

# ENGINEERING THERMODYNAMICS -II



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**1. IDEAL GASES AND THEIR MIXTURES** 

# **Objectives**

- Develop rules for determining non-reacting gas mixture properties from knowledge of mixture composition and the properties of the individual components.
- Define the quantities used to describe the composition of a mixture, such as mass fraction, mole fraction, and volume fraction.
- Predict the *P-v-T* behavior of gas mixtures based on Dalton's law of additive pressures and Amagat's law of additive volumes.
- Apply the rules for determining mixture properties to ideal-gas mixtures and real-gas mixtures.

# **1.1 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:

$$\begin{array}{c|c} H_2 \\ 6 \text{ kg} \end{array} + \begin{array}{c} O_2 \\ 32 \text{ kg} \end{array} \rightarrow \begin{array}{c} H_2 + O_2 \\ 38 \text{ kg} \end{array}$$

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



The number of moles of a nonreacting mixture is equal to the sum of the number of moles of its components.

- Molar analysis: specifying the number of moles of each component
- Gravimetric analysis: specifying the mass of each component

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

 $\mathrm{mf}_i = rac{m_i}{m_m}$  Mass fraction

$$y_i = rac{N_i}{N_m}$$
 Mole fraction



Gas constant

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

The molar mass of a mixture

$$M_{m} = \frac{m_{m}}{N_{m}} = \frac{m_{m}}{\sum m_{i}/M_{i}} = \frac{1}{\sum m_{i}/(m_{m}M_{i})} = \frac{1}{\sum_{i=1}^{k} \frac{\mathrm{mf}_{i}}{M_{i}}}$$

Mass and mole fractions of a mixture are related by

$$\mathrm{mf}_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m}$$

The sum of the mass and mole fractions of a mixture is equal to 1.

$$\sum_{i=1}^{k} \mathbf{m} \mathbf{f}_i = 1 \quad \text{and} \quad \sum_{i=1}^{k} y_i = 1$$

$$H_{2} + O_{2}$$

$$y_{H_{2}} = 0.75$$

$$y_{O_{2}} = \frac{0.25}{1.00}$$

The sum of the mole fractions of a mixture is equal to 1.

# EXAMPLE -1.1

Consider a gas mixture that consists of 3kg of  $o_2$ , 5kg of  $N_2$  and 12kg 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

# **1.2.** *P-v-T* BEHAVIOR OF GAS MIXTURES: IDEAL AND REAL GASES

- An 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 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 an *ideal gas* is expressed by the simple relation Pv=RT, which is called the *ideal-gas equation of state*.
- 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.

# *P-v-T* BEHAVIOR OF GAS MIXTURES: IDEAL AND REAL GASES



Dalton's law of additive pressures for a mixture of two ideal gases.



Amagat's law of additive volumes for a mixture of two ideal gases.

The prediction of the P-v-T behavior of gas mixtures is usually based on two models:

➤Dalton's law of additive pressures: 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.

➤Amagat's law of additive volumes: 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.

#### Dalton's law:

Amagat's law:

 $P_{m} = \sum_{i=1}^{k} P_{i}(T_{m}, V_{m})$ exact for ideal gases,  $V_{m} = \sum_{i=1}^{k} V_{i}(T_{m}, P_{m})$ for real gases

*P*<sub>*i*</sub> component pressure  $V_i$  component volume  $P_i / P_m$  pressure fraction  $V_i / V_m$  volume fraction



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  $y_i V_m$ ).

## **Ideal-Gas Mixtures**

For ideal gases, Dalton's and Amagat's laws are identical and give identical results.

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

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

- Note that for an ideal-gas mixture, the mole fraction, the pressure fraction, and the volume fraction of a component are identical.
- This equation is only valid for ideal-gas mixtures as it is derived by assuming ideal-gas behavior for the gas mixture and each of its components.
- The quantity  $y_i P_m$  is called the **partial pressure** (identical to the *component pressure* for ideal gases), and the quantity  $y_i V_m$  is called the **partial volume** (identical to the *component volume* for ideal gases).

