A-1
Real Gas Mixtures

Ideal Gas Eqn. of State: \( PV = Z N R T \)
for the mixture: \( P_m V_m = Z_m N_m R_m T_m \)
for gas \( i \) (Dalton’s law): \( P_i V_i = Z_i N_i R_i T_i \)

and

\[
P_m = \sum_{i=1}^{k} P_i
\]

Therefore,

\[
Z_m = \sum_{i=1}^{k} y_i Z_i
\]
\[
V_m = \sum_{i=1}^{k} V_i
\]

\( Z_m \) can be determined from both Dalton’s and Amagat’s Law.

Compressibility Factor of Gas Mixture (\( Z_m \))

- Amagat’s law find \( Z_i \) (table A-15) for each gas from in the mixture from their \( T_R \) and \( P_R \) and

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

- Dalton’s law find \( Z_i \) (table A-15) for each gas in the mixture from their \( V_R \) and \( P_R \) and

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

Then \( Z_m \) are different from different Laws. Amagat’s law is more accurate because intermolecular forces already consider.
Compressibility Factor Approached

Key's Rule:       

\[ P_{cr,m} = \sum_{i=1}^{k} y_i P_{cr,i} \]  \hspace{1cm} (12.11a) 

\[ T_{cr,m} = \sum_{i=1}^{l} y_i T_{cr,i} \]  \hspace{1cm} (12.11b) 

Where:  \( P_{cr,i} \) and \( T_{cr,i} \) can be determined in Table A-1

\( P_{cr,m} \) = Pseudocritical Pressure

\( T_{cr,m} \) = Pseudocritical Temperature

Then, \( T_R = \frac{T_m}{T_{cr,m}} \) and \( P_R = \frac{P_m}{P_{cr,m}} \)

Then, \( Z_m \) is easily determined by using these pseudocritical properties \( T_{R,m} \) and \( P_{R,m} \) (Table A-15).

Example 2

A rigid tank contains 2 kmol of \( N_2 \) and 6 kmol of \( CO_2 \) gases at 300 K and 15 MPa. Estimate the volume of the tank on the basis of (a) the ideal gas equation of state, (b) Key’s Rule, (c) Compressibility factor and Amagat’s law, and (d) compressibility factor and Dalton’s law.

Solution

(a) the ideal gas ,       \( 1.330 \) m\(^3\)

(b) Key’s Rule,       \( 0.652 \) m\(^3\)

(c) \( Z \) and Amagat’s law \( 0.638 \) m\(^3\)

(d) \( Z \) and Dalton’s law. \( 0.648 \) m\(^3\)
Properties of Ideal Gas Mixtures

Extensive properties of gas mixtures

\[ U_m = \sum U_i = \sum m_i \tilde{u}_i = \sum N_i \tilde{u}_i \]
\[ H_m = \sum H_i = \sum m_i \tilde{h}_i = \sum N_i \tilde{h}_i \]
\[ S_m = \sum S_i = \sum m_i s_i = \sum N_i s_i \]

Heat capacities of gas mixtures

\[ c_{v,m} = \sum c_{v,i} = \sum m_i c_{v,i} = \sum N_i \tilde{c}_{v,i} \]
\[ c_{p,m} = \sum c_{p,i} = \sum m_i c_{p,i} = \sum N_i \tilde{c}_{p,i} \]

Properties Change of Ideal Gas Mixtures

\[ \Delta U_m = \sum \Delta U_i = \sum m_i \Delta u_i = \sum N_i \Delta u_i \]

or \( (U_2 - U_1) = \sum m_i (u_2 - u_1) = \int_{T_1}^{T_2} \tilde{c}_{v,m} dT \)

\[ \Delta H_m = \sum \Delta H_i = \sum m_i \Delta h_i = \sum N_i \Delta h_i \]

or \( (H_2 - H_1) = \sum m_i (h_2 - h_1) = \int \tilde{c}_{p,m} dT \)

