Non-Reacting Gas Mixtures

Reading	**Problems**
13-1 → 13-3	13-57, 13-73
14-1 → 14-7	14-33, 14-36, 14-71, 14-75, 14-80, 14-83, 14-108, 14-116

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

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

- 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

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

- 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

$$\boldsymbol{\tilde{M} = \frac{m}{n} = \frac{\sum\limits_{i=1}^{j} n_i \tilde{M}_i}{n} = \sum_{i=1}^{j} Y_i \tilde{M}_i}$$

- $\boldsymbol{X_i}$ and $\boldsymbol{Y_i}$ are also related by the molecular weights

$$\boldsymbol{\frac{X_i}{Y_i} = \frac{(m_i/m)}{(n_i/n)} = \left(\frac{m_i}{n_i}\right)\left(\frac{n}{m}\right) = \left(\tilde{M}_i\right)\left(\frac{1}{\tilde{M}}\right)}$$

Therefore

$$\boldsymbol{\frac{X_i}{Y_i} = \frac{\tilde{M}_i}{\tilde{M}} \quad \rightarrow \quad X_i = Y_i \left[\frac{\tilde{M}_i}{\sum\limits_{i=1}^{j} Y_i \tilde{M}_i}\right]}$$

P-V-T Relationships for Ideal Gas Mixtures

Amagat Model (law of additive volumes)

- the volume of 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

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

- the volume that n_i moles of a component i would occupy at P and T is called the partial volume, V_i

$$V_i = \frac{n_i \mathcal{R} T}{P}$$

- dividing through by the total volume gives

$$\frac{V_i}{V} = \left(\frac{n_i \mathcal{R} T / P}{n \mathcal{R} T / P} \right) \Rightarrow \frac{n_i}{n} = Y_i \qquad (1)$$

which leads to

$$\sum_{i=i}^{j} V_i = \sum_{i=1}^{j} Y_i V = V \underbrace{\sum_{i=1}^{j} Y_i}_{=1}$$

where the sum of the mole fractions is 1.

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.

$$\boxed{V = \sum_{i=1}^{j} V_i}$$

Dalton Model (law of 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

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

- for a mixture of ideal gases the pressure is the sum of the partial pressures of the individual components
- the individual components do not exert the mixture pressure, P, but rather a partial pressure

$$P_i = \frac{n_i \mathcal{R} T}{V}$$

- dividing through by the total pressure

$$\frac{P_i}{P} = \frac{n_i \mathcal{R} T / V}{n \mathcal{R} T / V} = \frac{n_i}{n} = Y_i \qquad (2)$$

From (2)

$$\sum_{i=1}^{j} P_i = \sum_{i=1}^{j} Y_i P = P \underbrace{\sum_{i=1}^{j} Y_i}_{=1}$$

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

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

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

Therefore, Amagat's law and Dalton's law are equivalent to each other if the gases and the mixture are ideal gases.

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.

$$\begin{aligned} U = \sum U_i &= \sum m_i u_i = m \sum X_i u_i = mu \\ &= \sum n_i \overline{u}_i = n \sum Y_i \overline{u}_i = n\overline{u} \end{aligned}$$

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

$$\boxed{\begin{aligned} u &= \sum X_i\, u_i \\ h &= \sum X_i\, h_i \\ c_v &= \sum X_i\, c_{v_i} \\ c_p &= \sum X_i\, c_{p_i} \\ s &= \sum X_i\, s_i \end{aligned}}$$

Changes in internal energy and enthalpy of mixtures

$$\begin{aligned} u_2 - u_1 &= \sum X_i (u_2 - u_1)_i = \int_{T_1}^{T_2} c_v\, dT = c_v (T_2 - T_1) \\ h_2 - h_1 &= \sum X_i (h_2 - h_1)_i = \int_{T_1}^{T_2} c_p\, dT = c_p (T_2 - T_1) \\ s_2 - s_1 &= \sum X_i (s_2 - s_1)_i = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \end{aligned}$$

These relationships can also be expressed on a per mole basis.

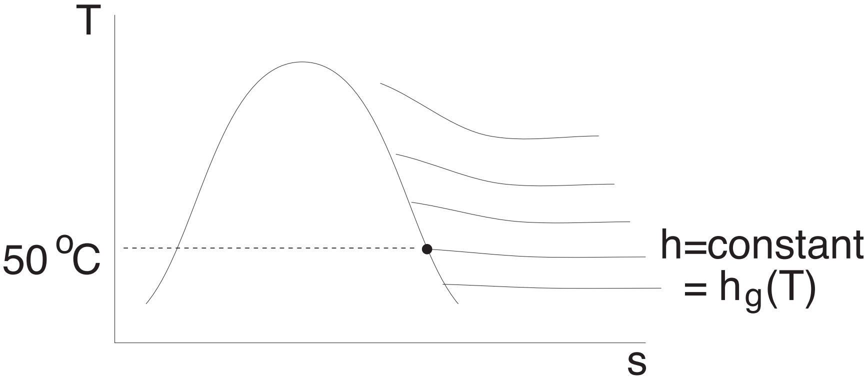
Entropy Change Due to Mixing of Ideal Gases

