

Non-Reacting Mixtures

Many important thermodynamic applications involve mixtures of several pure substances. A non-reacting gas mixture can be treated as a pure substance since it is usually a homogenous mixture of different gases (called components or constituents).

Homogeneous gas mixtures are frequently treated as a single compound rather than many individual constituents. For instance, air consists of oxygen, nitrogen, argon and water vapor. But dry air can be treated as a simple gas with a molar mass of 28.97 kg/kmol.

We need to develop equations to express the properties of mixtures in terms of the properties of their individual constituents.

Some definitions

The mass of a 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 number of the individual components:

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

Mass fraction, mf: the ratio of the mass of a component to the mass of the mixture

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

Mole fraction, y: the ratio of the mole number of a component to the mole number of the mixture

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

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

The mass of a substance can be expressed as: $m = NM$.

Apparent molar mass:

$$M_m = \frac{m_m}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum y_i M_i \quad \text{or}$$
$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i / M_i} = \frac{1}{\sum m_i / (m_m M_i)} = \frac{1}{\sum mf_i / M_i}$$

Gas constant of a mixture can be written as: $R_m = \frac{R_u}{M_m}$; and $R_u = 8.314 \text{ kPa}\cdot\text{m}^3/\text{kmol}\cdot\text{K}$

Mass and mole fractions of a mixture are related by:

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

P-V-T relationships for Ideal Gas Mixtures

An ideal gas is defined as a gas whose molecules are spaced so far apart so that the behavior of a molecule is not influenced by the presence of other molecules. At low pressures and high temperatures, gas mixtures can be modeled as ideal gas. The behavior of ideal gas can be expressed by simple relationship $Pv = RT$, or by using compressibility factor by $Pv = ZRT$.

Prediction of the P-v-T behavior of gas mixtures is typically based on the following two models:

Dalton's law (additive pressures): the pressure of a mixture of gases is the sum of the pressures of its components when each alone occupies the volume of the mixture, V , at the temperature, T , of the mixture.

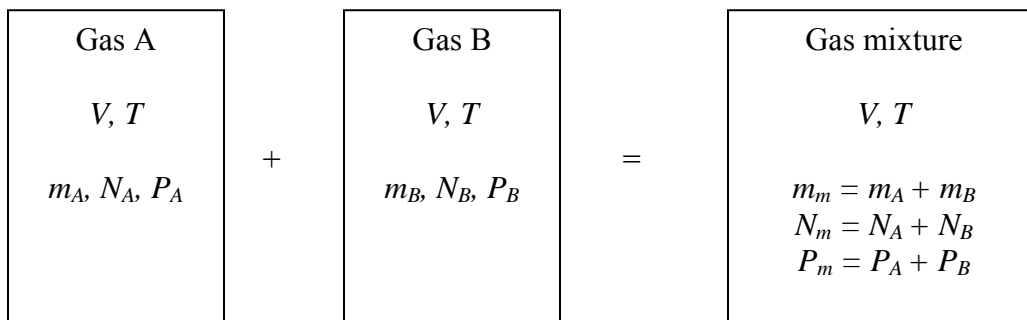


Fig.1: Dalton's law of additive pressures for a mixture of two gases.

Amagat's law (additive volumes): the volume of a mixture is the sum of the volumes that each constituent gas would occupy if each were at the pressure, P , and temperature, T , of the mixture.

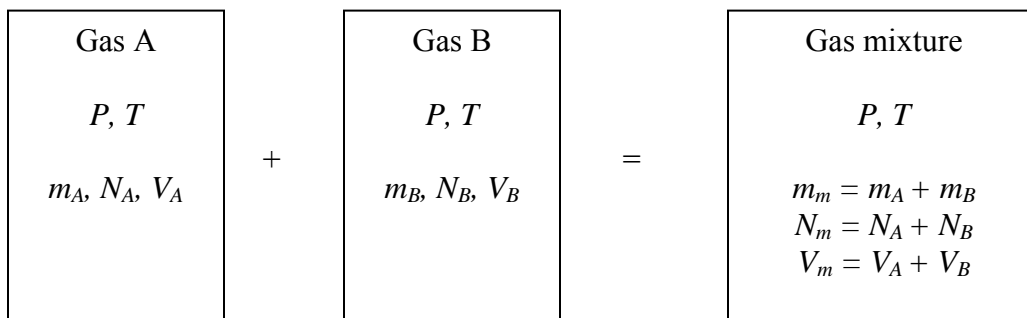


Fig.2: Amagat's law of additive volumes for a mixture of two gases.