## **Real-Gas Mixtures**

### **Compressibility factor**

 $PV = ZNR_uT$   $Z_m = \sum_{i=1}^k y_i Z_i$ 

 $Z_i$  is determined either at  $T_m$  and  $V_m$ Dalton's law) or at  $T_m$  and  $P_m$  (Amagat's law) for each individual gas.

✓ Amagat's law involves the use of mixture pressure  $P_m$ , which accounts for the influence of intermolecular forces between the molecules of different gases.



One way of predicting the *P*-*v*-*T* behavior of a real-gas mixture is to use compressibility factor.

✓ **Dalton's law** disregards the influence of dissimilar molecules in a mixture on each other. As a result, it tends to under predict the pressure of a gas mixture for a given Vm and Tm.

**Dalton's law** is more appropriate for gas mixtures at **low pressures**.

Amagat's law is more appropriate at high pressures.

# **Real-Gas Mixtures**

## Kay's rule

Another way of predicting the P-v-Tbehavior of a real-gas mixture is to treat it as a pseudopure substance with critical properties  $P'_{cr}$  and  $T'_{cr}$ .

 $Z_m$  is determined by using these pseudocritical properties.

The result by Kay's rule is accurate to within about 10% over a wide range of temperatures and pressures.

Pseudopure substance



## EXAMPLE-1.2

A rigid tank contains 2kmol of  $N_2$  and 6kmol of  $CO_2$  gases at 300 K and 15MPa. Estimate the volume of the tank on the basis of

- (*a*) the ideal-gas equation of state,
- (b) Kay's rule,

(c) compressibility factors and Amagat's law, and

(d) compressibility factors and Dalton's law. <u>Exercise</u>

#### **Solution** (a) the ideal-gas equation of state,

**Analysis** (a) When the mixture is assumed to behave as an ideal gas, the volume of the mixture is easily determined from the ideal-gas relation for the mixture:

$$V_m = \frac{N_m R_u T_m}{P_m} = \frac{(8 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(300 \text{ K})}{15,000 \text{ kPa}} = 1.330 \text{ m}^3$$
since  
$$N_m = N_{N_2} + N_{CO_2} = 2 + 6 = 8 \text{ kmol}$$

By using the critical-point properties of N2 and CO2 from Table A–1 and Fig. A-15b, we can easily the critical properties of mixtures

$$y_{N_2} = \frac{N_{N_2}}{N_m} = \frac{2 \text{ kmol}}{8 \text{ kmol}} = 0.25 \text{ and } y_{CO_2} = \frac{N_{CO_2}}{N_m} = \frac{6 \text{ kmol}}{8 \text{ kmol}} = 0.75$$
  

$$T'_{cr,m} = \sum y_i T_{cr,i} = y_{N_2} T_{cr,N_2} + y_{CO_2} T_{cr,CO_2}$$
  

$$= (0.25)(126.2 \text{ K}) + (0.75)(304.2 \text{ K}) = 259.7 \text{ K}$$
  

$$P'_{cr,m} = \sum y_i P_{cr,i} = y_{N_2} P_{cr,N_2} + y_{CO_2} P_{cr,CO_2}$$
  

$$= (0.25)(3.39 \text{ MPa}) + (0.75)(7.39 \text{ MPa}) = 6.39 \text{ MPa}$$

Then,

$$T_{R} = \frac{T_{m}}{T'_{cr,m}} = \frac{300 \text{ K}}{259.7 \text{ K}} = 1.16$$

$$P_{R} = \frac{P_{m}}{P'_{cr,m}} = \frac{15 \text{ MPa}}{6.39 \text{ MPa}} = 2.35$$

$$Z_{m} = 0.49 \quad \text{(Fig. A-15b)}$$

Thus,

$$V_m = \frac{Z_m N_m R_u T_m}{P_m} = Z_m V_{\text{ideal}} = (0.49)(1.330 \text{ m}^3) = 0.652 \text{ m}^3$$

