

UNIVERSITY OF NIGERIA, NSUKKA
DEPARTMENT OF MECHANICAL ENGINEERING

ME 561 – Thermodynamics III

Lecture Notes on
Mixtures and Solutions
for 2018/2019 Session
(Part I)

Lecturer:
Howard O. NJOKU *PhD*

April 25, 2019

Contents

1	Chemical Equilibrium	2
1.1	The Third Law of Thermodynamics and Absolute Entropy	2
1.2	Chemical Stoichiometry and Dissociation	2
1.3	Chemical Potential and the Gibbs Function	7
1.4	Chemical Equilibrium	9
1.5	Further discussions on Dissociation	15
1.6	Examples of the use of the equilibrium constant	17

1 Mixtures and Solutions

1. A non-reactive gas mixture is a multi-component system whose constituents do not react chemically with one another.
2. A reactive mixture is a multi-component system whose constituents may react chemically with one another.

The study of systems involving chemical reactions is an important topic in chemical thermodynamics. It has three main aspects corresponding to the three laws in nature, viz.:

- The principle of conservation of matter;
- The first law of thermodynamics; and
- The second law of thermodynamics.

1.1 Mixtures of ideal gases

Basic definitions:

1. The total mass, m of a mixture is the sum of the masses of each component i.e.,

$$m = m_1 + m_2 + m_3 + \dots = \sum_i m_i \quad (1)$$

and

$$1 = \frac{m_1}{m} + \frac{m_2}{m} + \frac{m_3}{m} + \dots = \sum_i \frac{m_i}{m} \quad (2)$$

The ratio $\frac{m_i}{m}$ is defined as the *mass fraction* of the i^{th} component in the mixture, and the analysis of gas mixtures on the basis of mass or weight is known as *gravimetric analysis*.

2. The total number of moles, n , for a mixture is the sum of the number of moles of the constituents, i.e.,

$$n = n_1 + n_2 + n_3 + \dots = \sum_i n_i \quad (3)$$

and

$$1 = \frac{n_1}{n} + \frac{n_2}{n} + \frac{n_3}{n} + \dots = \sum_i \frac{n_i}{n} = \sum_i x_i \quad (4)$$

where x_i is called the *molar fraction* of the i^{th} component, i.e., $x_i = \frac{n_i}{n}$, and the analysis of gas mixtures on the basis of moles is known as *molar analysis*.

For the i^{th} component of a mixture,

$$m_i = n_i M_i \quad (5)$$

This implies

$$m = \sum m_i = \sum_i n_i M_i \quad (6)$$

where M_i = molar mass or molecular weight of the i^{th} component. Average molecular weight, M , of the mixture is given as

$$\frac{m}{n} = M = \frac{\sum_i n_i M_i}{n} = \sum_i x_i M_i \quad (7)$$

$$\frac{M_i n_i}{M n} = \frac{m_i}{m} = \frac{M_i}{M} x_i \quad (8)$$

1.1.1 Dalton model

Consider a gas mixture of n moles occupying a volume, V at the equilibrium temperature and pressure of T and P , and treat the gas mixture as ideal, then

$$PV = n\bar{R}T \quad (9)$$

where $n = n_1 + n_2 + n_3 + \dots = \sum_i n_i$. For any i^{th} component,

$$P_i V = n_i \bar{R}T \quad (10)$$

where P_i is the partial pressure of the component in the mixture.

$$P = P_1 + P_2 + P_3 + \dots = \sum_i P_i \quad (11)$$

Equation (??) states the fact that *the total pressure of the mixture is the sum of the (partial) pressures which each component would exert if it alone occupied the whole volume of the mixture at the same temperature.* This is called Dalton's rule of partial pressures.

Dividing Equation (??) by Eqn. (??) gives

$$\frac{P_i}{P} = \frac{n_i}{n} = x_i$$

$$\text{or } P_i = x_i P \quad (12)$$

This states that the partial pressure of a component of an ideal gas mixture is the product of the mole fraction of that component and the total pressure of the mixture.

1.1.2 Amagat model (or the Amagat-Leduc model)

In the Amagat model, the properties of each component are considered as though each existed separately at the pressure and temperature of the mixture, i.e.,

$$V = V_1 + V_2 + V_3 + \dots = \sum_i V_i = \sum_i x_i V = V \sum_i x_i = V \quad (13)$$

where $\sum x_i = 1$ and $V_i = \frac{n_i \bar{R}T}{P}$ so that dividing by the equivalent form of Eqn. (??)

$$\frac{V_i}{V} = \frac{n_i}{n} = x_i$$

This is the Amagat-Leduc rule of partial volumes.

1.1.3 Internal energy, enthalpy and specific heats of an ideal gas mixture

Since each component of an ideal gas mixture behaves as if it occupies the volume of the mixture alone at the temperature of the mixture, the internal energy of each component may be given as

$$U_i = n_i \bar{u}_i \quad (14)$$

\bar{u}_i = molar internal energy of the i^{th} component and defined by T and V , or equivalently by T and P . Consider a mixture as a system consisting of several subsystem,

$$U = U_1 + U_2 + U_3 + \dots = \sum_i U_i = \sum_i n_i \bar{u}_i \quad (15)$$

Divide equation ?? by n ,

$$\frac{U}{n} = \bar{u} = \sum_i x_i \bar{u}_i \quad (16)$$

We can also go ahead to show that since

$$d\bar{u} = \bar{c}_v dT \quad (17)$$

then

$$\bar{c}_v = \sum_i x_i \bar{c}_{v,i} \quad (18)$$

but this will be left as an exercise.

