Chapter 13
GAS MIXTURES

Prof. Dr. Ali PINARBAŞI

**Yildiz Technical University**

Mechanical Engineering Department
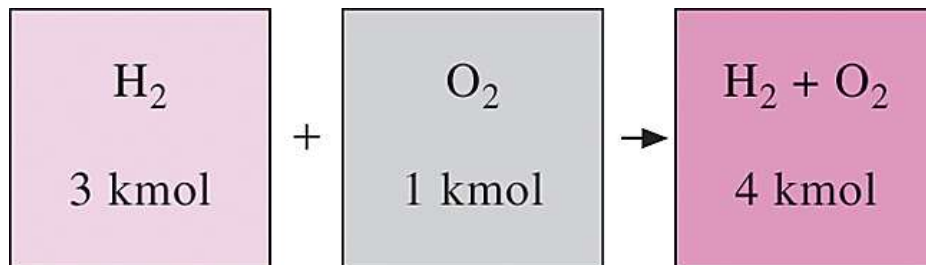
Yildiz, ISTANBUL

- Develop rules for determining nonreacting 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.

- Apply the rules for determining mixture properties to idealgas mixtures and real-gas mixtures.

- Predict the P-v-T behavior of gas mixtures based on Dalton's law of additive pressures and Amagat's law of additive volumes.

- Develop the concept of chemical potential and determine the separation work of mixtures...

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.**

H_2		O_2		$H_2 + O_2$
6 kg	+	32 kg	→	38 kg
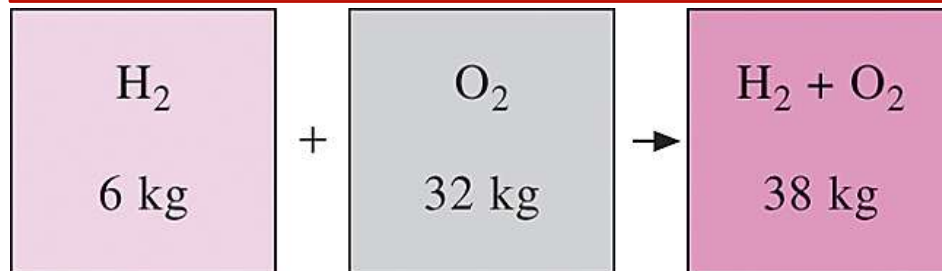
The mass of a mixture is equal to the sum of the masses of its components.

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

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

$$y_i = \frac{N_i}{N_m}$$

H_2		O_2		$H_2 + O_2$
3 kmol	+	1 kmol	→	4 kmol

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

The ratio of the mass of a component to the mass of the mixture is called the **mass fraction** m_f

$$mf_i = \frac{m_i}{m_m}$$

the apparent (or average) molar mass

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

the sum of the mass fractions or mole fractions for a mixture is equal to 1

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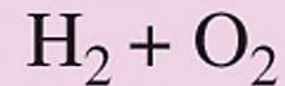
$$m = NM$$

gas constant

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

The molar mass of a mixture can also be expressed as

$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i/M_i} = \frac{1}{\sum m_i/(m_m M_i)} = \frac{1}{\sum_{i=1}^{k} \frac{\text{mf}_i}{M_i}}$$

$$H_2 + O_2$$

$$y_{H_2} = 0.75$$
$$y_{O_2} = \frac{0.25}{1.00}$$

Mass and mole fractions of a mixture

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

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

Prof. Dr. Ali PINARBAŞI

Example 13-1

Consider a gas mixture that 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.