- 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

$$\begin{aligned} \Delta S &= -\left(m_A R_A \ln \frac{P_A}{P} + m_B R_B \ln \frac{P_B}{P} + \cdots \right) \\ &= -\sum_{i=1}^{j} m_i R_i \ln \frac{P_i}{P} \\ &= -\mathcal{R} \sum_{i=1}^{j} n_i \ln Y_i \end{aligned}$$

Psychrometrics

- studies involving mixtures of dry air and water vapour
- used in the design of air-conditioning systems, cooling towers and most processes involving the control of vapour content in air
- for $T \leq 50°C \quad (P_{sat} \leq 13\, kPa) \;\Rightarrow\; h \approx h(T)$
  - water vapour can be treated as an ideal gas



Total Pressure

$$\begin{aligned} P &= P_a + P_w \\ P_a &= \frac{m_a R_a T}{V} \\ P_w &= \frac{m_w R_w T}{V} \end{aligned}$$

where P_a is the partial pressure of air and P_w is the partial pressure of water vapour. Typically $m_w << m_a$.

Relative Humidity - ϕ

$$\phi = \frac{P_w(T)}{P_{sat}(T)} = \frac{\text{vapour pressure at the prevailing T}}{\text{saturation pressure at the prevailing T}}$$

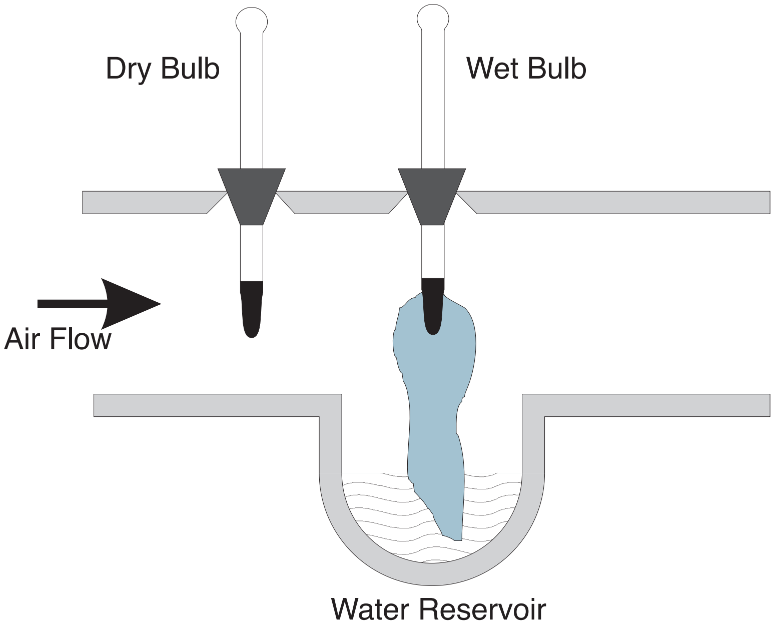
If $P_w = P_{sat}(T)$ the mixture is said to be saturated.

Specific Humidity (Humidity ratio) - ω

$$\begin{aligned}
\omega &= \frac{m_w}{m_a} = \frac{\text{mass of water vapour}}{\text{mass or air}} \\
&= \frac{\tilde{M}_w n_w}{\tilde{M}_a n_a} = \frac{\tilde{M}_w (P_w V/\mathcal{R}T)}{\tilde{M}_a (P_a V/\mathcal{R}T)} \\
&= \left(\frac{\tilde{M}_w}{\tilde{M}_a}\right)\left(\frac{P_w}{P_a}\right) \\
&= 0.622\left(\frac{P_w}{P_a}\right)
\end{aligned}$$