From the definition of enthalpy

$$H_i = U_i + P_i V \quad (19)$$

Hence

$$\begin{aligned}\sum_i H_i &= \sum_i U_i + \sum_i V P_i \\ &= \sum_i U_i + V \sum_i P_i\end{aligned}\tag{20}$$

But $\sum_i U_i = U$ and $\sum_i P_i = P$

$$\therefore \sum_i H_i = U + PV\tag{21}$$

But by definition, $H = U + PV$, thus

$$H = \sum_i H_i\tag{22}$$

Now, $H_i = n_i \bar{h}_i$. By Eqn. (??),

$$H = n \bar{h} = \sum_i H_i = \sum_i n_i \bar{h}_i\tag{23}$$

Dividing through by n ,

$$\bar{h} = \sum_i x_i \bar{h}_i\tag{24}$$

Noting once again that $d\bar{h} = c_p dT$, it can be shown that

$$\bar{c}_p = \sum_i x_i \bar{c}_{p,i}\tag{25}$$

The foregoing equations were obtained in terms of the mole fractions of the components. In terms of the mass fractions of the components, they are re-stated as follows:

$$U = \sum_i m_i u_i\tag{26}$$

$$u = \sum_i \frac{m_i}{m} u_i\tag{27}$$

$$c_v = \sum_i \frac{m_i}{m} c_{v,i}\tag{28}$$

$$H = \sum_i m_i h_i\tag{29}$$

$$h = \sum_i \frac{m_i}{m} h_i\tag{30}$$

$$c_p = \sum_i \frac{m_i}{m} c_{p,i}\tag{31}$$

1.1.4 Entropy of an ideal gas mixture

Using the same line of reasoning used in arriving at the relation for internal energy, we can express the entropy of a gaseous mixture in terms of the entropies of the mixture's components.

$$S = \sum_i S_i = \sum_i n_i \bar{s}_i \quad (32)$$

Equation (32) represents the Gibbs' rules which states that the entropy of an ideal gas mixture is equal to the sum of the entropies that each component of the mixture would have if it alone occupied the volume of the mixture at the temperature of the mixture. Dividing Eqn. (32) by n ,

$$\frac{S}{n} = \bar{s} = \sum_i x_i \bar{s}_i \quad (33)$$

$$d\bar{s}_i = \bar{c}_{p,i} \frac{dT_i}{T_i} - \bar{R} \frac{dP_i}{P_i} \quad (34)$$

Substituting equation (34) into the differential form of equation (33) gives

$$d\bar{s} = \sum_i x_i \bar{c}_{p,i} \frac{dT_i}{T_i} - \sum_i x_i \bar{R} \frac{dP_i}{P_i} \quad (35)$$

In terms of masses,

$$ds = \frac{1}{m} \sum_i m_i c_{p,i} \frac{dT_i}{T_i} - \frac{1}{m} \sum_i m_i R_i \frac{dP_i}{P_i} \quad (36)$$

The pressure to be used in Eqns. (34) and (35) for each component is that determined by its temperature and its total volume.

1.1.5 Concluding remarks

There are a number of ways defining a mixture of ideal gases. It is proposed to use the following definitions:

- i) The gas mixture as a whole obeys equation of state $PV = n\bar{R}T$.
- ii) The total pressure of the mixture is the sum of the pressures which each component would exert if it alone occupied the *whole volume* of the mixture at the same temperature.
- iii) The internal energy, enthalpy and entropy of the mixture are respectively equal to the sums of the internal energies, enthalpies and entropies which each component of the mixture would have if each alone occupied the *whole volume* of the mixture at the same temperature.

The first condition implies that the gas mixture acts as if it were a single component ideal gas. While the last two conditions are the well known Gibbs-Dalton laws. The first

condition both indicates that the gas molecules are considered to move independently of one another in the whole volume of the system.

1.2 Mixtures of ideal gases and vapour (Gas-vapour Mixtures)

Let us consider problems involving a mixture of ideal gases that is in contact with a solid or liquid phase of one of the components. Most familiar example being a mixture of air and water vapor in contact with liquid water or ice, such as the problems encountered in air conditioning or drying.

Assumptions in analysis

1. The solid or liquid phase contains no dissolved gases.
2. The gaseous phase can be treated as a mixture of ideal gases.
3. When the mixture and the condensed phase are at a given pressure and temperature, the equilibrium between the condensed phase and its vapor is not influenced by the pressure of the other component. This means that when equilibrium is achieved, the partial pressure of the vapor will be equal to saturation pressure corresponding to the temperature of the mixture.

Terms used in the analysis of gas vapor mixture

Saturated Mixture: If the partial pressure of the water vapor corresponds to the saturation pressure of water at the mixture temperature, the mixture is said to be saturated.

Saturated Air: Is a mixture of dry air and saturated water vapor.

Unsaturated Air: Is a mixture of dry air and superheated vapor.

Psychrometry: Is the study of steam-air mixtures and is particularly concerned with the measurement of their properties. It is of special importance to heating, ventilation and air conditioning (HVAC) engineers.

Dry-Bulb Temperature: The temperature registered by the thermometer wetted by the wick is known as the wet-bulb temperature. This is normally lower than the dry-bulb temperature. The difference between the two is a measure of the humidity of the air.

Dew Point: The dew point of a gas-vapor mixture is the temperature at which the vapor condenses or solidifies when it is cooled at constant pressure.

1.2.1 Humidity ratio or specific humidity, ω

This is the ratio of the mass of water vapor to the mass of dry air in a given volume of mixture.

$$\omega = \frac{m_v}{m_a}$$

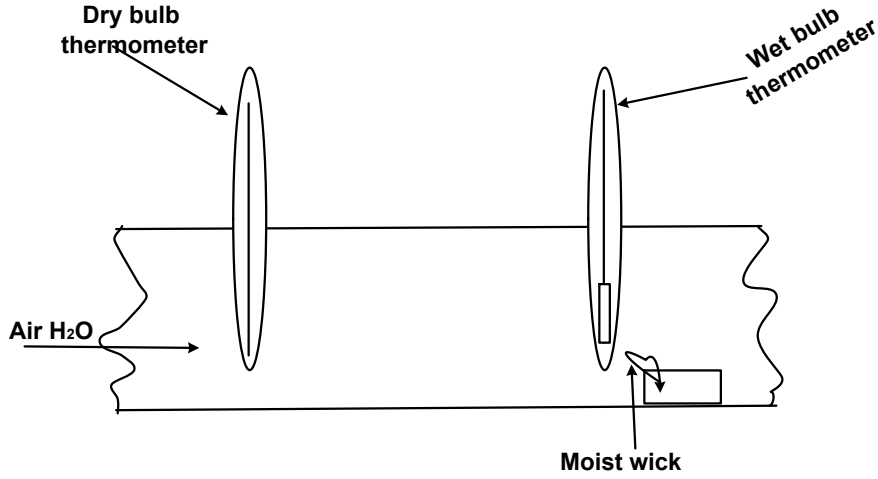


Figure 1: wet and dry bulb hygrometer

Assuming ideal-gas behaviour for both the dry air and vapor

$$m_v = \frac{P_v V}{R_v T}$$

and

$$m_a = \frac{P_a V}{R_a T}$$

$$\therefore \omega = \frac{R_a P_v}{R_v P_a}$$

For an air-water vapor mixture, this reduces to

$$\omega = 0.622 \frac{P_v}{P_a}$$

1.2.2 Relative humidity, ϕ

This is defined as the ratio of the mole fraction of the vapor in a mixture to the mole fraction of the vapor in a saturated mixture at same temperature and total pressure