3 kg O_2
5 kg N_2
12 kg CH_4

(a) the mass fraction of each component,

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

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

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

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

$$mf_{CH_4} = \frac{m_{CH_4}}{m_m} = \frac{12 \text{ kg}}{20 \text{ kg}} = 0.60$$

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

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

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

Prof. Dr. Ali PINARBAŞI

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

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

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

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

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

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

$$M_m = \sum y_i M_i = y_{O_2} M_{O_2} + y_{N_2} M_{N_2} + y_{CH_4} M_{CH_4}$$
$$= (0.092)(32) + (0.175)(28) + (0.733)(16)$$
$$= 19.6 \text{ kg/kmol}$$

$$R_m = \frac{R_u}{M_m} = \frac{8.314 \text{ kJ/(kmol} \cdot \text{K)}}{19.6 \text{ kg/kmol}} = \mathbf{0.424 \text{ kJ/kg} \cdot \text{K}}$$

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: *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.*
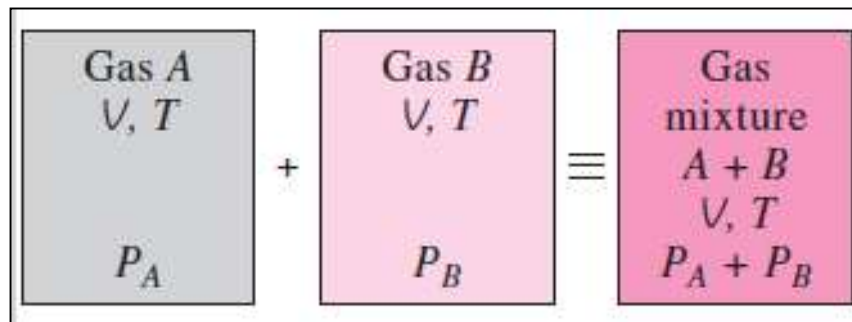
Dalton's law of additive pressures for a mixture of two ideal gases.
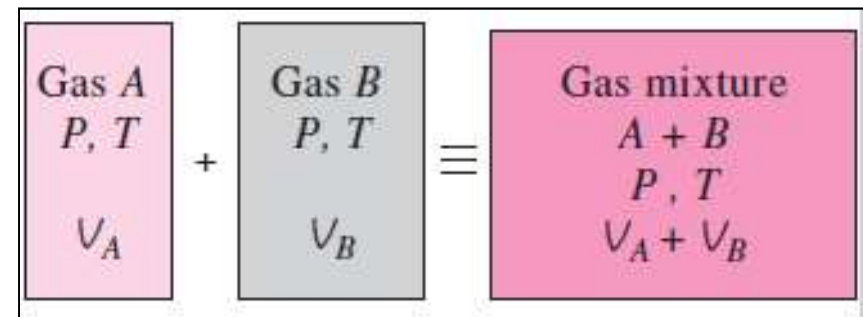
Amagat's law of additive volumes for a mixture of two ideal gases.

Dalton's law:

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

Amagat's law:

$$V_m = \sum_{i=1}^{k} V_i(T_m, P_m)$$
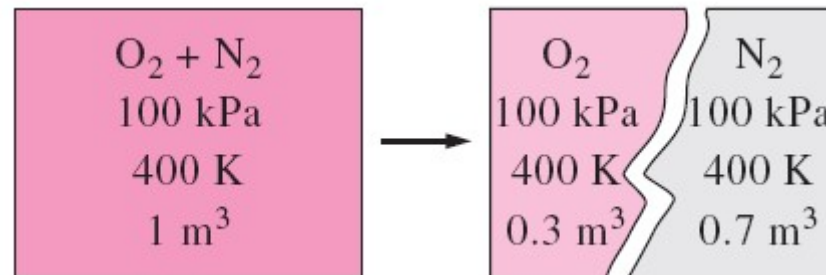
exact for ideal gases, approximate for real gases

P_i component pressure	V_i component volume
P_i/P_m pressure fraction	V_i/V_m volume fraction