\[ \Delta S_m = \sum \Delta S_i = \sum m_i \Delta s_i = \sum N_i \Delta s_i \]

or \( (S_2 - S_1) = \sum m_i (s_2 - s_1) \)

\[ = \sum m_i \int_{T_i}^{T_2} \tilde{c}_{p,m} d(\ln T) - \sum m_i R_i \ln \frac{P_{i,1}}{P_{i,2}} \]
Example 3: An insulated rigid tank is divided into two compartments by a partition. One compartment contains 7 kg of oxygen gas at 40°C and 100 kPa, and the other component contains 4 kg of nitrogen gas at 20°C and 150 kPa. Now the partition is removed, and the two gases are allowed to mix. Determine, (a) the mixture temperature, and (b) the mixture pressure after equilibrium has been established.

Solution

(a) The energy balance for the system (no heat transferred to/from the tank):

\[ E_{in} - E_{out} = \Delta E_{system} \]

0 = \( \Delta U = \Delta U_{N_2} + \Delta U_{O_2} \)

\[ [mc_v(T_m - T_1)]_{N_2} + [mc_v(T_m - T_1)]_{O_2} = 0 \]

\[ T_m = 32.2^\circ C \]

(b) The mixture pressure can be calculated from ideal-gas relation:

\[ P_m V_m = N_m R T_m \]

\[ N_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{7\text{kg}}{32\text{kg/kmol}} = 0.219\text{kmol} \]

\[ N_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{4\text{kg}}{28\text{kg/kmol}} = 0.143\text{kmol} \]

\[ N_m = N_{O_2} + N_{N_2} = 0.362\text{kmol} \]

\[ V_{O_2} = \left( \frac{NR T_1}{P_1} \right)_{O_2} = \frac{(0.219)(8.314)(313)}{100} = 5.70\text{m}^3 \]

\[ V_{N_2} = \left( \frac{NR T_1}{P_1} \right)_{N_2} = \frac{(0.143)(8.314)(293)}{150} = 2.32\text{m}^3 \]

\[ V_m = V_{O_2} + V_{N_2} = 8.02\text{m}^3 \]

Then,

\[ P_m = \frac{N_m R T_m}{V_m} = 114.4\text{kPa} \]
Example 4 An ideal-gas mixture has the following volumetric analysis:

<table>
<thead>
<tr>
<th>Component</th>
<th>% by Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>60</td>
</tr>
<tr>
<td>CO₂</td>
<td>40</td>
</tr>
</tbody>
</table>

(a) Find the analysis on a mass basis.

For ideal-gas mixtures, the percent by volume is the volume fraction. Recall:

\[ y_i = \frac{v_i}{v_m} \]

<table>
<thead>
<tr>
<th>Component</th>
<th>( y_i )</th>
<th>( M_i )</th>
<th>( y_i M_i )</th>
<th>( m_i = \frac{y_i M_i}{M_m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.60</td>
<td>28</td>
<td>16.8</td>
<td>0.488</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.40</td>
<td>44</td>
<td>17.6</td>
<td>0.512</td>
</tr>
</tbody>
</table>

\[ M_m = \sum y_i M_i = 34.4 \]

(b) What is the mass of 1 m³ of this gas when \( P = 1.5 \) MPa and \( T = 30^\circ C \)?

\[ R_m = \frac{R}{M_m} \quad (kJ / kg \cdot K) \]

\[ = \frac{8.314 \frac{kJ}{kmol \cdot K}}{34.4 \frac{kg}{kmol}} = 0.242 \frac{kJ}{kg \cdot K} \]

\[ m_m = \frac{P V_m}{R_m T_m} \]

\[ = \frac{15 MPa(1 m^3)}{(0.242 kJ / (kg \cdot K))(30 + 273)K m^3 MPa} \]

\[ = 20.45 \text{ kg} \]
(c) Find the specific heats at 300 K.

