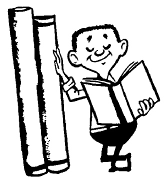
Non-Reacting Gas Mixtures



Reading	Problems
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Introduction

- homogeneous gas mixtures are frequently treated as a single compound rather than many individual constituents
- the individual properties of inert gases tend to be submerged, such that the gas behaves as a single pure substance
- equations can be derived to express the properties of mixtures in terms of the properties of their individual constituents

Formulations

- the total mass of a mixture, $\boldsymbol{m}$ is the sum of the masses of its components

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

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

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

- the total number of moles in a mixture, $\boldsymbol{n}$ is the sum of the number of moles of each of the components

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

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

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

- 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

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

- X_i and Y_i are also related by the molecular weights

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

  Therefore

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

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

T, P	T, P		T, P
m_A	m_B	remove	$m_C = m_A + m_B$
n_A	n_B	$\rightarrow$	$n_C = n_A + n_B$
V_A	V_B	partition	$V_C = V_A + V_B$

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.

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

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, $\boldsymbol{V}$, at the temperature, $\boldsymbol{T}$, of the mixture

$\boldsymbol{V, T}$		$\boldsymbol{V, T}$		$\boldsymbol{V, T}$
$\boldsymbol{m_A, n_A, P_A}$	+	$\boldsymbol{m_B, n_B, P_B}$	=	$\boldsymbol{m_C = m_A + m_B}$ $\boldsymbol{n_C = n_A + n_B}$ $\boldsymbol{P_C = P_A + P_B}$

The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at $\boldsymbol{T}$ *and* $\boldsymbol{V}$*.*

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

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

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 $\boldsymbol{U, H, c_p, c_v}$ and $\boldsymbol{S}$ can be found by adding the contribution of each component at the condition at which the component exists in the mixture.

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

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

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

Changes in internal energy and enthalpy of mixtures

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

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

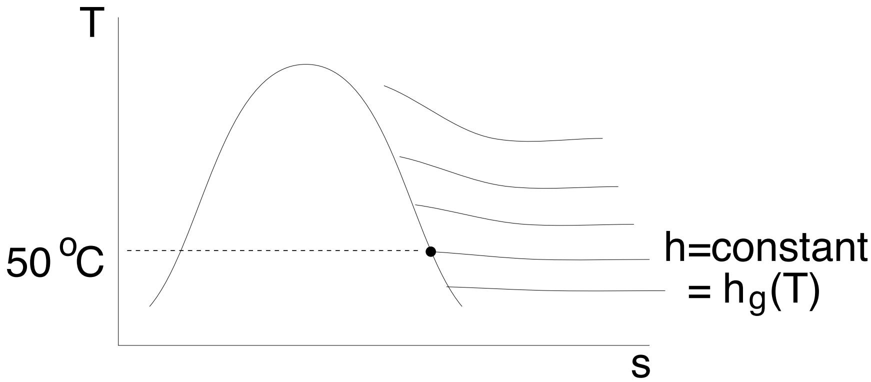
$$\begin{aligned} \Delta S &= -\left(m_A R_A \ln \frac{P_A}{P} + m_B R_B \ln \frac{P_B}{P} + \cdots \right) \\ &= -\sum_{i=1}^{j} m_i R_i \ln \frac{P_i}{P} \\ &= -\mathcal{R} \sum_{i=1}^{j} n_i \ln X_i \end{aligned}$$

Notes:

- -ve sign because $\ln \frac{Pi}{P} < 0$
- $m_i R_i = m_i \frac{\mathcal{R}}{\tilde{M}_i} = n_i \mathcal{R}$

Psychrometrics

- studies involving mixtures of dry air and water vapour
- for $T \leq 50°C \quad (P_{sat} \leq 13\ kPa) \quad \Rightarrow \quad h \approx h(T)$
  - 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 $\Rightarrow \quad P = \dfrac{mRT}{V}$

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 $m_w << m_a$.