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

$O_2 + N_2$
100 kPa
400 K
1 m³

$\longrightarrow$

O_2
100 kPa
400 K
0.3 m³

N_2
100 kPa
400 K
0.7 m³

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

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

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

$\longrightarrow$

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

This equation 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.
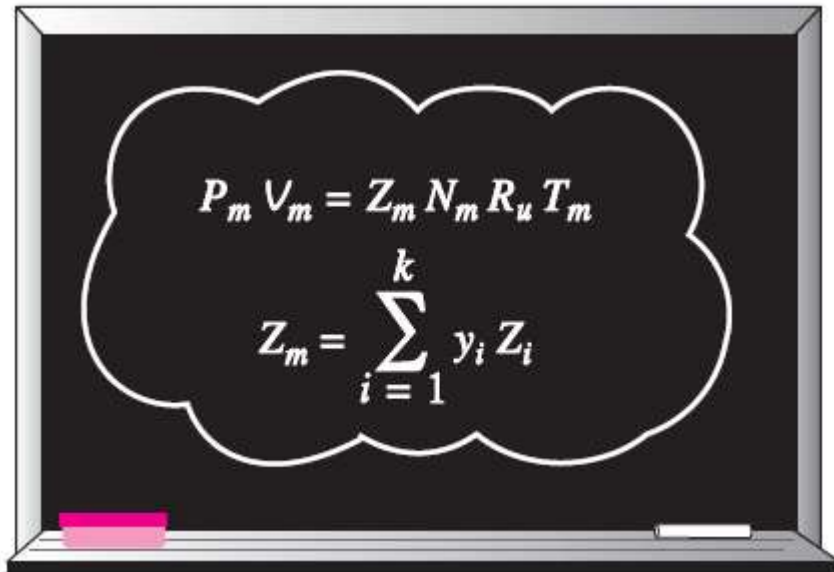
The quantity $y_i P_m$ is called the **partial pressure** (identical to the *component pressure* for ideal gases), and the quantity $y_i V_m$ is called the **partial volume**.

Note that for an ideal-gas mixture, the mole fraction, the pressure fraction, and the volume fraction of a component are identical.

Real-Gas Mixtures

| Compressibility factor | $PV = ZNR_uT$ |

$$P_m V_m = Z_m N_m R_u T_m$$

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

The compressibility-factor approach, in general, gives more accurate results when the Z_i's in below equation are evaluated by using Amagat's law instead of Dalton's law.

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

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

Another approach for predicting the *P-v-T* behavior of a gas mixture is to treat the gas mixture as a pseudo pure substance.

One such method, proposed by W. B. Kay in 1936 and called **Kay's rule,** involves the use of a *pseudo critical pressure* and *pseudo critical temperature* for the mixture, defined in terms of the critical pressures and temperatures of the mixture components as

Kay's Rule

$$P'_{cr,m} = \sum_{i=1}^{k} y_i P_{cr,i} \quad \text{and} \quad T'_{cr,m} = \sum_{i=1}^{k} y_i T_{cr,i}$$

Pseudopure substance

$$P'_{cr,m} = \sum_{i=1}^{k} y_i P_{cr,i}$$

$$T'_{cr,m} = \sum_{i=1}^{k} y_i T_{cr,i}$$

The compressibility factor of the mixture Z_m is then easily determined by using these pseudo critical properties.

The result obtained by using Kay's rule is accurate to within about 10 % over a wide range of temperatures and pressures, which is acceptable for most engineering purposes.

Prof. Dr. Ali PINARBAŞI

Example 13-2

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) Kay's rule,
(c) Compressibility factors and Amagat's law, and
(d) Compressibility factors and Dalton's law.

> 2 kmol N_2
> 6 kmol CO_2
> 300 K
> 15 MPa
> $V_m = ?$

(a) The ideal-gas equation of state,.

$$V_m = \frac{N_m R_u T_m}{P_m} = \frac{(8 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(300 \text{ K})}{15000 \text{ kPa}} = \textbf{1.330 m}^3$$

$$N_m = N_{N_2} + N_{CO_2} = 2 + 6 = 8 \text{ kmol}$$

(b) Kay's rule

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

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

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

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

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

Prof. Dr. Ali PINARBAŞI

$$T_R = \frac{T_m}{T'_{kr,m}} = \frac{300 \text{ K}}{259.7 \text{ K}} = 1.16$$
$$P_R = \frac{P_m}{P'_{kr,m}} = \frac{15 \text{ MPa}}{6.39 \text{ MPa}} = 2.35$$
$$\left.\right\} Z_m = 0.49$$