Using Table A-2, \( C_p \text{ N}_2 = 1.039 \text{ kJ/kg} \cdot \text{K} \) and \( C_p \text{ CO}_2 = 0.846 \text{ kJ/kg} \cdot \text{K} \)

\[
C_{p,m} = \sum_{i=1}^{2} m_f C_{p,i} = (0.488)(1.039) + (0.512)(0.846)
\]

\[
= 0.940 \frac{kJ}{kg_m \cdot K}
\]

\[
C_{v,m} = C_{p,m} - R_m = (0.940 - 0.242) \frac{kJ}{kg_m \cdot K}
\]

\[
= 0.698 \frac{kJ}{kg_m \cdot K}
\]

(d) This gas is heated in a steady-flow process such that the temperature is increased by 120°C. Find the required heat transfer. The conservation of mass and energy for steady-flow are

\[
\dot{m}_1 = \dot{m}_2 = \dot{m}
\]

\[
\dot{m}_1 h_1 + \dot{Q}_{in} = \dot{m}_2 h_2
\]

\[
\dot{Q}_{in} = \dot{m}(h_2 - h_1)
\]

\[
= \dot{m} C_{p,m}(T_2 - T_1)
\]

The heat transfer per unit mass flow is

\[
g_{in} = \frac{\dot{Q}_{in}}{\dot{m}} = C_{p,m}(T_2 - T_1)
\]

\[
= 0.940 \frac{kJ}{kg_m \cdot K}(120 \text{ K})
\]

\[
= 112.8 \frac{kJ}{kg_m}
\]
(e) This mixture undergoes an isentropic process from 0.1 MPa, 30°C, to 0.2 MPa. Find $T_2$.

The ratio of specific heats for the mixture is $k = \frac{C_{p,m}}{C_{v,m}} = \frac{0.940}{0.698} = 1.347$

Assuming constant properties for the isentropic process

$$T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{(k-1)/k}$$

$$= (30 + 273)K \left( \frac{0.2 \text{ MPa}}{0.1 \text{ MPa}} \right)^{(1.347-1)/1.347}$$

$$= 362.2K$$

(f) Find $\Delta S_m$ per kg of mixture when the mixture is compressed isothermally from 0.1 MPa to 0.2 MPa.

$$\Delta S_m = \frac{\Delta S_m}{m_m} = \sum_{i=1}^{n} m_f \Delta S_i$$

$$\Delta S_i = C_{v,i} \ln \left( \frac{T_2}{T_1} \right) - R_i \ln \left( \frac{P_{2,i}}{P_{1,i}} \right)$$

But, the compression process is isothermal, $T_2 = T_1$. The partial pressures are given by

$$P_i = y_i P_m$$

The entropy change becomes

$$\Delta S_i = -R_i \ln \left( \frac{y_{i,2} P_{m,2}}{y_{i,1} P_{m,1}} \right)$$

For this problem the components are already mixed before the compression process. So, $y_{i,2} = y_{i,1}$

Then,

$$\Delta S_i = -R_i \ln \left( \frac{P_{m,2}}{P_{m,1}} \right)$$

$$\Delta S_{N_2} = -0.296 \frac{kJ}{kg \cdot K} \ln \left( \frac{0.2 \text{ MPa}}{0.1 \text{ MPa}} \right)$$

$$= -0.206 \frac{kJ}{kg \cdot K}$$
\[
\Delta s_{CO_2} = -0.1889 \frac{kJ}{kg_{CO_2} \cdot K} \ln \left( \frac{0.2 \text{ MPa}}{0.1 \text{ MPa}} \right) \\
= -0.131 \frac{kJ}{kg_{CO_2} \cdot K}
\]

\[
\Delta s_m = \sum_{i=1}^{2} m_i \Delta s_i \\
= (0.488 \frac{kg_{N_2}}{kg_m})(-0.206 \frac{kJ}{kg_{N_2} \cdot K}) + (0.512 \frac{kg_{CO_2}}{kg_m})(-0.131 \frac{kJ}{kg_{CO_2} \cdot K}) \\
= -0.167 \frac{kJ}{kg_m \cdot K}
\]

Why is \( \Delta s_m \) negative for this problem? Find the entropy change using the average specific heats of the mixture. Is your result the same as that above? Should it be?

