Chapter 13

Gas Mixtures

Study Guide in PowerPoint

to accompany

Thermodynamics: An Engineering Approach, 7th edition
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The discussions in this chapter are restricted to nonreactive ideal-gas mixtures. Those interested in real-gas mixtures are encouraged to study carefully the material presented in Chapter 12.

Many thermodynamic applications involve mixtures of ideal gases. That is, each of the gases in the mixture individually behaves as an ideal gas. In this section, we assume that the gases in the mixture do not react with one another to any significant degree.

We restrict ourselves to a study of only ideal-gas mixtures. An ideal gas is one in which the equation of state is given by

$$PV = mRT \quad or \quad PV = NR_uT$$

Air is an example of an ideal gas mixture and has the following approximate composition.

Component	% by Volume
N2	78.10
O2	20.95
Argon	0.92
CO2 + trace elements	0.03

For more information and animations illustrating this topic visit the Animation Library developed by Professor S. Bhattacharjee, San Diego State University, at this link.
 test.sdsu.edu/testhome/vtAnimations/index.html

Definitions

Consider a container having a volume *V* that is filled with a mixture of *k* different gases at a pressure *P* and a temperature *T*.

A mixture of two or more gases of fixed chemical composition is called a *nonreacting gas mixture.* Consider *k* gases in a rigid container as shown here.

The properties of the mixture may be based on the mass of each component, called gravimetric analysis, or on the moles of each component, called molar analysis.

k gases
$T = T_m$ $V = V_m$
$P = P_m$ $m = m_m$

The total mass of the mixture m_m and the total moles of mixture N_m are defined as

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

The composition of a gas mixture is described by specifying either the *mass fraction* mf_i or the *mole fraction* y_i of each component *i*.

$$mf_i = \frac{m_i}{m_m} \quad \text{and} \quad y_i = \frac{N_i}{N_m}$$

Note that

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

The mass and mole number for a given component are related through the molar mass (or molecular weight).

$$m_i = N_i M_i$$

To find the average molar mass for the mixture M_m , note

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

Solving for the average or apparent molar mass M_m

$$M_m = \frac{m_m}{N_m} = \sum_{i=1}^{k} \frac{N_i}{N_m} M_i = \sum_{i=1}^{k} y_i M_i \qquad (kg\,/\,kmol)$$

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The *apparent* (or average) *gas constant* of a mixture is expressed as

$$R_m = \frac{R_u}{M_m} \qquad (kJ / kg \cdot K)$$

Can you show that R_m is given as

$$R_m = \sum_{i=1}^{k} mf_i R_i$$

To change from a mole fraction analysis to a mass fraction analysis, we can show that

$$mf_i = \frac{y_i M_i}{\sum_{i=1}^{k} y_i M_i}$$

To change from a mass fraction analysis to a mole fraction analysis, we can show that

$$y_i = \frac{mf_i / M_i}{\sum_{i=1}^{k} mf_i / M_i}$$

Volume fraction (Amagat model)

Divide the container into *k* subcontainers, such that each subcontainer has only one of the gases in the mixture at the original mixture temperature and pressure.

Gas 1	Gas 2		Gas k
$T = T_m$	$T = T_m$	. . . .	$T = T_m$
$P = P_m$	$P = P_m$		$P = P_m$
$V = V_1$	$V = V_2$		$V = V_k$

Amagat's law of additive volumes 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.

$$\text{Amagat's law:} \qquad V_m = \sum_{i=1}^{k} V_i(T_m, P_m)$$

The volume fraction of the vf_i of any component is

$$vf_i = \frac{V_i(T_m, P_m)}{V_m}$$

and

$$\sum_{i=1}^{k} vf_i = 1$$

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For an ideal gas mixture

$$V_i = \frac{N_i R_u T_m}{P_m} \quad and \quad V_m = \frac{N_m R_u T_m}{P_m}$$

Taking the ratio of these two equations gives

$$vf_i = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$

The volume fraction and the mole fraction of a component in an ideal gas mixture are the same.

