

Non-Reacting Gas Mixtures



Reading
13.1 → 13.5

Problems
13.17, 13.19, 13.22, 13.30, 13.39, 13.53
13.69, 13.78, 13.81, 13.84, 13.108, 13.109

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 and c_v)

Formulations

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

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

- 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

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

- 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_i 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

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

Therefore

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

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

$$\frac{X_i}{Y_i} = \frac{\tilde{M}_i}{\tilde{M}}$$

$$X_i R_i = Y_i \frac{\tilde{M}_i}{\tilde{M}} R_i = Y_i \frac{\mathcal{R}}{\tilde{M}} = Y_i R$$

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.

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

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

$u = \sum X_i u_i$
$h = \sum X_i h_i$
$c_v = \sum X_i c_{v_i}$
$c_p = \sum X_i c_{p_i}$
$s = \sum X_i s_i$

Changes in internal energy and enthalpy of mixtures

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

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

$$s_2 - s_1 = \sum X_i (s_2 - s_1)_i = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

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

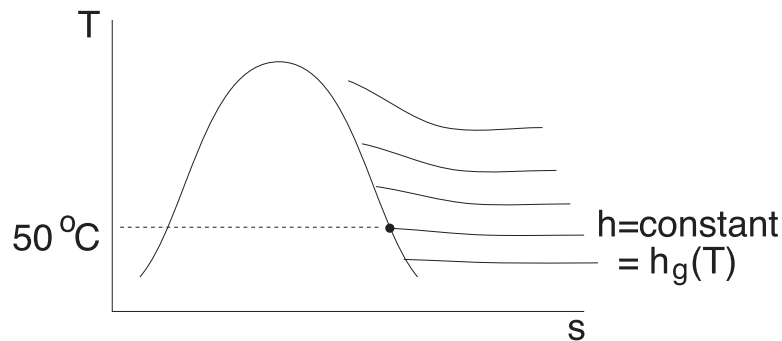
Entropy Change Due to Mixing of Ideal Gases

- 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

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

Psychrometrics

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

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 - 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

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

In addition ω can be written as

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

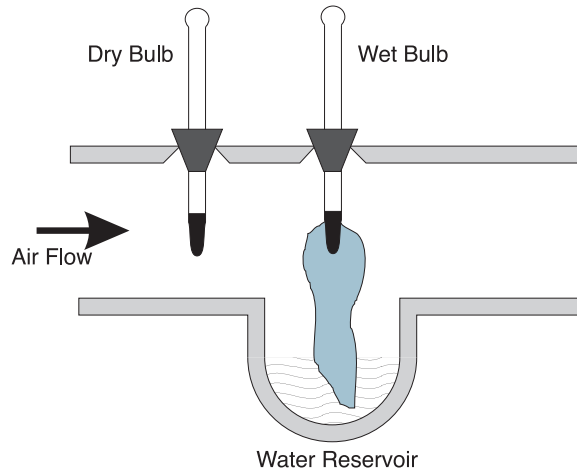
which can be rearranged in terms of relative humidity

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

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

Wet Bulb Temperature

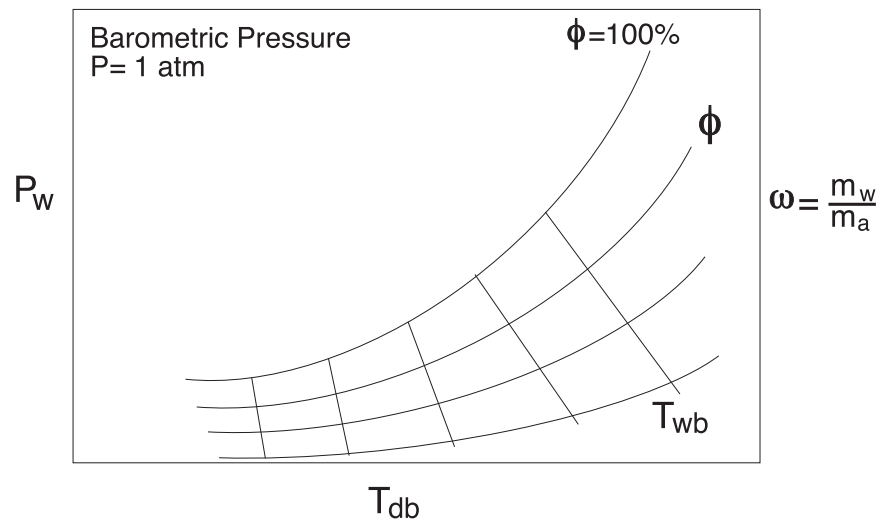
- thermometer surrounded by a saturated wick
- if air/water vapour mixture is not saturated, some water in the wick evaporates and diffuses into the air → cooling the water in the wick
- as the temperature of the water drops, heat is transferred to the water from both the air and the thermometer



- 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.