$$\phi = \frac{P_v}{P_g}$$

or from Fig. ??,

$$\phi = \frac{P_1}{P_g}$$

$$\phi = \frac{P_v}{P_g} = \frac{P_v}{P_a} \cdot \frac{P_a}{P_g} = \frac{\omega}{0.622} \frac{P_a}{P_g}$$

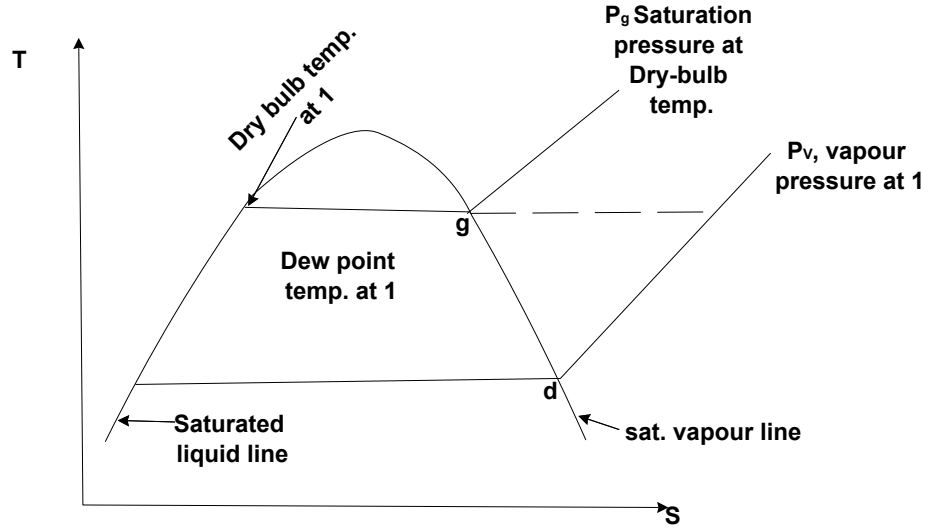


Figure 2: Vapor Pressure, Saturation pressure , Dew point temperature and dry bulb temperature. Dry-bulb temperature and Wet-bulb temperature.

or

$$\omega = 0.622\phi \frac{P_g}{P_a}$$

Noting that $P_v + P_a = P_g + P_a = P$,

$$\omega = 0.622\phi \frac{P_g}{P - P_g} = 0.622\phi \frac{P - P_a}{P_a}$$

Also noting that for a saturated mixture, $\phi = 1$,

$$\omega_{sat} = 0.622 \frac{P_g}{P_a}$$

1.2.3 Processes involving air-water-vapor mixture

The analysis of problems involving these kinds of processes will require the application of;

1. The principle of conservation of energy (The energy equation);
2. The principle of conservation of mass (The mass balance equation):
3. The principle of air water-vapor mixtures.
4. Gibb-Dalton relationships:

$$P = P_1 + P_2 + \dots$$

$$mh = m_1h_1 + m_2h_2 + \dots$$

$$mu = m_1u_1 + m_2u_2 + \dots$$

$$ms = m_1s_1 + m_2s_2 + \dots$$

The terms of the right hand side of each expression have to be evaluated for each component when that component is assumed to exist at the mixture's volume and temperature.

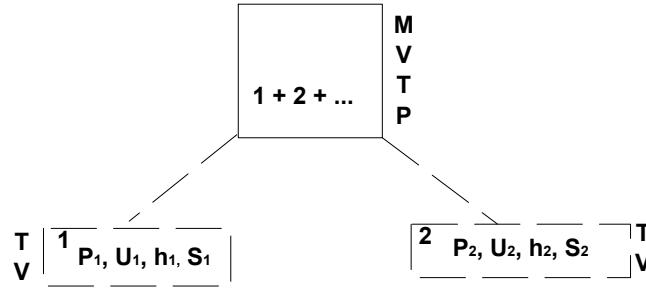


Figure 3: MVTP

The air - H₂O - mixtures considered includes all phases of H₂O. For a single-phase mixture, when only the gaseous phase is present i.e., the mixture is composed of air and steam, the Gibbs-Dalton law is applicable without modification.

Example

0.01 kg of steam and 0.99 kg of air from a gaseous mixture at a pressure of 100×10^3 N/m² and a temperature of 20°C. Determine

- The partial pressure of the steam and air.
- The specific volume of mixture and
- The enthalpy of the mixture.

Solutions (a) and (b) have to be solved simultaneously.

$$P = 100 \times 10^3 \text{ N/m}^2 = P_{\text{steam}} + P_{\text{air}}$$

For air,

$$P_{\text{air}} = \frac{R_{\text{air}}T}{v_{\text{air}}} = \frac{287 \times (293)}{v_{\text{air}}} \quad (37)$$

where $R_{\text{air}} = 8314.5 \text{ J/(kmol K)} \div 28.96 \text{ kg/kmol} \approx 287 \text{ J/(kg K)}$ is the gas constant for air. For steam, P_{steam} is related to v_{steam} by the data presented in the superheated steam table. Also,

$$V = \sum m_i \times v = (m_{steam} + m_{air}) \times v = m_{steam} \times v_{steam} = m_{air} \times v_{air} \quad (38)$$

where V and v are the volume and specific volume of the mixture, respectively.

$$1 \times v = 0.001 \times v_{steam} = 0.99 \times v_{air}$$

NB: Examination of the superheated steam table shows that it does not extend into the low pressure region which is required. Therefore we assume that at low pressure, steam can be treated as an ideal gas.