Partial pressure (Dalton model)

The partial pressure of component *i* is defined as the product of the mole fraction and the mixture pressure according to Dalton's law. For the component *i*

$$P_i = y_i P_m$$

Dalton's law: $\qquad P_m = \sum_{i=1}^{k} P_i(T_m, V_m)$

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Now, consider placing each of the k gases in a separate container having the volume of the mixture at the temperature of the mixture. The pressure that results is called the component pressure, P_i' .

i^{th} gas
$T = T_m$ $\qquad$ $V = V_m$
$P = P_i'$ $\qquad$ $m = m_i$

$$P_i' = \frac{N_i R_u T_m}{V_m} \quad and \quad P_m = \frac{N_m R_u T_m}{V_m}$$

Note that the ratio of P_i' to P_m is

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

For ideal-gas mixtures, the partial pressure and the component pressure are the same and are equal to the product of the mole fraction and the mixture pressure.

Other properties of ideal-gas mixtures

The *extensive properties* of a gas mixture, in general, can be determined by summing the contributions of each component of the mixture. The evaluation of *intensive properties* of a gas mixture, however, involves averaging in terms of mass or mole fractions:

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

$$H_m = \sum_{i=1}^{k} H_i = \sum_{i=1}^{k} m_i h_i = \sum_{i=1}^{k} N_i \bar{h}_i \quad (\text{kJ})$$

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

and

$$u_m = \sum_{i=1}^{k} mf_i u_i \quad \text{and} \quad \overline{u}_m = \sum_{i=1}^{k} y_i \overline{u}_i \quad \text{(kJ / kg or kJ / kmol)}$$

$$h_m = \sum_{i=1}^{k} mf_i h_i \quad \text{and} \quad \overline{h}_m = \sum_{i=1}^{k} y_i \overline{h}_i \quad \text{(kJ / kg or kJ / kmol)}$$

$$s_m = \sum_{i=1}^{k} mf_i s_i \quad \text{and} \quad \overline{s}_m = \sum_{i=1}^{k} y_i \overline{s}_i \quad \text{(kJ / kg} \cdot \text{K or kJ / kmol} \cdot \text{K)}$$

$$C_{v,m} = \sum_{i=1}^{k} mf_i C_{v,i} \quad \text{and} \quad \overline{C}_{v,m} = \sum_{i=1}^{k} y_i \overline{C}_{v,i}$$

$$C_{p,m} = \sum_{i=1}^{k} mf_i C_{p,i} \quad \text{and} \quad \overline{C}_{p,m} = \sum_{i=1}^{k} y_i \overline{C}_{p,i}$$

These relations are applicable to both ideal- and real-gas mixtures. The properties or property changes of individual components can be determined by using ideal-gas or real-gas relations developed in earlier chapters.

Ratio of specific heats k is given as

$$k_m = \frac{C_{p,m}}{C_{v,m}} = \frac{\overline{C}_{p,m}}{\overline{C}_{v,m}}$$

The entropy of a mixture of ideal gases is equal to the sum of the entropies of the component gases as they exist in the mixture. We employ the Gibbs-Dalton law that says each gas behaves as if it alone occupies the volume of the system at the mixture temperature. That is, the pressure of each component is the partial pressure.

For constant specific heats, the entropy change of any component is

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

The entropy change of the mixture per mass of mixture is

$$\Delta s_m = \frac{\Delta S_m}{m_m} = \sum_{i=1}^{2} mf_i \Delta s_i$$

$$= \sum_{i=1}^{k} mf_i \left(C_{p,i} \ln\left(\frac{T_2}{T_1}\right) - R_i \ln\left(\frac{P_{i,2}}{P_{i,1}}\right) \right)$$

The entropy change of the mixture per mole of mixture is

$$\Delta \bar{s}_m = \frac{\Delta S_m}{N_m} = \sum_{i=1}^{2} y_i \Delta \bar{s}_i$$

$$= \sum_{i=1}^{k} y_i \left(\overline{C}_{p,i} \ln\left(\frac{T_2}{T_1}\right) - R_u \ln\left(\frac{P_{i,2}}{P_{i,1}}\right) \right)$$

In these last two equations, recall that

$$P_{i,1} = y_{i,1} P_{m,1}$$

$$P_{i,2} = y_{i,2} P_{m,2}$$

Example 13-1

An ideal-gas mixture has the following volumetric analysis

Component	% by Volume
N_2	60
CO_2	40

(a) Find the analysis on a mass basis.

