Non-Reacting Gas Mixtures

Introduction

- homogeneous gas mixtures are frequently treated as a single compound
- the individual properties of inert gases tend to behave as a single pure substance

Definitions

\[ m \] - total mass of a mixture
\[ m_i \] - mass of the i’th component of the mixture
\[ n \] - total number of moles of a mixture
\[ n_i \] - number of moles of the i’th component of the mixture
\[ X_i \] - mass fraction of the i’th component of the mixture
\[ Y_i \] - mole fraction of the i’th component of the mixture
\[ \tilde{M} \] - molecular weight of the mixture (molar mass)
\[ \tilde{M}_i \] - molecular weight of the i’th component of the mixture
\[ \mathcal{R} \] - universal gas constant \( \equiv 8.3145 \text{ kJ/kmole} \cdot \text{K} \)
\[ R \] - gas constant for a particular gas
\[ R_i \] - gas constant of the i’th component of the mixture
\[ P \] - mixture pressure
\[ P_i \] - partial pressure of the i’th component of the mixture
\[ V \] - mixture volume
\[ V_i \] - partial volume of the i’th component of the mixture
\[ u \] - specific internal energy of the mixture
\[ u_i \] - specific internal energy of the i’th component of the mixture
\[ \bar{u} \] - specific internal energy of the mixture per mole of the mixture

(same as for \( h, s, c_p \text{ and } c_v \))
Formulations

• the total mass of a mixture, $m$ is the sum of the masses of its components

$$ m = m_1 + m_2 + \ldots + m_j = \sum_{i=1}^{j} m_i $$

• the relative amounts of the components present in the mixture can be specified in terms of mass fractions

$$ X_i = \frac{m_i}{m} \quad \Rightarrow \quad \sum_{i=1}^{j} X_i = 1 $$

• the total number of moles in a mixture, $n$ is the sum of the number of moles of each of the components

$$ n = n_1 + n_2 + \ldots + n_j = \sum_{i=1}^{j} n_i $$

• the relative amounts of the components present in the mixture can be specified in terms of mole fractions

$$ Y_i = \frac{n_i}{n} \quad \Rightarrow \quad \sum_{i=1}^{j} Y_i = 1 $$

• $m_1$ and $n_i$ are related by the molecular weight $\tilde{M}_i$

$$ m_i = n_i \tilde{M}_i $$

Therefore the total mass is

$$ m = \sum_{i=1}^{j} n_i \tilde{M}_i $$

• the mixture molecular weight can be calculated as a mole fraction average of the component molecular weights

$$ \tilde{M} = \frac{m}{n} = \frac{\sum_{i=1}^{j} n_i \tilde{M}_i}{n} = \sum_{i=1}^{j} Y_i \tilde{M}_i $$
• \( X_i \) and \( Y_i \) are also related by the molecular weights

\[
\frac{X_i}{Y_i} = \frac{m_i}{m} = \frac{n_i}{m} = \left( \frac{M_i}{M} \right) \left( \frac{1}{x} \right)
\]

Therefore

\[
\frac{X_i}{Y_i} = \frac{M_i}{M} \Rightarrow X_i = Y_i \left[ \frac{M_i}{\sum_{i=1}^{j} Y_i \tilde{M}_i} \right]
\]

**P-V-T Relationships for Ideal Gas Mixtures**

**Amagat Model (law of additive volumes)**

*The volume of the gas mixture is equal to the sum of the volumes each gas would occupy if it existed at the mixture temperature and pressure.*

\[
V = \sum_{i=1}^{j} V_i
\]

**Dalton Model (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 \( T \) and \( V \).*

By combining the results of the Amagat and Dalton models i.e. (1) and (2), we obtain for ideal gas mixtures

\[
\frac{P_i}{P} = \frac{V_i}{V} = \frac{n_i}{n}
\]

Therefore, Amagat’s law and Dalton’s law are equivalent to each other if the gases and the mixture are ideal gases.
Ideal Gas Law for a Mixture

The gas constant can be expressed as

\[ R = \sum_{i=1}^{j} X_i R_i \]