$$\therefore P_{steam} = \frac{R_{steam} T}{v_{steam}} \frac{462 \times 293}{v_{steam}} \quad (39)$$

where $R_{steam} = 8314.5 \text{ J/(kmol K)} \div 18.015 \text{ kg/kmol} \approx 462 \text{ J/(kg K)}$ is the gas constant for H_2O . Dividing Eqn. (??) by Eqn. (??) gives

$$\frac{P_{steam}}{P_{air}} = \frac{462}{287} \times \frac{v_{air}}{v_{steam}} = \frac{462}{287} \times \frac{0.01}{0.99} = 0.01626$$

or

$$P_{air} = \frac{P_{steam}}{0.01626}$$

But $P_{steam} + P_{air} = 100 \times 10^2 \text{ N/m}^2$,

$$\therefore P_{steam} + \frac{P_{steam}}{0.01626} = 100 \times 10^2$$

and so

$$P_{steam} = \frac{0.01626}{1 + 0.01626} \times 100 \times 10^2 = 1.60 \times 10^3 \text{ N/m}^2$$

$$P_{air} = P - P_{steam} = 100 \times 10^3 - 1.60 \times 10^3 = 98.40 \times 10^3 \text{ N/m}^2$$

From Eqn. (??),

$$v_{steam} = \frac{462 \times 293}{1.60 \times 10^3} = 84.4 \text{ m}^3/\text{kg}$$

From Eqn. (??),

$$V = 0.01 \times 0.846 \text{ m}^3/\text{kg of air}$$

Note: A solution by means of steam tables would be a trial and error process. The steps are as follows:

- i) Select a value of P_{steam} ;
- ii) From the steam table, at $T = 20^\circ\text{C}$, look up the corresponding value of v_{steam} ;
- iii) Evaluate P_{air} from $P = P_{steam} + P_{air}$;
- iv) Evaluate v_{air} from the ideal gas rule;

v) The values of v_{steam} and v_{air} have to satisfy

$$mv = m_{air}v_{air} + m_{steam}v_{steam}$$

$$\text{i.e } 0.01v_s = 0.99v_a$$

Select values of P_{steam} until agreement is reached.

Solution (c):

$$mh = m_{steam}h_{steam} + m_{air}h_{air} = 0.01h_{steam} + 0.99h_{air}$$

Since the supersaturated-steam table does not extend to the value of P_s , take h_s equal to h_g at 20°C, in conformity with our ideal gas assumption that $h = f(T)$. For air let $c_p = 1.0 \text{ kJ/Kg K}$. Note that for our selected approach for determining the specific enthalpies, the datum state (i.e., zero values of enthalpy) for saturated water is at the triple point, while for air it is at $T = 0.01^\circ\text{C}$.

$$1 \times h = (0.01 \times 2537.5) + (0.99 \times 1.0 \times 283.15) = 305.6935 \text{ kJ/kg}$$

Note that an inconsistency arises because of the different datums for the air and steam and the final quantity obtained has no physical meaning. This is not a problem in practice because what is usually required is not the specific enthalpy a given state but the enthalpy change as the mixture undergoes processes between two states. When this is so, a consistency should be maintained in the method for obtaining the specific enthalpies of the air and steam.

Example

A sample of atmospheric air contains 0.012 kg of water and 1.0 kg of dry air at 22°C and 95 kPa. During the night, the temperature drops to 10°C at the same pressure. Determine

- (a) the initial relative humidity;
- (a) the initial dew point, and
- (a) the mass of water condensed per unit mass of dry air.

Solution:

$$P = 95 \text{ kPa}, T_1 = 22^\circ\text{C}, T_2 = 10^\circ\text{C}$$

	m_i	M_i	$n_i = m_i/M_i$	$y_i = n_i / \sum n_i$
H ₂ O	0.012	18	0.000667	0.0191
Air	1.0	28.97	0.0345	0.981
			$\sum n_i = 0.035167$	

(a)

$$\phi = \frac{P_v}{P_g}$$

$$P_v = y_i \times P = 0.0190 \times 95 \text{ kPa} = 1.805 \text{ kPa} \equiv 0.01805 \text{ bar}$$

$$P_g = P_{sat} @ 22^\circ\text{C} = 0.02645 \text{ bar. Hence}$$

$$\phi = \frac{0.01805}{0.02645} = 0.682$$

(b) By interpolation from the steam tables,

$$\frac{T_{dew} - 15}{16 - 15} = \frac{0.01805 - 0.01705}{0.01818 - 0.01705}$$

From which we obtain $T_{dew} = 15.885^\circ\text{C}$.

(c) Since 10°C is below the dew point, condensation will occur. At 10°C $\phi = 1$ (100%), and thus $P_{v,2} = P_g @ 10^\circ\text{C}$ which is 0.01228 bar ($\equiv 1.228 \text{ kPa}$). The molar fraction of the steam at 10°C is

$$y_{v,2} = \frac{P_{v,2}}{P} = \frac{1.228 \text{ kPa}}{95 \text{ kPa}} = 0.0129$$

The molar fraction of air at 10°C will be

$$y_{a,2} = 1 - y_{v,2} = 1 - 0.0129 = 0.9871$$

The total number of moles in the mixture @ 10°C is

$$\sum n_{i,2} = \frac{n_a}{y_{a,2}} = \frac{0.03495}{0.9871} = 0.03495$$

Thus the number of moles of water vapour @ 10°C is

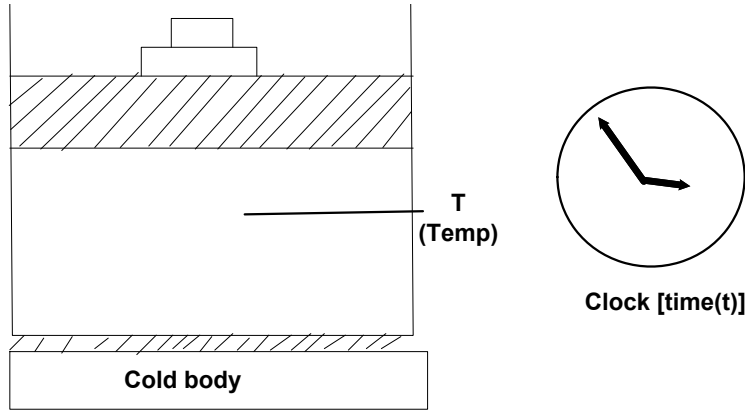
$$n_{v,2} = \sum n_{i,2} - n_a = 0.03495 - 0.0345 = 0.000451$$

and the mass of water vapour in the mixture @ 10°C is

$$m_{v,2} = n_{v,2} \times M_{H_2O} = 0.000451 \times 18 = 0.008118 \text{ kg}$$

Finally the mass of water condensed is

$$m_{v,1} - m_{v,2} = 0.012 - 0.008118 = 0.003882 \text{ kg}$$



1.2.4 Constant-pressure cooling experiments

Figure ?? above shows temperature-time curves for air-H₂O mixtures cooling at atmospheric pressure.