(*c*) compressibility factors and Amagat's law First determine the *Z* of each component on the basis of Amagat's law:

$$N_{2}: \quad T_{R,N_{2}} = \frac{T_{m}}{T_{cr,N_{2}}} = \frac{300 \text{ K}}{126.2 \text{ K}} = 2.38}$$

$$P_{R,N_{2}} = \frac{P_{m}}{P_{cr,N_{2}}} = \frac{15 \text{ MPa}}{3.39 \text{ MPa}} = 4.42$$

$$Z_{N_{2}} = 1.02 \quad (\text{Fig. A-15}b)$$

$$CO_{2}: \quad T_{R,CO_{2}} = \frac{T_{m}}{T_{cr,CO_{2}}} = \frac{300 \text{ K}}{304.2 \text{ K}} = 0.99}$$

$$P_{R,CO_{2}} = \frac{P_{m}}{P_{cr,CO_{2}}} = \frac{15 \text{ MPa}}{7.39 \text{ MPa}} = 2.03$$

$$Z_{CO_{2}} = 0.30 \quad (\text{Fig. A-15}b)$$

Mixture: 
$$Z_m = \sum y_i Z_i = y_{N_2} Z_{N_2} + y_{CO_2} Z_{CO_2}$$
  
= (0.25)(1.02) + (0.75)(0.30) = 0.48

Thus,

$$V_m = \frac{Z_m N_m R_u T_m}{P_m} = Z_m V_{\text{ideal}} = (0.48)(1.330 \text{ m}^3) = 0.638 \text{ m}^3$$

### Assignment: 1.1

• 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.



# **1.3. PROPERTIES OF GAS MIXTURES:** IDEAL AND REAL GASES

#### Extensive properties of a gas mixture

$$U_m = \sum_{i=1}^k U_i = \sum_{i=1}^k m_i u_i = \sum_{i=1}^k N_i \overline{u}_i \qquad (kJ)$$
$$H_m = \sum_{i=1}^k H_i = \sum_{i=1}^k m_i h_i = \sum_{i=1}^k N_i \overline{h}_i \qquad (kJ)$$

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

 $\overline{z} = 1$ 

#### Changes in properties of a gas mixture

 $\overline{z} = 1$ 

2-1

$$\Delta U_m = \sum_{i=1}^k \Delta U_i = \sum_{i=1}^k m_i \,\Delta u_i = \sum_{i=1}^k N_i \,\Delta \overline{u}_i \qquad (kJ)$$

$$\Delta H_m = \sum_{i=1}^k \Delta H_i = \sum_{i=1}^k m_i \,\Delta h_i = \sum_{i=1}^k N_i \,\Delta \overline{h}_i \qquad (kJ)$$

$$\Delta S_m = \sum_{i=1}^k \Delta S_i = \sum_{i=1}^k m_i \,\Delta s_i = \sum_{i=1}^k N_i \,\Delta \overline{s}_i \qquad (kJ/K)$$

2 kmol A 6 kmol B  $U_A = 1000 \text{ kJ}$   $U_B = 1800 \text{ kJ}$   $\bigcup_{m} = 2800 \text{ kJ}$ 

The extensive properties of a mixture are determined by simply adding the properties of the components.





The **intensive properties** of a mixture are determined by weighted averaging.

Properties per unit mass involve mass fractions  $(mf_i)$  and properties per unit mole involve mole fractions  $(y_i)$ .

The relations are exact for ideal-gas mixtures, and approximate for real-gas mixtures.

#### **Ideal-Gas Mixtures**

**Gibbs–Dalton law:** Under the ideal-gas approximation, the properties of a gas are not influenced by the presence of other gases, and each gas component in the mixture behaves as if it exists alone at the mixture temperature  $T_m$  and mixture volume  $V_m$ .