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

(c) Compressibility factors and Amagat's law,

$$N_2: \quad T_{R,N_2} = \frac{T_m}{T_{kr,N_2}} = \frac{300 \text{ K}}{126.2 \text{ K}} = 2.38$$
$$P_{R,N_2} = \frac{P_m}{P_{kr,N_2}} = \frac{15 \text{ MPa}}{3.39 \text{ MPa}} = 4.42$$
$$\left.\right\} Z_{N_2} = 1.02$$

$$CO_2: \quad T_{R,CO_2} = \frac{T_m}{T_{kr,CO_2}} = \frac{300 \text{ K}}{304.2 \text{ K}} = 0.99$$
$$P_{R,CO_2} = \frac{P_m}{P_{kr,CO_2}} = \frac{15 \text{ MPa}}{7.39 \text{ MPa}} = 2.03$$
$$\left.\right\} Z_{CO_2} = 0.30$$

Mixture:

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

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

Prof. Dr. Ali PINARBAŞI

$$V_{R,N_2} = \frac{\bar{v}_{N_2}}{R_u T_{kr,N_2}/P_{cr,N_2}} = \frac{V_m/N_{N_2}}{R_u T_{kr,N_2}/P_{kr,N_2}}$$

$$= \frac{(1.33 \text{ m}^3)/(2 \text{ kmol})}{(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(126.2 \text{ K})/(3390 \text{ kPa})} = 2.15$$

$$V_{R,CO_2} = \frac{(1.33 \text{ m}^3)/(6 \text{ kmol})}{(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(304.2 \text{ K})/(7390 \text{ kPa})} = 0.648$$

$Z_{N_2} = 0.99$ ve $Z_{CO_2} = 0.56$

$$Z_m = y_{N_2} Z_{N_2} + y_{CO_2} Z_{CO_2} = (0.25)(0.99) + (0.75)(0.56) = 0.67$$

$$V_m = \frac{Z_m N_m R T_m}{P_m} = Z_m V_{mükemmel} = (0.67)(1.330 \text{ m}^3) = 0.891 \text{ m}^3 \qquad V_m = \mathbf{0.648 \text{ m}^3}$$

Discussion Notice that the results obtained in parts (*b*), (*c*), and (*d*) are very close. But they are very different from the values obtained from the ideal-gas relation. Therefore, treating a mixture of gases as an ideal gas may yield unacceptable errors at high pressures.

extensive properties

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

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

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

the changes in internal energy, enthalpy, and entropy

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

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

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

2 kmol A

6 kmol B

$U_A = 1000$ kJ

$U_B = 1800$ kJ

$U_m = 2800$ kJ

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

$$u_m = \sum_{i=1}^{k} mf_i u_i \quad (kJ/kg) \qquad ve \qquad \bar{u}_m = \sum_{i=1}^{k} y_i \bar{u}_i \quad (kJ/kmol)$$

$$h_m = \sum_{i=1}^{k} mf_i h_i \quad (kJ/kg) \qquad ve \qquad \bar{h}_m = \sum_{i=1}^{k} y_i \bar{h}_i \quad (kJ/kmol)$$

$$s_m = \sum_{i=1}^{k} mf_i s_i \quad (kJ/kg \cdot K) \qquad ve \qquad \bar{s}_m = \sum_{i=1}^{k} y_i \bar{s}_i \quad (kJ/kmol \cdot K)$$

$$c_{v,m} = \sum_{i=1}^{k} mf_i c_{v,i} \quad (kJ/kg \cdot K) \qquad ve \qquad \bar{c}_{v,m} = \sum_{i=1}^{k} y_i \bar{c}_{v,i} \quad (kJ/kmol \cdot K)$$

$$c_{p,m} = \sum_{i=1}^{k} mf_i c_{p,i} \quad (kJ/kg \cdot K) \qquad ve \qquad \bar{c}_{p,m} = \sum_{i=1}^{k} y_i \bar{c}_{p,i} \quad (kJ/kmol \cdot K)$$