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

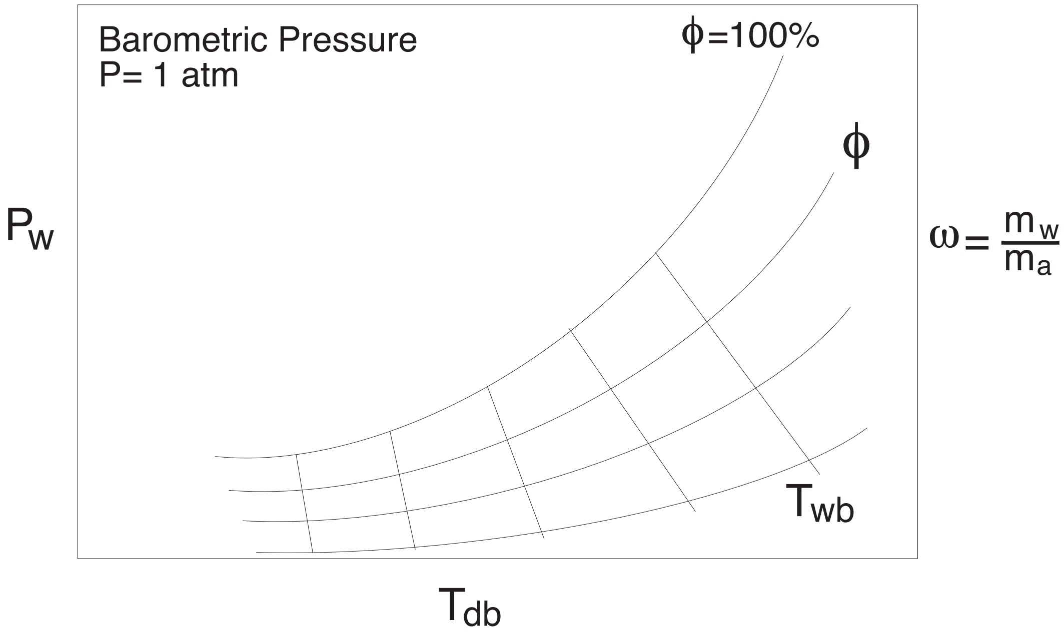
Wet Bulb Temperature



- thermometer surrounded by a saturated wick

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.

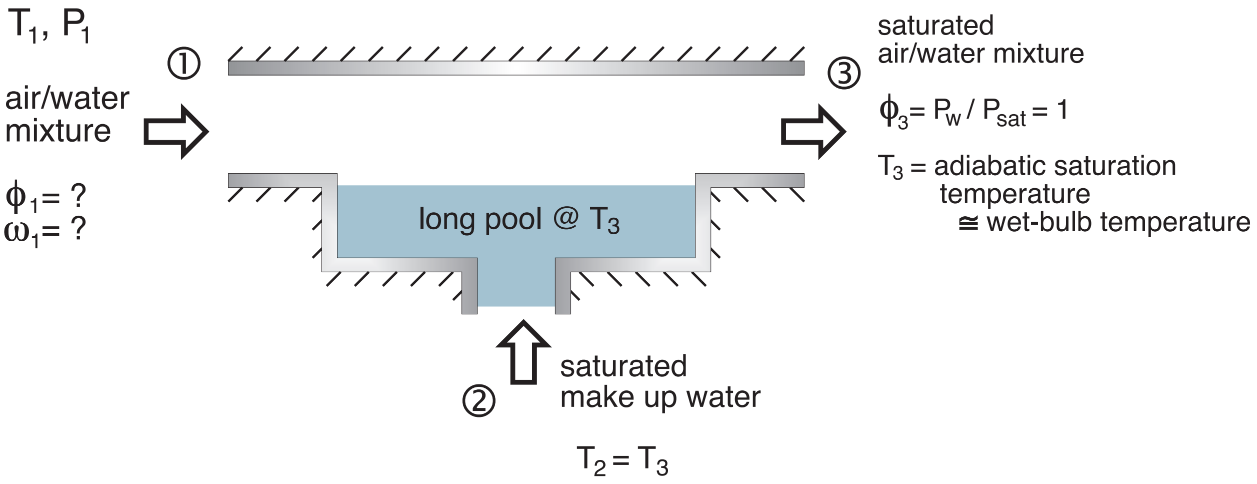
The Psychrometric Chart



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?



- the adiabatic saturator is used to measure humidity

Adiabatic Saturator Analysis

Conservation of Mass

$$\dot{m}_{a,1} = \dot{m}_{a,3} \qquad \text{air} \qquad (1)$$

$$\dot{m}_{w,1} + \dot{m}_{w,2} = \dot{m}_{w,3} \qquad \text{water} \qquad (2)$$

Conservation of Energy

$$(\dot{m}h)_{a,1} + (\dot{m}h)_{w,1} + (\dot{m}h)_{w,2} = (\dot{m}h)_{a,3} + (\dot{m}h)_{w,3} \qquad (3)$$

By definition

$$\omega_1 = \left(\frac{\dot{m}_w}{\dot{m}_a}\right)_1 \qquad (4)$$

$$\omega_3 = \left(\frac{\dot{m}_w}{\dot{m}_a}\right)_3 \qquad (5)$$

From (2) and (1)

$$\left(\frac{\dot{m}_{w,2}}{\dot{m}_{a,1}}\right) = \left(\frac{\dot{m}_{w,3}}{\underbrace{\dot{m}_{a,1}}_{\dot{m}_{a,3}}}\right) - \left(\frac{\dot{m}_{w,1}}{\dot{m}_{a,1}}\right) = \omega_3 - \omega_1$$

Dividing (3) by $\dot{m}_{a,1}$ and noting $m_{a_1} = m_{a_3}$ and $\dfrac{m_{w_2}}{m_{a_1}} = \omega_3 - \omega_1$

$$h_{a,1} + \omega_1\, h_{w,1} + (\omega_3 - \omega_1)\, h_{w,2} = h_{a,3} + \omega_3\, h_{w,3} \qquad (6)$$

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