1.2.5 The enthalpy-composition diagram

The composition of a mixture, f is given as

$$f = \frac{\text{mass of H}_2\text{O}}{\text{mass of mixture}} = \frac{m_{\text{H}_2\text{O}}}{m_{\text{air}} + m_{\text{H}_2\text{O}}}$$

Thus $f = 1$ denotes pure water, while $f = 0$ denotes pure air. Alternatively, if the composition is given in terms of the mass of air, i.e.,

$$f = \frac{\text{mass of air}}{\text{mass of mixture}}$$

then $f = 1$ denotes pure air and $f = 0$ denotes pure H₂O. It is thus important to note that composition is another property to be specified while dealing with the type of problem. Since steam-air mixture is not a pure substance, three properties are needed to fix its state viz, temperature, specific volume and composition.

1.2.6 Application of the first law to mixtures

In applying the first law of thermodynamics to gas-vapor mixtures. It is helpful to realize that because of our assumption that ideal gas are involved, the various components can be treated separately when calculating changes of internal energy and enthalpy. When dealing with air-water vapor mixtures, the changes in enthalpy and internal energy of the water vapor can be found from the steam tables and the ideal gas relations can be applied to the air.

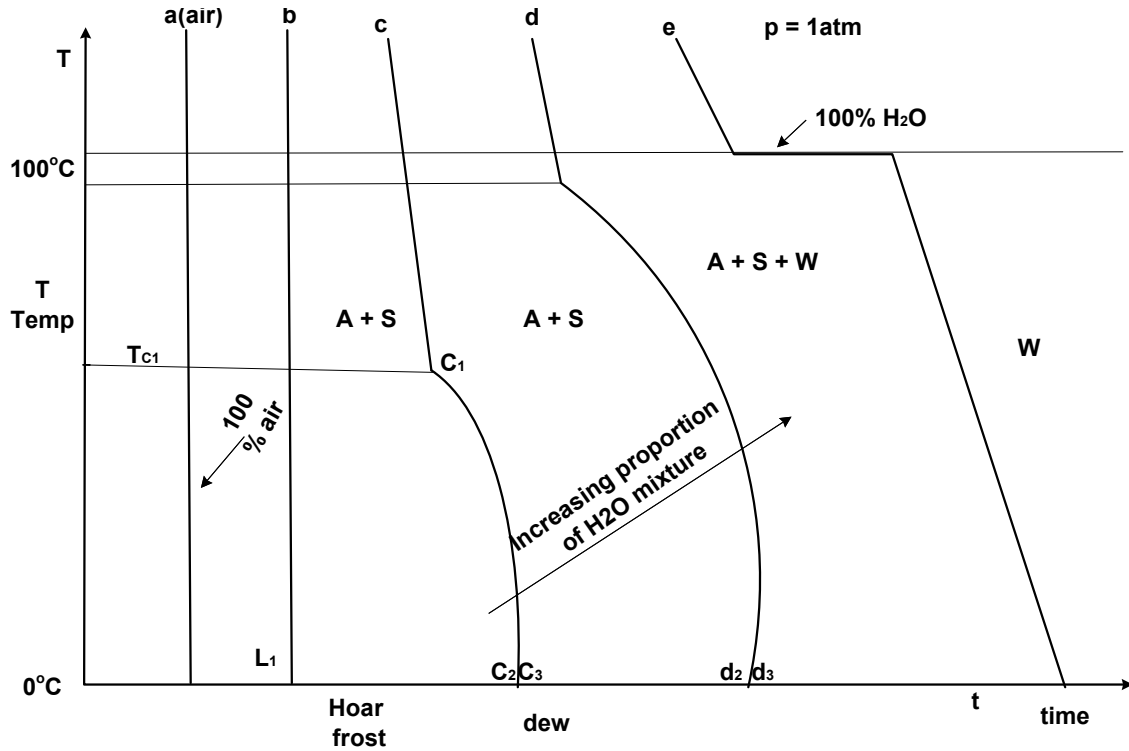


Figure 4: Constant pressure cooling for air-H₂O mixture.

- a 100 % air
- b Small ratio $\frac{m_{H_2O}}{m_{air}}$ (air + superheated steam)
- c Large ratio $\frac{m_{H_2O}}{m_{air}}$
- d 100% H₂O

Sample Problem

A rigid insulated vessel of 1 m³ capacity contains pure hydrogen at a pressure of 104×10^2 N/m² and a temperature of 16°C. It is connected to a compressed-air main in which the air at a gauge pressure of 280×10^3 N/m² and a temperature of 25°C. Air enters the vessel until the pressure in the main and in the vessel are equal. What is the final temperature of the mixture in the vessel?

Note: This problem is important because if a mixture of hydrogen and air becomes hot enough, it will explode.