2 kmol A

3 kmol B

$\bar{u}_A = 500$ kJ/kmol

$\bar{u}_B = 600$ kJ/kmol

$\bar{u}_m = 560$ kJ/kmol

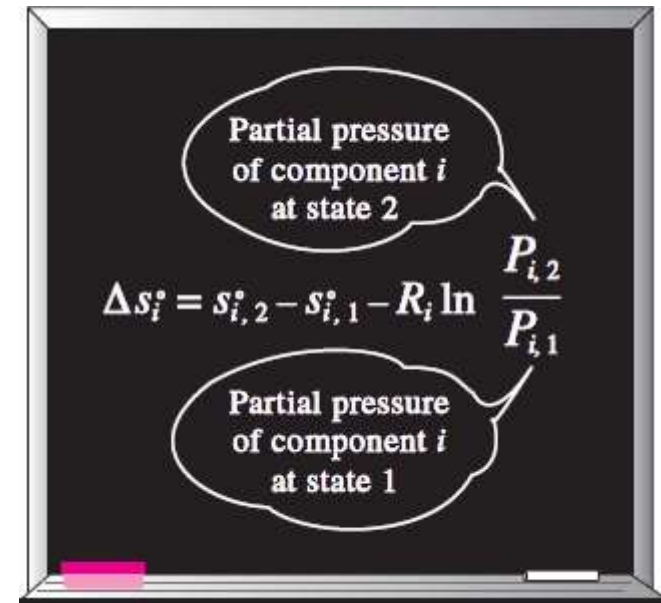The intensive properties of a mixture are determined by weighted averaging

Notice that *properties per unit mass involve mass fractions* (m_{f_i}) *and properties per unit mole involve mole fractions* (y_i).

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

Ideal-Gas Mixtures

Gibbs–Dalton's 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.

Partial pressure of component i at state 2

$$\Delta s_i^\circ = s_{i,2}^\circ - s_{i,1}^\circ - R_i \ln \frac{P_{i,2}}{P_{i,1}}$$

Partial pressure of component i at state 1

$$\Delta s_i = s_{i,2}^\circ - s_{i,1}^\circ - R_i \ln \frac{P_{i,2}}{P_{i,1}} \cong c_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_i \ln \frac{P_{i,2}}{P_{i,1}}$$

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

$$\Delta \overline{s}_i = \overline{s}_{i,2}^\circ - \overline{s}_{i,1}^\circ - R_u \ln \frac{P_{i,2}}{P_{i,1}} \cong \overline{c}_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_u \ln \frac{P_{i,2}}{P_{i,1}}$$

$$P_{i,2} = y_{i,2} P_{m,2} \quad \text{ve} \quad P_{i,1} = y_{i,1} P_{m,1}$$

Example 13-3

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 compartment 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.

O_2	N_2
7 kg	4 kg
40°C	20°C
100 kPa	150 kPa
	←Partition
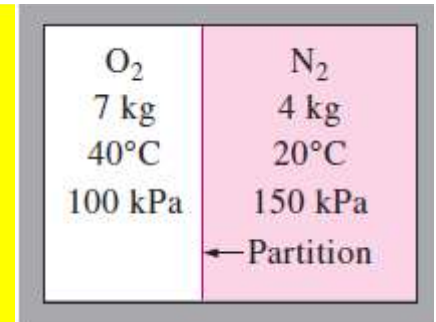
(a) the mixture temperature

$$E_g - E_ç = \Delta E_{sistem}$$

$$0 = \Delta U = \Delta U_{N_2} + \Delta U_{O_2}$$

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

$$(4 \text{ kg})(0.743 \text{ kJ/kg} \cdot \text{K})(T_m - 20°C) + (7 \text{ kg})(0.658 \text{ kJ/kg} \cdot \text{K})(T_m - 40°C) = 0$$