The mixture molecular weight can be written as

\[ \tilde{M} = \sum_{i=1}^{j} Y_i \tilde{M}_i \]

and

\[ \frac{X_i}{Y_i} = \frac{\tilde{M}_i}{\tilde{M}} \]

\[ X_i R_i = Y_i \frac{\tilde{M}_i}{\tilde{M}} R_i = Y_i \frac{R}{\tilde{M}} = Y_i R \]

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

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

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.

\[ U = \sum U_i = \sum m_i u_i = m \sum X_i u_i = mu \]

\[ = \sum n_i \bar{u}_i = n \sum Y_i \bar{u}_i = n \bar{u} \]

where \( \bar{u} \) is the specific internal energy of the mixture per mole of the mixture.
Changes in internal energy and enthalpy of mixtures

\[
\begin{align*}
    u &= \sum X_i u_i \\
    h &= \sum X_i h_i \\
    c_v &= \sum X_i c_{v_i} \\
    c_p &= \sum X_i c_{p_i} \\
    s &= \sum X_i s_i \\
\end{align*}
\]

These relationships 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 systems
- if the initial temperature of all constituents are the same and the mixing process is adiabatic
  - temperature does not change
  - but entropy does

\[
\Delta S = -\left( m_A R_A \ln \frac{P_A}{P} + m_B R_B \ln \frac{P_B}{P} + \cdots \right)
\]

\[
= -\sum_{i=1}^{j} m_i R_i \ln \frac{P_i}{P}
\]

\[
= -\mathcal{R} \sum_{i=1}^{j} n_i \ln Y_i
\]
Psychrometrics

- studies involving mixtures of dry air and water vapour
- for \( T \leq 50^\circ C \) \( (P_{sat} \leq 13 \, kPa) \) \( \Rightarrow \) \( h \approx h(T) \)
  - water vapour can be treated as an ideal gas

Definitions

Moist Air

- a mixture of dry air and water vapour where dry air is treated as if it were a pure component
- the overall mixture is given as \( P = \frac{mRT}{V} \)

Total Pressure

\[
P = P_a + P_w \\
P_a = \frac{m_a R_a T}{V} \\
P_w = \frac{m_w R_w T}{V}
\]

where \( P_a \) is the partial pressure of air and \( P_w \) is the partial pressure of water vapour. Typically \( m_w \ll m_a \).

Relative Humidity - \( \phi \)

\[
\phi = \frac{P_w(T)}{P_{sat}(T)} = \frac{\text{vapour pressure at the prevailing } T}{\text{saturation pressure at the prevailing } T}
\]
If \( P_w = P_{sat}(T) \) the mixture is said to be saturated.

**Specific Humidity (Humidity ratio) - \( \omega \)**

\[
\omega = \frac{m_w}{m_a} = \frac{\text{mass of water vapour}}{\text{mass or air}}
\]

\[
= \frac{\dot{M}_w n_w}{\dot{M}_a n_a} = \frac{\dot{M}_w (P_w V/RT)}{\dot{M}_a (P_a V/RT)}
\]

\[
= \left( \frac{\dot{M}_w}{\dot{M}_a} \right) \left( \frac{P_w}{P_a} \right)
\]

\[
= 0.622 \left( \frac{P_w}{P_a} \right)
\]

In addition \( \omega \) can be written as

\[
\omega = 0.622 \left( \frac{P_w}{P_a} \right) = 0.622 \left( \frac{P_w}{P - P_w} \right) = 0.622 \left( \frac{\phi P_{sat}}{P - \phi P_{sat}} \right)
\]

which can be rearranged in terms of relative humidity

\[
\phi = \frac{P \omega}{P_{sat} \left( \omega + \frac{\dot{M}_w}{\dot{M}_a} \right)} = \frac{P \omega}{P_{sat} (\omega + 0.622)}
\]

**Dry Bulb Temperature** - the temperature measured by a thermometer placed in a mixture of air and water vapour

**Wet Bulb Temperature**

- thermometer surrounded by a saturated wick
- if air/water vapour mixture is not saturated, some water in the wick evaporates and diffuses into the air → cooling the water in the wick
- as the temperature of the water drops, heat is transferred to the water from both the air and the thermometer
- the steady state temperature is the wet-bulb temperature

**Sling Psychrometer** - a rotating set of thermometers one of which measures wet bulb temperature and the other dry bulb temperature. $T_{DB}$ and $T_{WB}$ are sufficient to fix the state of the mixture.