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

$$y_i = vf_i$$

Comp.	y_i	M_i	$y_i M_i$	$mf_i = y_i M_i / M_m$
		kg/kmol	kg/kmol	kgi/kgm
N_2	0.60	28	16.8	0.488
CO_2	0.40	44	17.6	0.512

$$M_m = \Sigma y_i M_i = 34.4$$

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

$$R_m = \frac{R_u}{M_m} \qquad (kJ / kg \cdot K)$$

$$= \frac{8.314 \dfrac{kJ}{kmol \cdot K}}{34.4 \dfrac{kg}{kmol}} = 0.242 \frac{kJ}{kg \cdot K}$$

$$m_m = \frac{P_m V_m}{R_m T_m}$$

$$= \frac{1.5 MPa(1m^3)}{(0.242 kJ / (kg \cdot K))(30 + 273) K} \frac{10^3 kJ}{m^3 MPa}$$

$$= 20.45 \ kg$$

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(c) Find the specific heats at 300 K.

Using Table A-2, C_p N_2 = 1.039 kJ/kg·K and C_p CO_2 = 0.846 kJ/kg·K
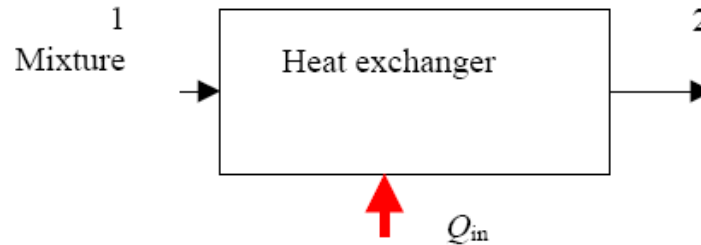
$$C_{p,m} = \sum_1^2 mf_i C_{p,i} = (0.488)(1.039) + (0.512)(0.846)$$

$$= 0.940 \frac{kJ}{kg_m \cdot K}$$

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

$$= 0.698 \frac{kJ}{kg_m \cdot K}$$

(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

$$q_{in} = \frac{\dot{Q}_{in}}{\dot{m}} = C_{p,m}(T_2 - T_1)$$

$$= 0.940 \frac{kJ}{kg_m \cdot K}(120\, K)$$

$$= 112.8 \frac{kJ}{kg_m}$$

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(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

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

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

$$= 362.2 \, K$$

(f) Find ΔS_m per kg of mixture when the mixture is compressed isothermally from 0.1 MPa to 0.2 MPa.

$$\Delta s_m = \frac{\Delta S_m}{m_m} = \sum_{i=1}^{2} mf_i \Delta s_i$$

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

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,

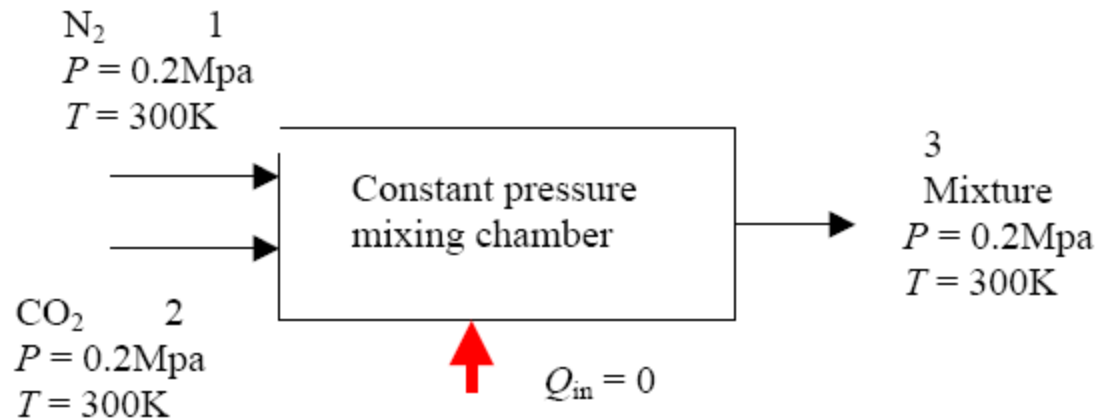$$\Delta s_i = -R_i \ln\left(\frac{P_{m,2}}{P_{m,1}}\right)$$