Also, the *h*, *u*,  $c_v$ , and  $c_p$  of an ideal gas depend on temperature only and are independent of the pressure or the volume of the ideal-gas mixture.

$$\Delta s_{i} = s_{i,2}^{\circ} - s_{i,1}^{\circ} - R_{i} \ln \frac{P_{i,2}}{P_{i,1}} \cong c_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_{i} \ln \frac{P_{i,2}}{P_{i,1}}$$
$$\Delta \overline{s}_{i} = \overline{s}_{i,2}^{\circ} - \overline{s}_{i,1}^{\circ} - R_{u} \ln \frac{P_{i,2}}{P_{i,1}} \cong \overline{c}_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_{u} \ln \frac{P_{i,2}}{P_{i,1}}$$

 $P_{i,2} = y_{i,2}P_{m,2}$   $P_{i,1} = y_{i,1}P_{m,1}$ 



Partial pressures (not the mixture pressure) are used in the evaluation of entropy changes of ideal-gas mixtures.

## Example 1.3

A 0.9-m3 rigid tank is divided into two equal compartments by a partition. One compartment contains Ne at 20°C and 100 kPa, and the other compartment contains Ar at 50°C and 200 kPa. Now the partition is removed, and the two gases are allowed to mix. Heat is lost to the surrounding air during this process in the amount of 15 kJ. Determine (*a*) *the* final mixture temperature and (*b*) *the final mixture pressure*.

*Properties* The molar masses and specific heats of Ne and Ar are 20.18 kg/kmol, 39.95 kg/kmol, 0.6179 kJ/kg.°C, and 0.3122 kJ/kg.°C, respectively. (Tables A-1 and A-2).

Analysis The mole number of each gas is

$$N_{\text{Ne}} = \left(\frac{P_{1}\boldsymbol{V}_{1}}{R_{u}T_{1}}\right)_{\text{Ne}} = \frac{(100 \text{ kPa})(0.45 \text{ m}^{3})}{(8.314 \text{ kPa} \cdot \text{m}^{3}/\text{kmol} \cdot \text{K})(293 \text{ K})} = 0.0185 \text{ kmol}$$

$$N_{\text{Ar}} = \left(\frac{P_{1}\boldsymbol{V}_{1}}{R_{u}T_{1}}\right)_{\text{Ar}} = \frac{(200 \text{ kPa})(0.45 \text{ m}^{3})}{(8.314 \text{ kPa} \cdot \text{m}^{3}/\text{kmol} \cdot \text{K})(323 \text{ K})} = 0.0335 \text{ kmol}$$

$$N_{\text{Ar}} = \left(\frac{P_{1}\boldsymbol{V}_{1}}{R_{u}T_{1}}\right)_{\text{Ar}} = \frac{(200 \text{ kPa})(0.45 \text{ m}^{3})}{(8.314 \text{ kPa} \cdot \text{m}^{3}/\text{kmol} \cdot \text{K})(323 \text{ K})} = 0.0335 \text{ kmol}$$

15 kJ

Thus,

 $N_m = N_{\text{Ne}} + N_{\text{Ar}} = 0.0185 \text{ kmol} + 0.0335 \text{ kmol} = 0.0520 \text{ kmol}$ 

(a) We take both gases as the system. No work or mass crosses the system boundary, therefore this is a closed system with W = 0. Then the conservation of energy equation for this closed system reduces to

$$E_{\rm in} - E_{\rm out} = \Delta E_{\rm system}$$
$$-Q_{\rm out} = \Delta U = \Delta U_{\rm Ne} + \Delta U_{\rm Ar} \longrightarrow -Q_{\rm out} = \left[mc_v (T_m - T_1)\right]_{\rm Ne} + \left[mc_v (T_m - T_1)\right]_{\rm Ar}$$

Using  $c_v$  values at room temperature and noting that m = NM, the final temperature of the mixture is determined to be

$$-15 \text{ kJ} = (0.0185 \times 20.18 \text{ kg})(0.6179 \text{ kJ/kg} \cdot ^{\circ}\text{C})(T_m - 20^{\circ}\text{C}) + (0.0335 \times 39.95 \text{ kg})(0.3122 \text{ kJ/kg} \cdot ^{\circ}\text{C})(T_m - 50^{\circ}\text{C}) T_m = 16.2^{\circ}\text{C} (289.2 \text{ K})$$