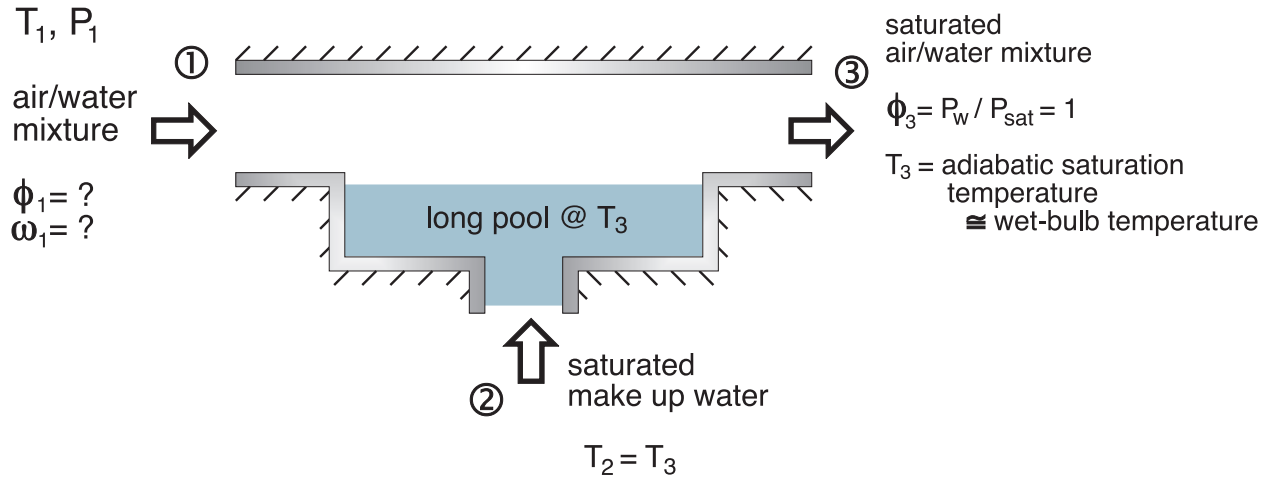
The Psychrometric Chart



where the **dry bulb** temperature is the temperature measured by a thermometer placed in the mixture and the **wet bulb** temperature is the adiabatic saturation temperature.

An Adiabatic Saturator

How can we measure humidity?



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

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

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

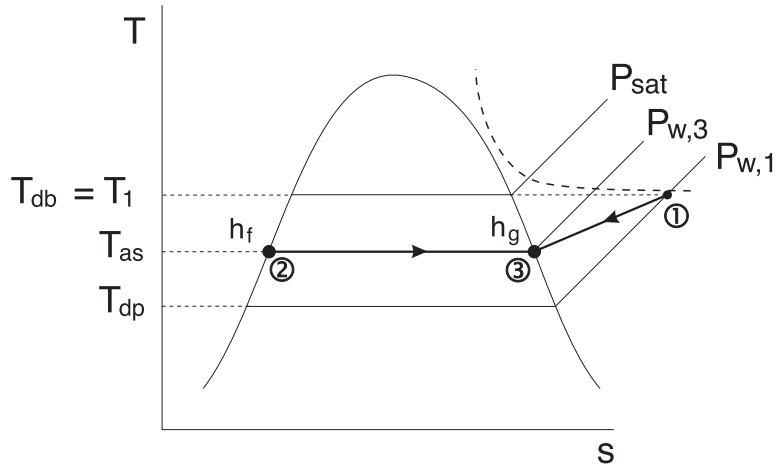
From (2) and (1)

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

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

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

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



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

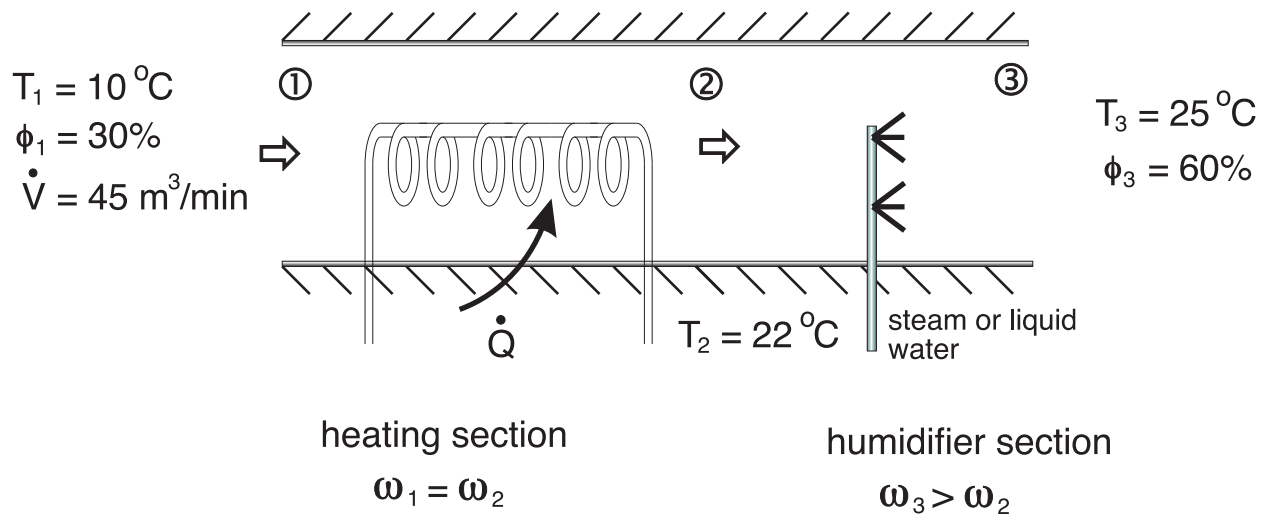
then we can write ω_1 as a function of T_1 and T_3 only

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

PROBLEM STATEMENT:

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

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



PROBLEM STATEMENT:

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

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