$$\Delta s_{N_2} = -0.296\frac{kJ}{kg_{N_2} \cdot K} \ln\left(\frac{0.2\,MPa}{0.1\,MPa}\right)$$

$$= -0.206\frac{kJ}{kg_{N_2} \cdot K}$$

$$\Delta s_{CO_2} = -0.1889\frac{kJ}{kg_{CO_2} \cdot K} \ln\left(\frac{0.2\,MPa}{0.1\,MPa}\right)$$

$$= -0.131\frac{kJ}{kg_{CO_2} \cdot K}$$

$$\Delta s_m = \sum_{i=1}^{2} m f_i \Delta s_i$$

$$= (0.488 \frac{kg_{N_2}}{kg_m})(-0.206 \frac{kJ}{kg_{N_2} \cdot K}) + (0.512 \frac{kg_{CO_2}}{kg_m})(-0.131 \frac{kJ}{kg_{CO_2} \cdot K})$$

$$= -0.167 \frac{kJ}{kg_m \cdot K}$$

Why is Δs_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.

N₂   1
P = 0.2Mpa
T = 300K

Constant pressure mixing chamber

3
Mixture
P = 0.2Mpa
T = 300K

CO₂   2
P = 0.2Mpa
T = 300K

$Q_{in} = 0$

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.

$$\Delta s_m = \frac{\Delta S_m}{m_m} = \sum_{i=1}^{2} mf_i \Delta s_i$$

$$\Delta s_i = C_{p,i} \ln\left(\frac{T_3}{T_{i,\,initial}}\right) - R_i \ln\left(\frac{P_{i,3}}{P_{i,\,initial}}\right)$$

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

$$\Delta s_{N_2} = -R_{N_2} \ln\left(\frac{y_{N_2,3} P_3}{y_{N_2,1} P_1}\right)$$

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

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,

$$\Delta s_{N_2} = -0.296 \frac{kJ}{kg_{N_2} \cdot K} \ln\left(\frac{(0.6)0.2\,MPa}{0.2\,MPa}\right)$$

$$= 0.152 \frac{kJ}{kg_{N_2} \cdot K}$$

$$\Delta s_{CO_2} = -0.1889 \frac{kJ}{kg_{CO_2} \cdot K} \ln\left(\frac{(0.4)0.2\,MPa}{0.2\,MPa}\right)$$
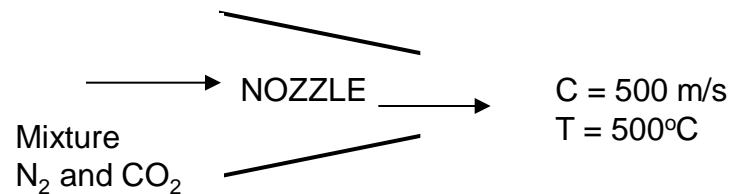
$$= 0.173 \frac{kJ}{kg_{CO_2} \cdot K}$$

Then,

$$\Delta s_m = \sum_{i=1}^{2} mf_i \Delta s_i$$

$$= (0.488 \frac{kg_{N_2}}{kg_m})(0.152 \frac{kJ}{kg_{N_2} \cdot K}) + (0.512 \frac{kg_{CO_2}}{kg_m})(0.173 \frac{kJ}{kg_{CO_2} \cdot K})$$

$$= 0.163 \frac{kJ}{kg_m \cdot K}$$

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

$$C = \sqrt{kRT}$$

NOZZLE

C = 500 m/s
T = 500°C

Mixture
N_2 and CO_2

Answer: $y_{N2} = 0.589$, $y_{CO2} = 0.411$