$$T_m = \textbf{32.2°C}$$

(b) The final pressure of the mixture is determined from the ideal-gas relation

$$P_m V_m = N_m R_u T_m$$

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

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

Prof. Dr. Ali PINARBAŞI

$$N_m = N_{O_2} + N_{N_2} = 0.219 + 0.143 = 0.362 \text{ kmol}$$

$$V_{O_2} = \left(\frac{N R_u T_1}{P_1} \right)_{O_2} = \frac{(0.219 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(313 \text{ K})}{100 \text{ kPa}} = 5.70 \text{ m}^3$$

$$V_{N_2} = \left(\frac{N R_u T_1}{P_1} \right)_{N_2} = \frac{(0.143 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(293 \text{ K})}{150 \text{ kPa}} = 2.32 \text{ m}^3$$

$$V_m = V_{O_2} + V_{N_2} = 5.70 + 2.32 = 8.02 \text{ m}^3$$

$$P_m = \frac{N_m R_u T_m}{V_m} = \frac{(0.362 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(305.2 \text{ K})}{8.02 \text{ m}^3} = \textbf{114.5 kPa}$$

Discussion We could also determine the mixture pressure by using $P_m V_m = m_m R_m T_m$, where R_m is the apparent gas constant of the mixture. This would require a knowledge of mixture composition in terms of mass or mole fractions.

Prof. Dr. Ali PINARBAŞI

Example 13-4

An insulated rigid tank is divided into two compartments by a partition. One compartment contains 3 kmol of O_2, and the other compartment contains 5 kmol of CO_2. Both gases are initially at 25°C and 200 kPa. Now the partition is removed, and the two gases are allowed to mix. Assuming the surroundings are at 25°C and both gases behave as ideal gases, determine the entropy change and exergy destruction associated with this process.

O_2	CO_2
25°C	25°C
200 kPa	200 kPa
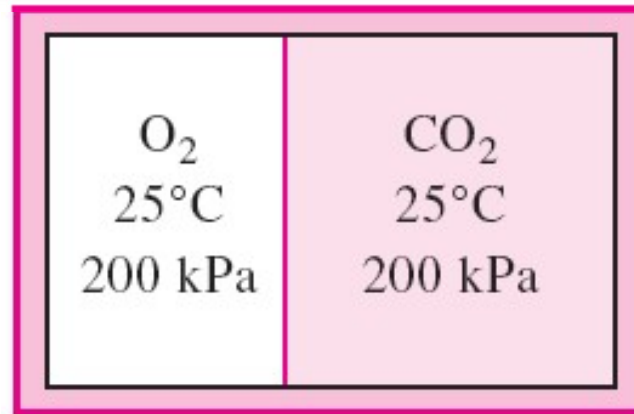
$P_{m,2}=P_{i,1}=200$ kPa

$$\Delta S_m = \sum \Delta S_i = \sum N_i \, \Delta \bar{s}_i = \sum N_i \left(\bar{c}_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} \nearrow^0 - R_u \ln \frac{P_{i,2}}{P_{i,1}} \right)$$

$$= -R_u \sum N_i \ln \frac{y_{i,2} P_{m,2}}{P_{i,1}} = -R_u \sum N_i \ln y_{i,2}$$

Prof. Dr. Ali PINARBAŞI

$$N_m = N_{O_2} + N_{CO_2} = (3 + 5) \text{ kmol} = 8 \text{ kmol}$$

$$y_{O_2} = \frac{N_{O_2}}{N_m} = \frac{3 \text{ kmol}}{8 \text{ kmol}} = 0.375 \qquad y_{CO_2} = \frac{N_{CO_2}}{N_m} = \frac{5 \text{ kmol}}{8 \text{ kmol}} = 0.625$$

$$\Delta S_m = -R_u(N_{O_2} \ln y_{O_2} + N_{CO_2} \ln y_{CO_2})$$

$$= -(8.314 \text{ kJ/kmol} \cdot \text{K})[(3 \text{ kmol})(\ln 0.375) + (5 \text{ kmol})(\ln 0.625)] = \mathbf{44.0 \text{ kJ/K}}$$

