Non-Reacting Gas Mixtures

Reading	**Problems**
13-1 → 13-3	13-52, 13-60
14-1 → 14-7	14-32, 14-35, 14-68, 14-71, 14-75
	14-79, 14-103, 14-112

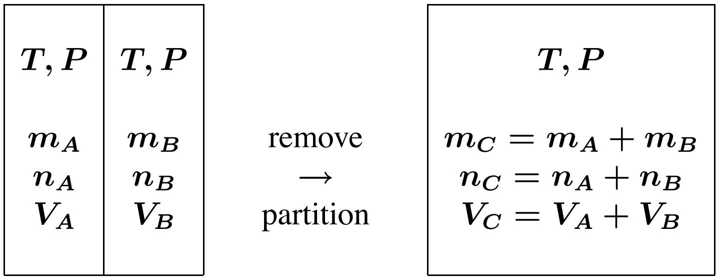
Introduction

- 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
- eg. - air consists of oxygen, nitrogen, argon and water vapour. But dry air can be treated as a simple gas with a molar mass of $28.97\ kg/kmole$
- equations can be derived to express the properties of mixtures in terms of the properties of their individual constituents
- it is assumed that each constituent is unaffected by the other constituents in the mixture

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



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

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

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 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

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

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

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

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

$$
\begin{aligned}
&= \frac{\tilde{M}_w n_w}{\tilde{M}_a n_a} = \frac{\tilde{M}_w (P_w V/\mathcal{R}T)}{\tilde{M}_a (P_a V/\mathcal{R}T)} \\
&= \left(\frac{\tilde{M}_w}{\tilde{M}_a}\right)\left(\frac{P_w}{P_a}\right) \\
&= 0.622 \left(\frac{P_w}{P_a}\right)
\end{aligned}
$$

In addition ω can be written as

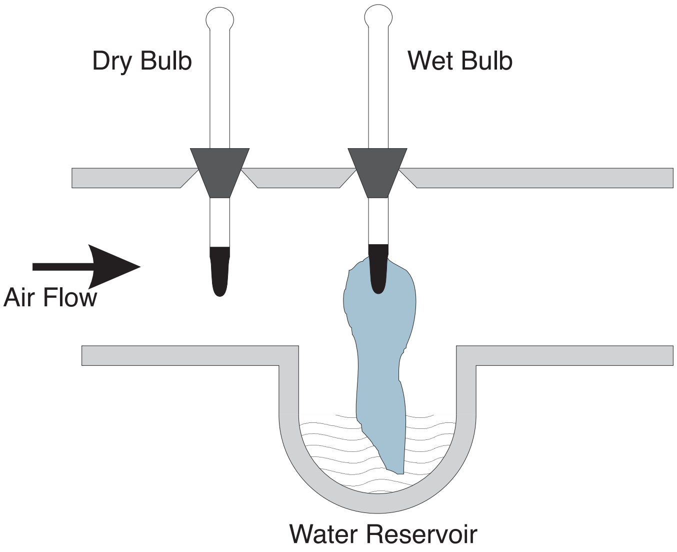
$$\omega = 0.622 \left(\frac{P_w}{P_a}\right) = 0.622 \left(\frac{P_w}{P - P_w}\right) = 0.622 \left(\frac{\phi P_{sat}}{P - \phi P_{sat}}\right)$$

which can be rearranged in terms of relative humidity

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

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

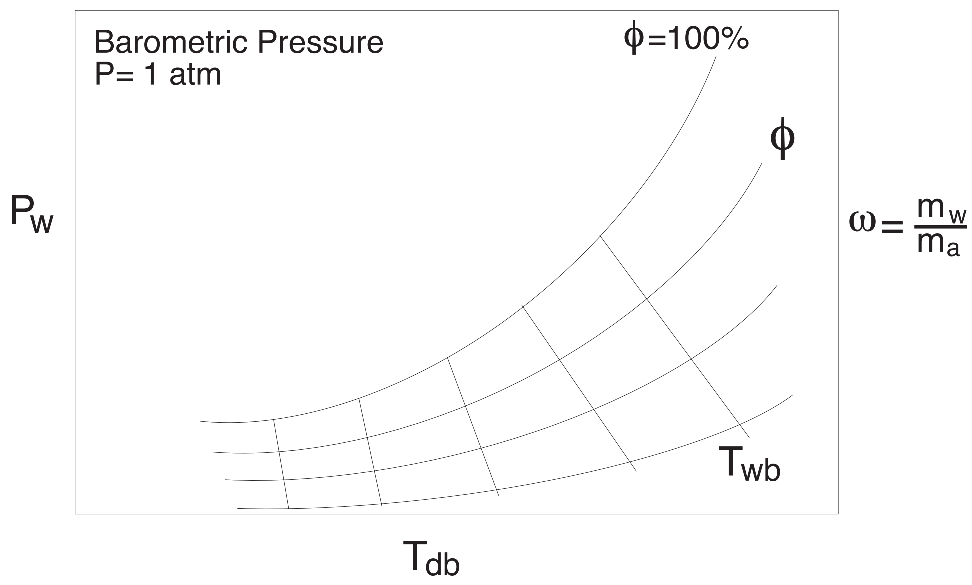
Wet Bulb Temperature



- 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 → 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.