Data needed:

For air, $R = 287$ J/kg K, $c_v = 717$ J/kg K

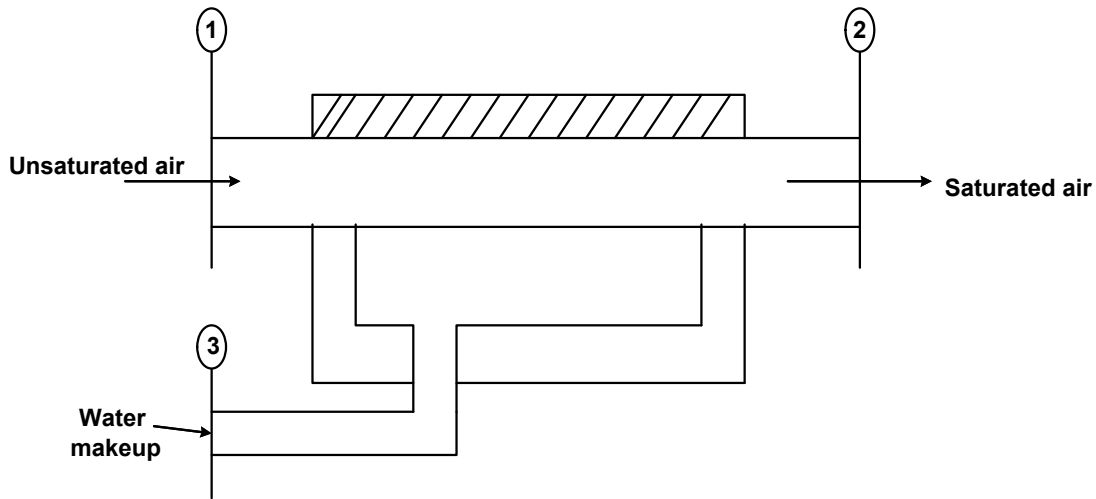
For hydrogen, $R = 4160$ J/Kg K, $c_v = 1008$ J/kg K.

Sample Problem

0.1 kmol of CO₂ initially at 2 bars and 27°C is mixed adiabatically with 0.2 kmol of O₂ initially at 5 bars and 152°C. during the constant-volume mixing process, electric energy equal to 670 kJ/kmol of the mixture is added. Determine

- the final temperature of the mixture, in °C, using tabular data and
- the final pressure in bars.

1.2.7 Adiabatic saturation process



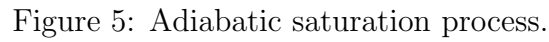
An important process involving an air-water vapor mixture is the adiabatic saturation process, in which an air-vapor mixture comes in contact with a body of water in a well insulated duct. An unsaturated air of dry bulb temperature T_1 enters an insulated chamber containing a body of water. It leaves as saturated air with a temperature of T_2 . When the unsaturated air passes over the water surface, some of the water is evaporated. The energy for evaporation comes from both the moist air and the water in the chamber. Since the system is insulated, the temperature of the air decreases. Therefore T_2 will be lower than T_1 . If the water being added to the air is equal to T_2 , the final equilibrium temperature is called the thermodynamic wet bulb temperature, also known as the **adiabatic saturation temperature**.

The energy balance for the adiabatic saturator is stated as

$$\dot{m}_{a,1}h_1 + \dot{m}_{w,3}h_{w,3} = \dot{m}_{a,2}h_2$$

But $h = h_a + \omega h_v$

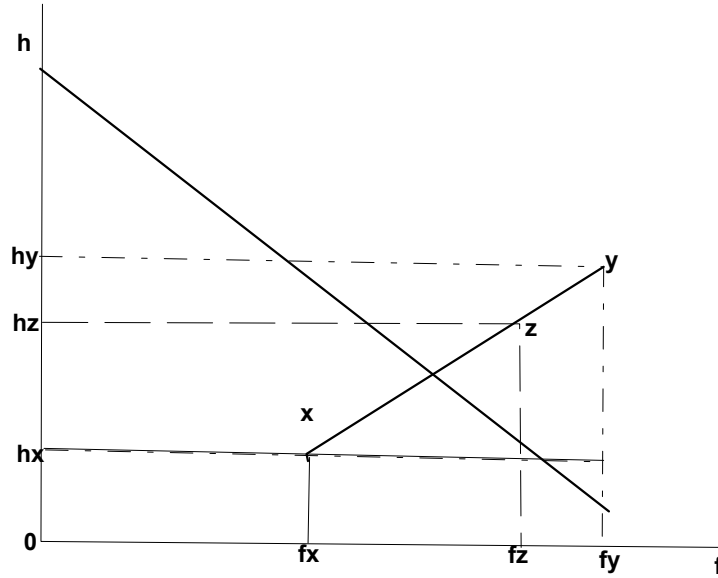
$$\therefore \dot{m}_{a,1}(h_a + \omega h_v)_1 + \dot{m}_{w,3}h_{w,3} = \dot{m}_{a,2}(h_a + \omega h_v)_2 \quad (a)$$


$$\dot{m}_{a,1} = \dot{m}_{a,2} = \dot{m}_a$$
$$\dot{m}_{v,1} + \dot{m}_{w,3} = \dot{m}_{v,2} \implies \dot{m}_{w,3} = \dot{m}_{v,2} - \dot{m}_{v,1}$$
$$\dot{m}_{w,3} = \omega_2 \dot{m}_a - \omega_1 \dot{m}_a = \dot{m}_a (\omega_2 - \omega_1)$$
$$\dot{m}_a(h_a + \omega h_v)_1 + \dot{m}_a(\omega_2 - \omega_1)h_{w,3} = \dot{m}_a(h_a + \omega h_v)_2$$
$$h_{a,1} + \omega_1 h_{v,1} + (\omega_2 - \omega_1) h_{w,3} = h_{a,2} + \omega_2 h_{v,2}$$
$$\begin{aligned}
\omega_1(h_{v,1} - h_{w,3}) &= h_{a,2} - h_{a,1} + \omega_2(h_{v,2} - h_{w,3}) \\
\Rightarrow \omega_1 &= \frac{h_{a,2} - h_{a,1} + \omega_2(h_{v,2} - h_{w,3})}{(h_{v,1} - h_{w,3})} \\
&\approx \frac{c_{p,a}(T_2 - T_1) + \omega_2(h_{g,2} - h_{w,3})}{(h_{g,1} - h_{w,3})} \quad (40)
\end{aligned}$$

Earlier, it had been stated that $T_2 \equiv T_{ad,1}$, the specific enthalpy of the make-up fluid is the saturation enthalpy at $T_3 = T_2$, i.e., $h_{w,3} = h_{f,2}$ thus $h_{g,2} - h_{w,3} = h_{fg,2}$. Substituting these into Eqn. (??),

$$\omega_1 = \frac{c_{p,a}(T_2 - T_1) + \omega_2(h_{g,2} - h_{w,3})}{(h_{g,1} - h_{w,3})} \quad (41)$$