\( (g) \) Both the \( N_2 \) and \( CO_2 \) are supplied in separate lines at 0.2 MPa and 300 K to a mixing chamber and are mixed adiabatically. The resulting mixture has the composition as given in part (a). Determine the entropy change due to the mixing process per unit mass of mixture.
Take the time to apply the steady-flow conservation of energy and mass to show that the temperature of the mixture at state 3 is 300 K.

\[ \Delta S_n = \frac{\Delta S_m}{m_m} = \sum_{i=1}^{n} m_f \Delta s_i \]

\[ \Delta s_i = C_p \ln \left( \frac{T_i}{T_0} \right) - R \ln \left( \frac{P_{i,m}}{P_{i,ref}} \right) \]

But the mixing process is isothermal, \( T_3 = T_2 = T_1 \). The partial pressures are given by

\[ P_i = y_i P_m \]

The entropy change becomes

\[ \Delta s_{H} = -R \ln \left( \frac{y_{H_i} P_i}{y_{H_i} P_1} \right) \]

\[ \Delta s_{CO_2} = -R \ln \left( \frac{y_{CO_2,3} P_3}{y_{CO_2,2} P_2} \right) \]

But here the components are not mixed initially. So,

\[ y_{N_2,1} = 1 \]

\[ y_{CO_2,2} = 1 \]

and in the mixture state 3,

\[ y_{N_2,3} = 0.6 \]

\[ y_{CO_2,3} = 0.4 \]

Then,

\[ \Delta s_{N_2} = -0.296 \frac{k}{R_{N_2}} \ln \left( \frac{(0.6)0.2 \text{ MPa}}{0.2 \text{ MPa}} \right) \]

\[ = 0.152 \frac{k}{R_{N_2}} \cdot \ln \left( \frac{(0.6)0.2 \text{ MPa}}{0.2 \text{ MPa}} \right) \]

\[ \Delta s_{CO_2} = -0.1889 \frac{k}{R_{CO_2}} \ln \left( \frac{(0.4)0.2 \text{ MPa}}{0.2 \text{ MPa}} \right) \]

\[ = 0.173 \frac{k}{R_{CO_2}} \cdot \ln \left( \frac{(0.4)0.2 \text{ MPa}}{0.2 \text{ MPa}} \right) \]
Then,

\[
\Delta s_{\text{m}} = \sum_{j} mf_{j} \Delta s_{j}
\]

\[
= \left(0.488 \frac{\text{kg}_{N_{2}}}{\text{kg}_{\text{m}}} \right) \left(0.152 \frac{\text{kJ}}{\text{kg}_{N_{2}}} \cdot \text{K} \right) + \left(0.512 \frac{\text{kg}_{CO_{2}}}{\text{kg}_{\text{m}}} \right) \left(0.173 \frac{\text{kJ}}{\text{kg}_{CO_{2}}} \cdot \text{K} \right)
\]

\[
= 0.163 \frac{\text{kJ}}{\text{kg}_{\text{m}}} \cdot \text{K}
\]

If the process is adiabatic, why did the entropy increase?

---

Extra Assignment

Nitrogen and carbon dioxide are to be mixed and allowed to flow through a convergent nozzle. The exit velocity to the nozzle is to be the speed of sound for the mixture and have a value of 500 m/s when the nozzle exit temperature of the mixture is 500°C. Determine the required mole fractions of the nitrogen and carbon dioxide to produce this mixture. From Chapter 17, the speed of sound is given by

\[ C = \sqrt{kRT} \]

\[
\text{Mixture} \quad \text{N}_2 \text{ and CO}_2 \quad \text{NOZZLE} \quad C = 500 \text{ m/s} \quad T = 500^\circ\text{C}
\]

Answer: \(y_{N_2} = 0.589, \ y_{CO_2} = 0.411\)