Week 10: Lecture 2

P-V-T Relationships for Ideal Gas Mixtures

Amagat Model (law of additive volumes)

- each component mixture behaves as an ideal gas as if it existed separately at the pressure, P and the temperature, T, of the mixture

$$\begin{array}{|c|c|}\hline T,P & T,P \\ & \\ m_A & m_B \\ n_A & n_B \\ V_A & V_B \\ & \\ \hline \end{array} \quad \begin{array}{c} \text{remove} \\ \rightarrow \\ \text{partition} \end{array} \quad \begin{array}{|c|}\hline T,P \\ \\ m_C = m_A + m_B \\ n_C = n_A + n_B \\ V_C = V_A + V_B \\ \\ \hline \end{array}$$

$$\frac{V_i}{V} = \frac{n_i}{n} = X_i$$

which leads to

$$V = \sum_{i=i}^{j} V_i$$

Dalton Model (law of additive pressures)

- each mixture component behaves as an ideal gas as if it were alone at the temperature, T and the volume, V of the mixture

$$\begin{array}{|c|}\hline V,T \\ \\ m_A, n_A, P_A \\ \\ \\ \hline \end{array} + \begin{array}{|c|}\hline V,T \\ \\ m_B, n_B, P_B \\ \\ \\ \hline \end{array} = \begin{array}{|c|}\hline V,T \\ \\ m_C = m_A + m_B \\ n_C = n_A + n_B \\ P_C = P_A + P_B \\ \hline \end{array}$$

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for a mixture of ideal gases the pressure is the sum of the partial pressures of the individual components

$$P = \sum_{i=i}^{j} P_i$$

By combining the results of the Amagat and Dalton models, we obtain

$$\frac{P_i}{P} = \frac{V_i}{V} = \frac{n_i}{n}$$

Ideal Gas Law for a Mixture

- the gas constant can be expressed as

$$R = \sum_{i=1}^{j} Y_i R_i$$

- the relative mass fractions and mole fractions can be related in terms of the gas constant as

$$X_i = Y_1 \left[\frac{R_i}{\displaystyle\sum_{i=1}^{j} Y_i R_i} \right]$$

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Non-Reacting Mixtures

Changes in Internal Energy, Enthalpy and Entropy of Mixtures

$$u_2 - u_1 = \sum Y_i (u_2 - u_1)_i = \int_{T_1}^{T_2} c_v dT$$

$$h_2 - h_1 = \sum Y_i (h_2 - h_1)_i = \int_{T_1}^{T_2} c_p dT$$

$$s_2 - s_1 = \sum Y_i (s_2 - s_1)_i = \int_{T_1}^{T_2} c_p \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$

The above equations can also be expressed on a per mole basis.

Entropy Change Due to Mixing of Ideal Gases

- when ideal gases are mixed, a change in entropy occurs as a result of the increase in disorder in the system
- if the initial temperatures of all constituents are the same and the mixing process is adiabatic

$$\begin{aligned}\mathcal{P}_s = \Delta S &= -\left(m_A R_A \ln \frac{P_A}{P} + m_B R_B \ln \frac{P_B}{P} + \ldots\right) \\ &= -\sum m_i R_i \ln \frac{P_i}{P} \\ &= -\mathcal{R} \sum n_i \ln X_i\end{aligned}$$