1.2.8 The mixing rule



If X and Y are the state-points of two air-H₂O systems on an $h - f$ diagram and these two systems are mixed together adiabatically at constant pressure in the mass proportions m_x to m_y , the state point, Z for the resultant system lies on the line XY and divides it so that

$$\frac{ZY}{XZ} = \frac{m_x}{m_y}$$

Proof: Applying first law,

$$Q - W = \Delta U$$

Since the mixing process is adiabatic, $Q = 0$,

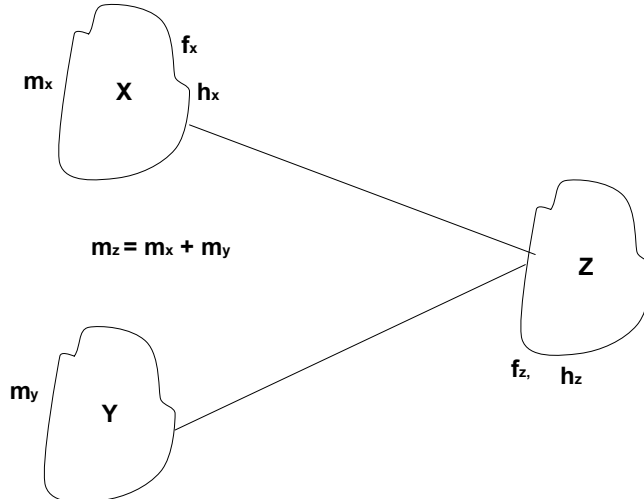
$$0 - W = \Delta U$$

For constant pressure, this equation reduces to

$$\Delta H = 0$$

i.e., Final H = Initial H

$$(m_x + m_y)h_z = m_x h_x = m_y h_y$$



$$\frac{m_x}{m_y} = \frac{h_y - h_z}{h_z - h_x}$$

Applying the conservation of mass, the principle of conservation of mass applied to H_2O in the process

$$(m_{H_2O})_z = (m_{H_2O})_x + (m_{H_2O})_y$$

$$m_z f_z = m_x f_x + m_y f_y$$

$$\frac{m_x}{m_y} = \frac{f_y - f_z}{f_z - f_x}$$

These show that we have a straight line relationship between enthalpy and composition.

1.2.9 Adiabatic saturation on a $h - f$ diagram

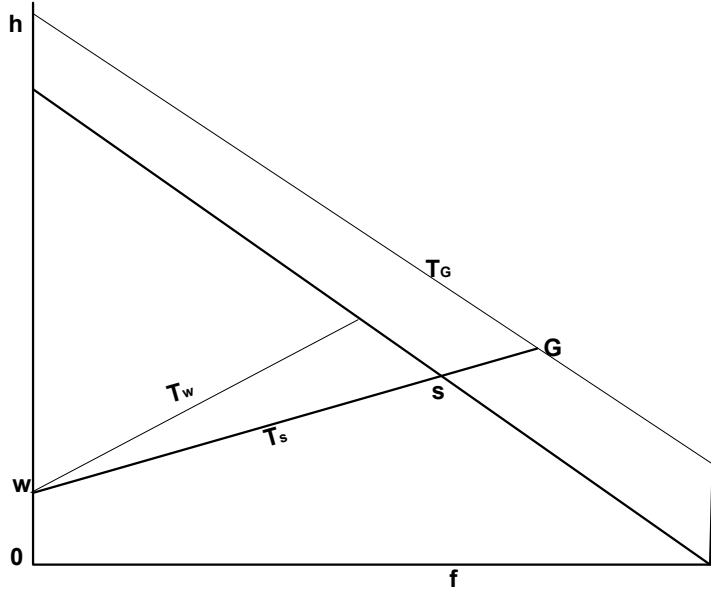
G represents the initial state the air-steam mixture while W represents the state of the water which is to be mixed with it. How much water must be added to produce S ?

The mixing rule shows that the state point for the resultant mixture must lie on the line WG . But it must also lie on the saturation line. The required state point is S where WG cuts the saturation line.

$$\frac{mw}{mg} = \frac{SG}{WS}$$

Example

The pressure of the mixture entering and leaving the adiabatic saturation is 1 bar, the entering temperature of 30°C and the temperature of mixture leaving is 20°C which is the adiabatic saturation temperature. Calculate the humidity ratio and relative humidity of



the air-water vapor entering the saturator.

Solution:

Since the water leaving is saturated,

$$P_{v2} = P_{g2}$$

and ω_2 can be calculated from

$$\omega_2 = 0.622 \times \left(\frac{2.339}{100 - 2.34} \right) = 0.0149$$

$$\omega_1 = \frac{c_{pa}(T_2 - T_1) + \omega_2 h_{fg,2}}{h_{v,1} - h_{f,2}} \quad (42)$$

$$= \frac{1.0035(20 - 30) + 0.0149 \times 2454.1}{2556.3 - 83.96} = 0.0107 \quad (43)$$

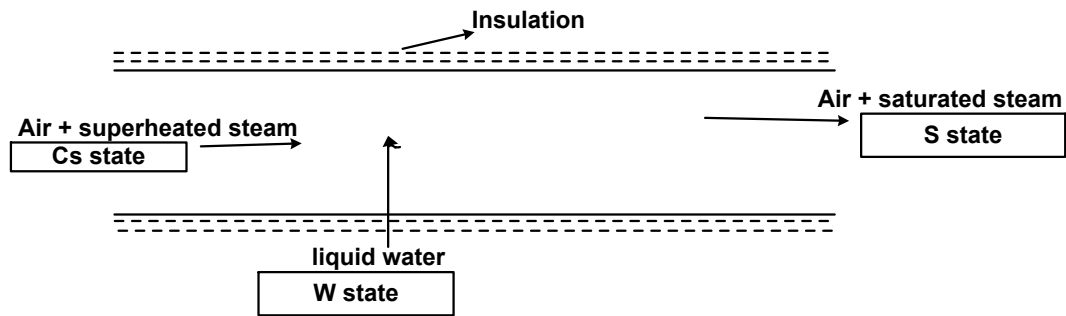
$$\omega_1 = 0.0107 = 0.622 \times \left(\frac{P_{v,1}}{100 - P_{v,1}} \right)$$

Hence $P_{v,1} = 1.691$ kPa

$$\phi = \frac{P_{v,1}}{P_{g,1}} = \frac{1.691}{4.246} = 0.398$$

1.2.10 Psychrometric chart

The numerous property data for air-water vapour mixtures have been presented graphically in the *psychrometric chart* for ease. The chart is widely used for HVAC applications as well as drying applications. The dry-bulb temperature is represented on the abscissa of



the chart while humidity ratio is represented on the ordinate. Other properties include the specific volume, relative and specific humidities, vapour pressures, and specific enthalpy. The specific enthalpy is defined in terms of the mass of air, i.e.,

$$H = m_a h = m_a h_a + m_v h_v$$

$$\therefore h = h_a + \omega h_v$$

A sample of the psychrometric chart is presented in the figure below.