The exergy destruction associated with this mixing process is determined from

$$X_{\text{yok olan}} = T_0 S_{\text{üretim}} = T_0 \Delta S_{\text{sistem}}$$

$$= (298 \text{ K})(44.0 \text{ kJ/K}) = \mathbf{13.1 \text{ MJ}}$$

Gerçek Gaz Karışımları

Bir gaz karışımı için T ds bağıntısı

$$dh_m = T_m \, ds_m + v_m \, dP_m$$

$$d\left(\sum mf_i h_i\right) = T_m \, d\left(\sum mf_i s_i\right) + \left(\sum mf_i v_i\right) dP_m$$

$$\sum mf_i(dh_i - T_m \, ds_i - v_i \, dP_m) = 0$$

$$dh_i = T_m \, ds_i + v_i \, dP_m$$

Gerçek gaz A	Gerçek gaz B
25°C	25°C
0.4 m³	0.6 m³
100 kPa	100 kPa

Gerçek gaz karışımı
A + B
25°C
1 m³
102 kPa ?

Gerçek gaz karışımlarının davranışlarını belirlemek zordur, çünkü birbirinden farklı moleküllerin karşılıklı etkilerini göz önüne almak gerekir.

$$dh_i = T_m\, ds_i + \mathsf{v}_i\, dP_m$$

Denklem entalpi ve entropi için genelleştirilmiş bağıntıları ve diyagramları geliştirmenin başlangıç noktasıdır. Ayrıca gerçek gazlar için geliştirilen genelleştirilmiş özelik bağıntılarının ve diyagramlarının, gerçek gaz karışımını oluşturan gazlar için de kullanılabileceğini belirtmektedir.

Fakat her karışım için indirgenmiş sıcaklık, T_R ve indirgenmiş basınç P_m, karışım sıcaklığı T_m ve karışım basıncı P_m'de hesaplanmalıdır.
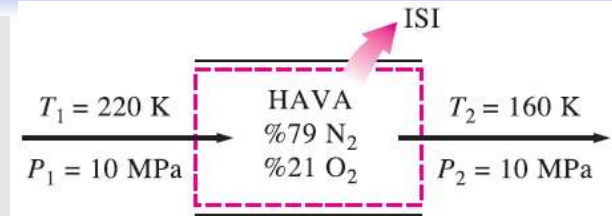
Karışım basıncı ve sıcaklığı yerine karışım hacim ve sıcaklığı verilirse izlenecek olan yol, Dalton'un toplanan basınçlar yasasını kullanarak yaklaşık bir karışım basıncı belirlemektir.

Gerçek bir gaz karışımının özeliklerini belirlemenin bir başka yolu da, karışımı sanki-kritik özelikleri olan, sanki-saf bir madde gibi ele almaktır. Burada sanki-kritik özelikler, karışanların kritik özeliklerinden Kay kuralını kullanarak belirlenir.

Örnek 13-5

Hava genellikle N_2 ve O_2'den oluşan bir karışım olarak ele alınır. Bu karışımda N_2 ve 0_2'nin mol oranları sırasıyla % 79 ve % 21'dir. Sürekli akışlı bir açık sistemde, hava 10 MPa sabit basınçta, 220 K'den 160 K sıcaklığa soğutulmaktadır. Havadan çevreye olan ısı geçişini, (a) mükemmel gaz yaklaşımıyla, (b) Kay kuralını kullanarak, (c) Amagat yasasını kullanarak hesaplayın..

$$e_g - e_ç = \Delta e_{sistem}^{\nearrow 0} = 0 \rightarrow e_g = e_ç \rightarrow \bar{h}_1 = \bar{h}_2 + \bar{q}_ç$$

$$\bar{q}_ç = \bar{h}_1 - \bar{h}_2 = y_{N_2}(\bar{h}_1 - \bar{h}_2)_{N_2} + y_{O_2}(\bar{h}_1 - \bar{h}_2)_{O_2}$$