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.

The relative humidity can also be written as

$$\phi = \frac{P_w}{P_{sat}} = \frac{\rho_w}{\rho_s at} = \frac{v_g}{v_w} = \frac{mixture\ volume}{water\ volume}$$

where v_g is the mixture specific volume and v_w is water specific volume.

Specific Humidity (Humidity ratio) - ω

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

In addition ω can be written as

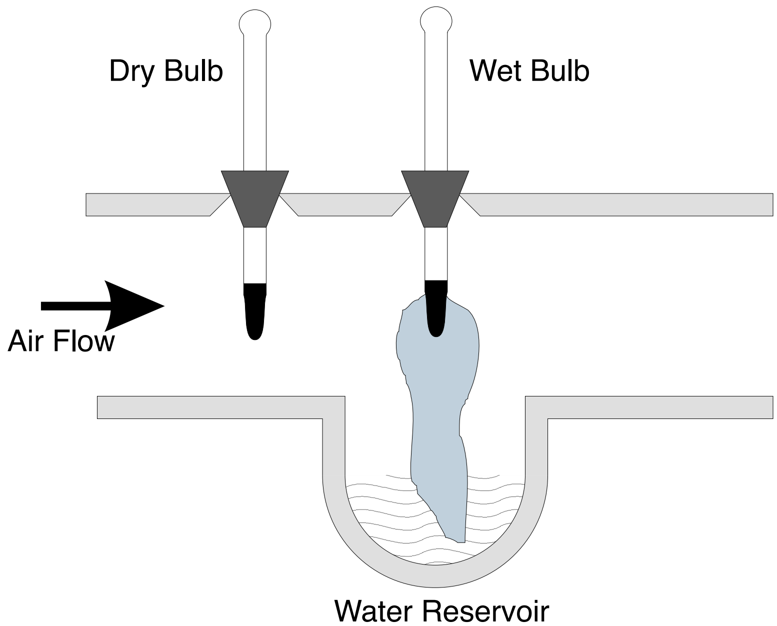
$$\omega = 0.622 \left(\frac{P_w}{P_a}\right) = 0.622 \left(\frac{P_w}{P - P_w}\right) = 0.622 \left(\frac{\phi P_{sat}}{P - \phi P_{sat}}\right)$$

which can be rearranged in terms of relative humidity

$$\phi = \frac{P\gamma}{P_{sat}\left(\omega + \dfrac{\tilde{M}_w}{\tilde{M}_a}\right)} = \frac{P\omega}{P_{sat}(\omega + 0.622)}$$