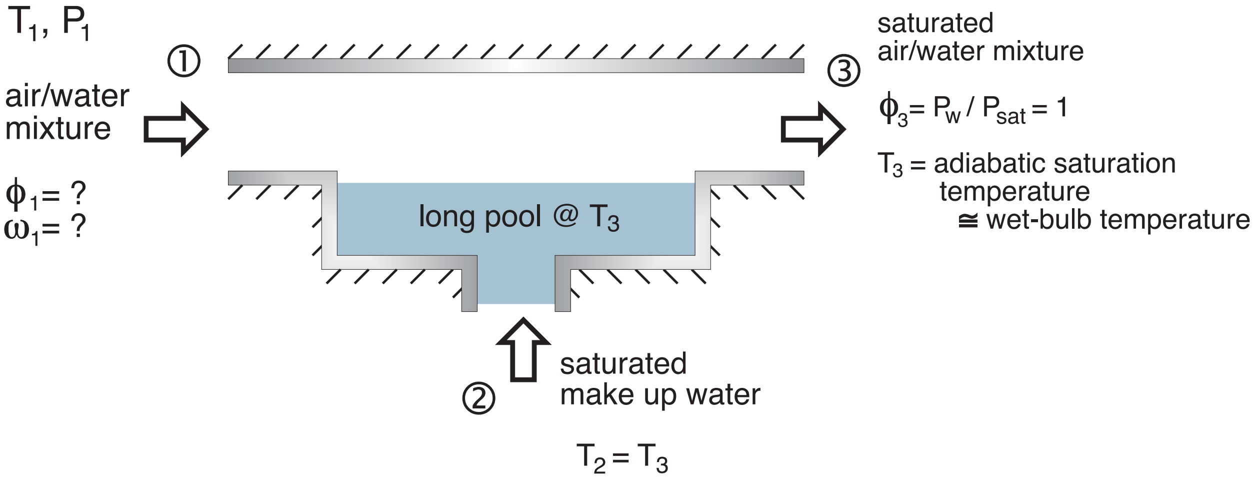
The Psychrometric Chart



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?



- 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, ($\phi < 100\%$), some water from the pool will evaporate
- the energy required to evaporate the water comes from the moist air → mixture temperature decreases
- for a sufficiently long duct, the moisture exits with $\phi_3 = 1$
- the temperature of the exiting mixture is called the adiabatic saturation temperature

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

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

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

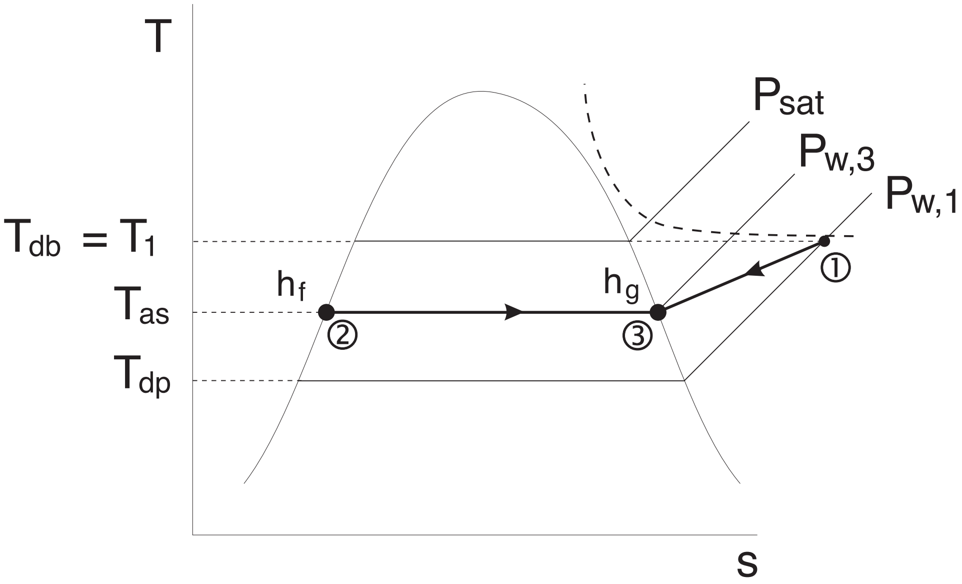
From (2) and (1)

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

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

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

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



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 ω_1 as a function of T_1 and T_3 only

$$\omega_1 = \frac{c_{p_a}(T_3 - T_1) + \omega_3\, h_{fg}(T_3)}{h_g(T_1) - h_f(T_3)}$$

Aside: Since $h_f << h_g$ very little is lost if the denominator is approximated as $h_{fg}(T_1)$

During the adiabatic saturation process, the vapour pressure increases and the temperature decreases; so the adiabatic saturation temperature is higher than the dew point temperature and lower than the dry bulb temperature. For the limiting case of a saturated mixture, the dry bulb, dew point and adiabatic saturation temperature are the same.

Equation 6 can be written as

$$h_1^* + \underbrace{(\omega_3 - \omega_1)}_{negligible} h_{\ell,2} = h_3^*$$

where

$$h^* = h_a + \omega\, h_w$$

Therefore $h_1^* \approx h_3^*(T_{wb})$. The lines of wet bulb temperature and h^* coincide on the psychrometric chart. Since h_3^* is solely a function of T_{wb}, lines of h_1^* are proportional to T_{wb}.