(b) The final pressure in the tank is determined from

$$P_m = \frac{N_m R_u T_m}{V_m} = \frac{(0.052 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3 / \text{kmol} \cdot \text{K})(289.2 \text{ K})}{0.9 \text{ m}^3} = 138.9 \text{ kPa}$$

#### Example 1.4

 A mixture that is 20 percent carbon dioxide, 10 percent oxygen, and 70 percent nitrogen by volume undergoes a process from 300 K and 100 kPa to 500 K and 400 kPa. Determine the makeup of the mixture on a mass basis and the enthalpy change per unit mass of mixture.

Properties The molar masses of CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> are 44.0, 32.0, and 28.0 kg/kmol, respectively (Table A-1).

Analysis Noting that volume fractions are equal to mole fractions in ideal gas mixtures, the molar mass of the mixture is determined to be

 $M_m = y_{\rm CO_2} M_{\rm CO_2} + y_{\rm O_2} M_{\rm O_2} + y_{\rm N_2} M_{\rm N_2} = (0.20)(44 \text{ kg/kmol}) + (0.10)(32) + (0.70)(28) = 31.60 \text{ kg/kmol}$ 

The mass fractions are



The enthalpy change of each gas and the enthalpy change of the mixture are (from Tables A-18-20)

$$\Delta h_{\rm CO_2} = \frac{\overline{h_{@.500\,\rm K} - \overline{h_{@.300\,\rm K}}}}{M_{\rm CO_2}} = \frac{(17,678 - 9431)\,\rm kJ/kmol}{44\,\rm kg/kmol} = 187.43\,\rm kJ/kg$$

$$\Delta h_{\rm O_2} = \frac{\overline{h_{@.500\,\rm K} - \overline{h_{@.300\,\rm K}}}}{M_{\rm O_2}} = \frac{(14,770 - 8736)\,\rm kJ/kmol}{32\,\rm kg/kmol} = 188.56\,\rm kJ/kg$$

$$\Delta h_{\rm N_2} = \frac{\overline{h_{@.500\,\rm K} - \overline{h_{@.300\,\rm K}}}}{M_{\rm N_2}} = \frac{(14,581 - 8723)\,\rm kJ/kmol}{28\,\rm kg/kmol} = 209.21\,\rm kJ/kg$$

$$\Delta h_m = \rm mf_{\rm CO_2}\,\Delta h_{\rm CO_2} + \rm mf_{O_2}\,\Delta h_{O_2} + \rm mf_{N_2}\,\Delta h_{N_2}$$

$$= (0.2785)(187.43) + (0.1013)(188.56) + (0.6203)(209.21)$$

$$= 201.1\,\rm kJ/kg$$

## Assignment 1.2

Air, which may be considered as a mixture of 79 percent  $N_2$  and 21 percent  $O_2$  by mole numbers, is compressed isothermally at 200 K from 4 to 8MPa in a steady-flow device. The compression process is internally reversible, and the mass flow rate of air is 2.9 kg/s. Determine the power input to the compressor and the rate of heat rejection by treating the mixture (*a*) as an ideal gas and (*b*) as a non-ideal gas and using Amagat's law.



#### Assignment 1.3

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.
- b) What is the mass of 1 m<sup>3</sup> of this gas when P = 1.5MPa and  $T = 30^{\circ}C$ ?
- c) Find the specific heats at 300 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.
- e) This mixture undergoes an isentropic process from 0.1MPa, 30°C, to 0.2MPa. Find  $T_2$ .
- f) Find  $\Delta$ Sm per kg of mixture when the mixture is compressed isothermally from 0.1MPa to 0.2MPa.
- g) Both the  $N_2$  and  $CO_2$  are supplied in separate lines at 0.2MPa 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.

# **Thank You for your attention!**