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

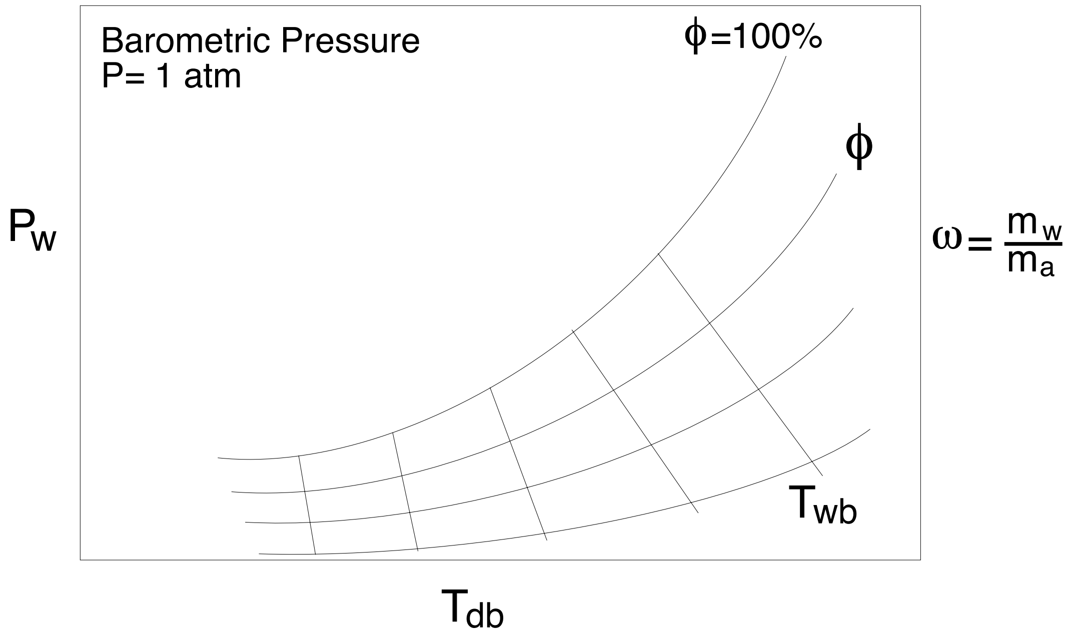
Wet Bulb Temperature



- 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 $\longrightarrow$ cooling the water in the wick
- at 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 Thermometer - a rotating set of thermometers one of which measures wet bulb temperature and the other dry bulb temperature. $\boldsymbol{T_{DB}}$ and $\boldsymbol{T_{WB}}$ are sufficient to fix the state of the mixture.

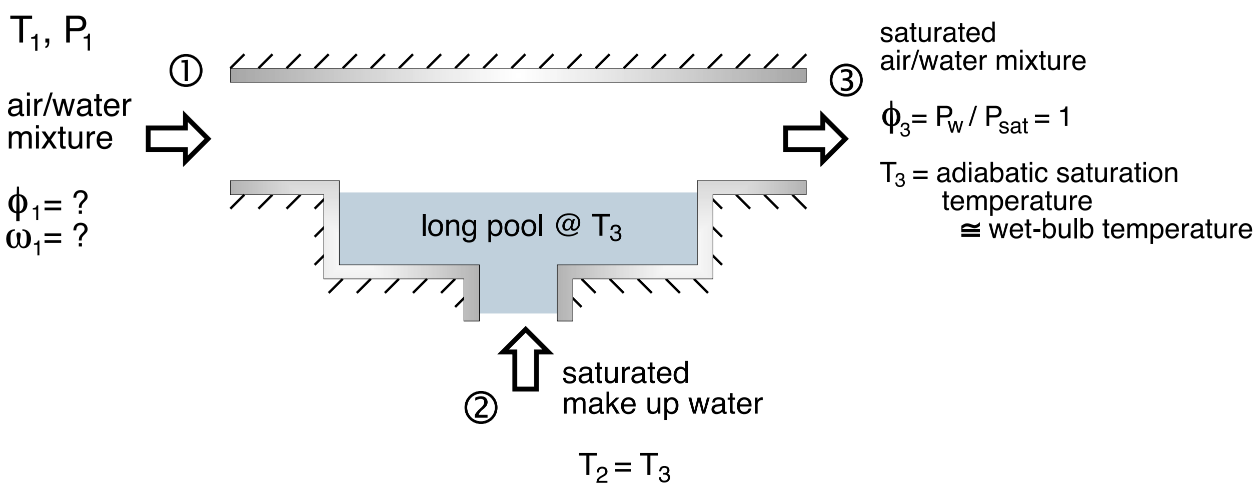
The Psychrometric Chart



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

- two inlets, single exit device through which moist air passes
- air-water mixture of unknown humidity enters at a known pressure and temperature
- if air/water mixture is not saturated, ($\boldsymbol{\phi < 100\%}$), some water from the pool will evaporate
- the energy required to evaporate the water comes from the moist air $\longrightarrow$ mixture temperature decreases
- for a sufficiently long duct, the moisture exits with $\boldsymbol{\phi_3 = 1}$
- the temperature of the exiting mixture is called the adiabatic saturation temperature