The volume fraction is defined as the ratio V_i/V_m . Also we define the pressure fraction as the ratio of P_i/P_m

$$P_m = \sum_{i=1}^k P_i \quad \text{and} \quad V_m = \sum_{i=1}^k V_i$$

By combining the results of the Amagat and Dalton models, we obtain for **ideal gas** mixtures:

$$\frac{P_i}{P} = \frac{V_i}{V} = \frac{N_i}{N_m} = y_i$$

Therefore, Amagat's law and Dalton's law are equivalent to each other if the gases and the mixture are ideal gases. This is strictly valid for ideal-gas mixtures.

Real Gas Properties

Dalton's law and Amagat's law can also be used for real gases, often with reasonable accuracy. However; the component pressure or volume should be calculated using relationships that take into account the deviation of each component from ideal gas behavior. One way of doing this is to use the compressibility factor:

$$PV = ZNR_uT$$

The compressibility factor of the mixture Z_m can be calculated from:

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

where 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. It should be noted that for real-gas mixtures, these two laws give different results.

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 mixtures components as:

$$P'_{cr,m} = \sum y_i P_{cr,i} \quad \text{and} \quad T'_{cr,m} = \sum y_i T_{cr,i}$$

The compressibility factor of the mixture is then easily determined by using these pseudo-critical properties. The result obtained by using Kay's rule is accurate to within 10%.

Example 1

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.

Analysis:

a) Assuming ideal gas, the volume of the mixture is calculated from:

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

since

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

The molar fractions are:

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

b) Kay's rule; critical temperatures and pressures of N_2 and CO_2 can be found from Table A-1.

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

$$= 0.25(126.2K) + 0.75(304.2K) = 259.7K$$

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

$$= 0.25(3.39MPa) + 0.75(7.39MPa) = 6.39MPa$$

then;

$$\left. \begin{aligned} T_R &= \frac{T_m}{T'_{cr,m}} = \frac{300K}{259.7K} = 1.16 \\ P_R &= \frac{P_m}{P'_{cr,m}} = \frac{15MPa}{6.39MPa} = 2.35 \end{aligned} \right\} \text{Fig.A-15b} \rightarrow Z_m = 0.49$$

thus;

$$V_m = \frac{Z_m N_m R_u T_m}{P_m} = \frac{(0.49)(8 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3 / \text{kmol} \cdot \text{K})(300K)}{15,000 \text{ kPa}} = 0.652 \text{ m}^3$$

c) Amagat's law:

$$N_2 : \left. \begin{aligned} T_{R,N_2} &= \frac{T_m}{T_{cr,N_2}} = \frac{300K}{126.2K} = 2.38 \\ P_{R,N_2} &= \frac{P_m}{P_{cr,N_2}} = \frac{15MPa}{3.39MPa} = 4.42 \end{aligned} \right\} \text{Fig.A-15b} \rightarrow Z_{N_2} = 1.02$$

$$CO_2 : \left. \begin{aligned} T_{R,CO_2} &= \frac{T_m}{T_{cr,CO_2}} = \frac{300K}{304.2K} = 0.99 \\ P_{R,CO_2} &= \frac{P_m}{P_{cr,CO_2}} = \frac{15MPa}{7.39MPa} = 2.03 \end{aligned} \right\} \text{Fig.A-15b} \rightarrow Z_{CO_2} = 0.3$$

Mixture:

$$Z_m = \sum y_i Z_i = y_{N_2} Z_{N_2} + y_{CO_2} Z_{CO_2}$$

$$= 0.25(1.02) + 0.75(0.3) = 0.48$$

Thus;

$$V_m = \frac{Z_m N_m R_u T_m}{P_m} = \frac{(0.48)(8 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3 / \text{kmol} \cdot \text{K})(300K)}{15,000 \text{ kPa}} = 0.638 \text{ m}^3$$

Note that the compressibility factor in this case turned out to be almost the same as the one determined by using Kay's rule.

d) Dalton's law

This time the compressibility factor of each component is to be determined at the mixture temperature and volume, which is not known. Therefore, an iterative solution is required. We start the calculations by assuming that the volume of the gas mixture is 1.330 m^3 , the value determined by assuming ideal-gas behavior.