**The Psychrometric Chart**

where the **dry bulb** temperature is the temperature measured by a thermometer place in the mixture and the **wet bulb** temperature is the adiabatic saturation temperature.
**An Adiabatic Saturator**

How can we measure humidity?

![Diagram of an adiabatic saturator](image)

**Conservation of Mass**

\[
\dot{m}_{a,1} = \dot{m}_{a,3} \quad \text{air} \quad (1)
\]

\[
\dot{m}_{w,1} + \dot{m}_{w,2} = \dot{m}_{w,3} \quad \text{water} \quad (2)
\]

**Conservation of Energy**

\[
(\dot{m}h)_{a,1} + (\dot{m}h)_{w,1} + (\dot{m}h)_{w,2} = (\dot{m}h)_{a,3} + (\dot{m}h)_{w,3} \quad (3)
\]

By definition

\[
\omega_1 = \left( \frac{\dot{m}_w}{\dot{m}_a} \right)_{1} \quad (4)
\]

\[
\omega_3 = \left( \frac{\dot{m}_w}{\dot{m}_a} \right)_{3} \quad (5)
\]

From (2) and (1)

\[
\left( \frac{\dot{m}_{w,2}}{\dot{m}_{a,1}} \right) = \left( \frac{\dot{m}_{w,3}}{\dot{m}_{a,1}} \right) - \left( \frac{\dot{m}_{w,1}}{\dot{m}_{a,1}} \right) = \omega_3 - \omega_1
\]
Dividing (3) by \( \dot{m}_{a,1} \) and noting \( m_{a,1} = m_{a,3} \) and \( \frac{m_{w,2}}{m_{a,1}} = \omega_3 - \omega_1 \)

\[
h_{a,1} + \omega_1 h_{w,1} + (\omega_3 - \omega_1) h_{w,2} = h_{a,3} + \omega_3 h_{w,3}
\]

(6)

\[
\omega_1 = \frac{(h_{a,3} - h_{a,1}) + \omega_3 (h_{w,3} - h_{w,2})}{(h_{w,1} - h_{w,2})}
\]

If we assume:

i) air is an ideal gas and \( (h_{a,3} - h_{a,1}) = c_{p_a} (T_3 - T_1) \)

ii) \( (h_{w,3} - h_{w,2}) = h_g - h_f = h_{fg} (T_3) \)

iii) \( h_{w,1} \approx h_g (T_1) \)

iv) \( h_{w,2} = h_f (T_2) = h_f (T_3) \)

then we can write \( \omega_1 \) as a function of \( T_1 \) and \( T_3 \) only

\[
\omega_1 = \frac{c_{p_a} (T_3 - T_1) + \omega_3 h_{fg} (T_3)}{h_g (T_1) - h_f (T_3)}
\]
**PROBLEM STATEMENT:**

Outdoor air at $T_1 = 10 \, ^\circ C$ and $\phi = 30\%$ is first to be heated to $T_2 = 22 \, ^\circ C$ and then humidified to $T_3 = 25 \, ^\circ C$ and $\phi_3 = 60\%$ at atmospheric pressure. The volumetric flow rate is $\dot{V} = 45 \, m^3/min$.

i) find the heating requirement, $\dot{Q}$  
ii) find the mass flow rate of steam, $\dot{m}_{steam}$ required to complete the process.  
iii) what would you expect if liquid water was sprayed instead of steam?

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**PROBLEM STATEMENT:**

A mixture of 5 $kg$ carbon dioxide and 10 $kg$ nitrogen is at $27 \, ^\circ C$ and $101.325 \, kPa$. Determine:

a) the volumetric analysis [% by volume] of this mixture  
b) the specific heat of the mixture, $c_v$, $c_p$ [kJ/kg · K] and $\bar{c}_v$, $\bar{c}_p$ [kJ/kmol · K]  
c) the heat transfer [kJ] to reduce the temperature to 0 $^\circ C$,  
   if the mixture is confined in a rigid tank  
d) the increase in availability [kJ] of the mixture during this cooling process