ISI

$T_1 = 220$ K $\quad$ HAVA $\quad$ $T_2 = 160$ K
$P_1 = 10$ MPa $\quad$ %79 N_2 / %21 O_2 $\quad$ $P_2 = 10$ MPa

$$\bar{h}_1 - \bar{h}_2 = \bar{h}_{1,mük} - \bar{h}_{2,mük} - R_u T_{kr}(Z_{h1} - Z_{h2})$$

(a) N_2, O_2 karışımının mükemmel gaz olduğu kabul edilirse

$$T_1 = 220 \text{ K} \rightarrow \bar{h}_{1,mük,N_2} = 6391 \text{ kJ/kmol}$$

$$\bar{h}_{1,mük,O_2} = 6404 \text{ kJ/kmol}$$

$$T_2 = 160 \text{ K} \rightarrow \bar{h}_{2,mük,N_2} = 4648 \text{ kJ/kmol}$$

$$\bar{h}_{2,mük,O_2} = 4657 \text{ kJ/kmol}$$

$$\bar{q}_ç = y_{N_2}(\bar{h}_1 - \bar{h}_2)_{N_2} + y_{O_2}(\bar{h}_1 - \bar{h}_2)_{O_2}$$
$$= (0.79)(6391 - 4648) \text{ kJ/kmol} + (0.21)(6404 - 4657) \text{ kJ/kmol}$$
$$= \textbf{1744 kJ/kmol}$$

(b) Kay kuralına göre, sanki-saf bir madde gibi davranan bir gaz karışımının kritik sıcaklığı ve basıncı;

$$T'_{kr,m} = \sum y_i T_{kr,i} = y_{N_2} T_{kr,N_2} + y_{O_2} T_{kr,O_2}$$
$$= (0.79)(126.2 \text{ K}) + (0.21)(154.8 \text{ K}) = 132.2 \text{ K}$$

$$P'_{kr,m} = \sum y_i P_{kr,i} = y_{N_2} P_{kr,N_2} + y_{O_2} P_{kr,O_2}$$
$$= (0.79)(3.39 \text{ MPa}) + (0.21)(5.08 \text{ MPa}) = 3.74 \text{ MPa}$$

$$T_{R,1} = \frac{T_{m,1}}{T_{kr,m}} = \frac{220 \text{ K}}{132.2 \text{ K}} = 1.66$$

$$\left.\begin{array}{l} P_R = \dfrac{P_m}{P_{kr,m}} = \dfrac{10 \text{ MPa}}{3.74 \text{ MPa}} = 2.67 \end{array}\right\} \quad Z_{h_1,m} = 1.0$$

$$\left.\begin{array}{l} T_{R,2} = \dfrac{T_{m,2}}{T_{kr,m}} = \dfrac{160 \text{ K}}{132.2 \text{ K}} = 1.21 \end{array}\right\} \quad Z_{h_2,m} = 2.6$$

$$\overline{h}_{m_1,\text{mük}} = y_{N_2}\overline{h}_{1,\text{mük},N_2} + y_{O_2}\overline{h}_{1,\text{mük},O_2}$$

$$= (0.79)(6391 \text{ kJ/kmol}) + (0.21)(6404 \text{ kJ/kmol})$$

$$= 6394 \text{ kJ/kmol}$$

$$\overline{h}_{m_2,\text{mük}} = y_{N_2}\overline{h}_{2,\text{mük},N_2} + y_{O_2}\overline{h}_{2,\text{mük},O_2}$$

$$= (0.79)(4648 \text{ kJ/kmol}) + (0.21)(4657 \text{ kJ/kmol})$$

$$= 4650 \text{ kJ/kmol}$$

$$\overline{q}_ç = (\overline{h}_{m_1,\text{mük}} - \overline{h}_{m_2,\text{mük}}) - R_u T_{\text{kr}}(Z_{h_1} - Z_{h_2})_m$$

$$= [(6394 - 4650) \text{ kJ/kmol}] - (8.314 \text{ kJ/kmol} \cdot \text{K})(132.2 \text{ K})(1.0 - 2.6)$$

$$= \textbf{3503 kJ/kmol}$$