Exercises

- (A) A mixture at 300 K and 160 kPa has the following volumetric analysis: O₂, 60 %; CO₂, 40 %. Compute (a) the mass analysis, (b) the partial pressure of O₂, in kPa, (c) the apparent molar mass, and (d) the volume occupied by 0.13 kg of the mixture, in m³.

(B) A gas mixture at 120 kPa and 0.063 m³ has the following gravimetric analysis: O₂, 32%; CO₂, 56 %; He, 12 %. Determine (a) the volumetric analysis, (b) the apparent gas constant in kJ/(kg K), and (c) the temperature of 0.050 kg of the mixture, in K.
- A gas mixture is made up of 64% O₂ and 36 % H₂, by mass. The total pressure is 3 bars, and the volume is 0.10 m³. Determine (a) the partial pressure of hydrogen, in bars, (b) the apparent molar mass in kg/kmol, (c) the gas constant, in kJ/(kg K), and (d) the temperature, in K, if the mass of the mixture is 0.052 kg.
- A gas at 77°C and 100 kPa has the following volumetric analysis: H₂, 4 %; CO, 12

- %, CO_2 25 %; and N_2 , 59 %. The initial mixture passes at $20 \text{ m}^3/\text{min}$ through a steady-flow heat exchanger until the temperature reaches 227°C . Determine (a) the gravimetric analysis, (b) the heat transfer based on tabular ideal-gas tables, (c) the heat transfer based on average specific-heat data, in kJ/kg and (d) the heat transfer rate in kJ/min .
4. Carbon monoxide and argon in separate streams enter an adiabatic mixing chamber in a 2:1 ratio. At the inlet the CO is at 120 kPa and 300 K, and the Ar is at 120 kPa and 450 K. The mixture leaves at 110 kPa. Determine (a) the final temperature of the mixture in K, and (b) the entropy production for the process, in kJ/K per kmol of mixture.
 5. Hydrogen and nitrogen in separate streams enter an adiabatic mixing chamber in a 3:1 molar ratio. At the inlet the H_2 is at 2 bars and 77°C , and the N_2 is at 2 bars and 277°C . The mixture leaves at 1.9 bars. (a) Determine the final temperature of the mixture, in K. (b) Compute the entropy production of the overall process, in $\text{kJ}/(\text{kmol K})$.
 6. **(A)** A rigid tank with a volume of 300 L initially contains 0.34 kg of dry air at 60°C . Water vapor is added until the gas is saturated at the same temperature. Determine (a) the mass of water added, in kg, and (b) the final total pressure, in kPa.
(B) Atmospheric air at 1 bar has dry-bulb temperature of 25°C and a relative humidity of 50 %. Use a psychrometric chart to estimate (a) the wet-bulb temperature, (b) dew point, (c) specific humidity and (d) specific enthalpy.
 7. **(A)** A tank contains 10 kg of dry air and 0.15 kg of water vapour at 26°C and 100 kPa. Determine (a) the specific humidity, (b) the relative humidity, and (c) the volume of the tank in m^3 .
(B) Atmospheric air at 1 bar has dry-bulb and wet-bulb temperatures of 25 and 20°C . By use of a psychrometric chart, estimate the values of (a) relative humidity, (b) dew point, (c) specific humidity, and (d) specific enthalpy.
 8. **(A)** Atmospheric air initially at 20°C , 1 bar, and 70 % relative humidity is compressed isothermally until the pressure reaches 2 bars. (a) Show that condensation must occur. (b) Determine the amount of water condensed, in kg of H_2O / kg of dry air.
(B) Atmospheric air at 1 bar has dry-bulb temperature of 28°C and a specific humidity of $0.0090 \text{ kg H}_2\text{O}/\text{kg dry air}$. Use a psychrometric chart to estimate (a) the wet-bulb temperature, (b) relative humidity, (c) dew point, and (d) specific enthalpy.

9. If the partial pressure of water vapour in atmospheric air at 1 bar is 30 mbars at 30°C, calculate (a) the relative humidity, (b) the dew-point temperature, (c) the humidity ratio, (d) the enthalpy, kJ/kg (based on $h = 0$ at 0°C for both dry air and water), and (e) the specific volume of the mixture, in m³/kg dry air. Use steam-table data where necessary.
10. **(A)** Atmospheric air at 22°C and 99 kPa has an enthalpy of 40.0 kJ/kg dry air (based on $h = 0$ at 0°C for dry air). Calculate (a) the specific humidity in kg/kg, (b) the vapour pressure of water, in kPa, (c) the relative humidity, and (d) the specific volume, in m³/kg dry air.
- (B)** Atmospheric air at 1 bar has dry-bulb temperature of 26°C and a specific enthalpy of 65 kJ/kg dry air. Use a psychrometric chart to estimate (a) the wet-bulb temperature, (b) relative humidity, (c) specific humidity, and (d) the specific volume.
11. A gas mixture is made up of 50% O₂ and 50 % H₂, by mass. The total pressure is 3 bars, and the volume is 0.10 m³. Determine (a) the partial pressure of hydrogen, in bars, (b) the apparent molar mass in kg/kmol, (c) the gas constant, in kJ/(kg K), and (d) the temperature, in K, if the mass of the mixture is 0.052 kg.



PSYCHROMETRIC CHART

NORMAL TEMPERATURES

SI METRIC UNITS

Barometric Pressure 101,325 kPa

SEA LEVEL