The T_R values are identical to those obtained in part c).

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

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

Similarly,

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

From Fig. A-15, we read $Z_{N_2} = 0.99$ and $Z_{CO_2} = 0.56$, thus,

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

and,

$$V_m = \frac{Z_m N_m R_u T_m}{P_m} = \frac{(0.67)(8 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3 / \text{kmol} \cdot \text{K})(300 \text{ K})}{15,000 \text{ kPa}} = 0.891 \text{ m}^3$$

This is 33% lower than the assumed value. Therefore, we should repeat the calculations, using the new value of V_m . When calculations are repeated we obtain 0.738 m^3 after the second iteration, 0.678 m^3 after the third iteration, and 0.648 m^3 after the fourth iteration. This value does not change with more iteration. Therefore:

$$V_m = 0.648 \text{ m}^3$$

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

Mixture Properties

Extensive properties such as U , H , c_p , c_v and S can be found by adding the contribution of each component at the condition at which the component exists in the mixture.

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

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

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

where \bar{u} is the specific internal energy of the mixture per mole of the mixture.

Also;

$$\begin{aligned}
 u_m &= \sum_{i=1}^k mf_i u_i \quad (\text{kJ/kg}) \quad \text{and} \quad \bar{u}_m = \sum_{i=1}^k y_i \bar{u}_i \quad (\text{kJ/kmol}) \\
 h_m &= \sum_{i=1}^k mf_i h_i \quad (\text{kJ/kg}) \quad \text{and} \quad \bar{h}_m = \sum_{i=1}^k y_i \bar{h}_i \quad (\text{kJ/kmol}) \\
 s_m &= \sum_{i=1}^k mf_i s_i \quad (\text{kJ/kg}) \quad \text{and} \quad \bar{s}_m = \sum_{i=1}^k y_i \bar{s}_i \quad (\text{kJ/kmol}) \\
 c_{v,m} &= \sum_{i=1}^k mf_i c_{v,i} \quad (\text{kJ/kg.K}) \quad \text{and} \quad \bar{c}_{v,m} = \sum_{i=1}^k y_i \bar{c}_{v,i} \quad (\text{kJ/kmol.K}) \\
 c_{p,m} &= \sum_{i=1}^k mf_i c_{p,i} \quad (\text{kJ/kg.K}) \quad \text{and} \quad \bar{c}_{p,m} = \sum_{i=1}^k y_i \bar{c}_{p,i} \quad (\text{kJ/kmol.K})
 \end{aligned}$$

Changes in internal energy and enthalpy of mixtures:

$$\begin{aligned}
 \Delta U_m &= \sum_{i=1}^k \Delta U_i = \sum_{i=1}^k m_i \Delta u_i = \sum_{i=1}^k N_i \Delta \bar{u}_i \quad (\text{kJ}) \\
 \Delta H_m &= \sum_{i=1}^k \Delta H_i = \sum_{i=1}^k m_i \Delta h_i = \sum_{i=1}^k N_i \Delta \bar{h}_i \quad (\text{kJ}) \\
 \Delta S_m &= \sum_{i=1}^k \Delta S_i = \sum_{i=1}^k m_i \Delta s_i = \sum_{i=1}^k N_i \Delta \bar{s}_i \quad (\text{kJ/K})
 \end{aligned}$$

Care should be exercised in evaluating the Δ s of the components since the entropy of an ideal gas depends on the pressure or volume of the component as well as on its temperature.

$$(s_2 - s_1)_m = \sum_{i=1}^k mf_i (s_2 - s_1)_i = \sum_{i=1}^k mf_i \left(c_{p,i} \ln \frac{T_2}{T_1} - R_i \ln \frac{P_{i,2}}{P_{i,1}} \right)_i$$

This relationship can also be expressed on a per mole basis.

Notes:

- when ideal gases are mixed, a change in entropy occurs as a result of the increase in disorder in the systems
- if the initial temperature of all constituents are the same, the mixing process is adiabatic; i.e., temperature does not change – but entropy does!

$$\begin{aligned}
 \Delta S_m &= - \left(m_1 R_1 \ln \frac{P_1}{P} + m_2 R_2 \ln \frac{P_2}{P} + \dots \right) \\
 &= - \sum_{i=1}^k m_i R_i \frac{P_i}{P}
 \end{aligned}$$