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Chapter 14

GAS-VAPOR MIXTURES AND AIR-CONDITIONING

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GAS-VAPOR MIXTURES AND AIR-CONDITIONING

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Simple Heating and Cooling (ω =constant) Heating with Humidification Cooling with Dehumidification Evaporative Cooling Adiabatic Mixing of Airstreams Wet Cooling Towers

Objectives

- Explain the meaning of the terms dry air and atmospheric air.
- Define and calculate the specific and relative humidity of atmospheric air.
- Calculate the dew-point temperature of atmospheric air.
- Relate the adiabatic saturation temperature and wet-bulb temperatures of atmospheric air.
- Use the psychrometric chart as a tool to determine the properties of atmospheric air.
- Relate the desire for human comfort to air-conditioning requirements.
- Solve problems associated with the conservation of mass and energy for various air-conditioning processes.

DRY AND ATMOSPHERIC AIR

Atmospheric air : Air is a mixture of nitrogen, oxygen, and small amounts of some other gases.

We will be concerned with the mixture of dry air and water vapor. This mixture is often called atmospheric air.

Dry air: air that contains no water vapor is called dry air.

$$h_{\rm dry\,air} = c_p T = (1.005 \text{ kJ/kg} \cdot ^{\circ}\text{C})T \qquad (\text{kJ/kg})$$

 $\Delta h_{\rm dry\,air} = c_p \Delta T = (1.005 \,\text{kJ/kg} \cdot ^\circ\text{C}) \,\Delta T \qquad (\text{kJ/kg})$

where T is the air temperature in °C and T is the change in temperature.

In air-conditioning processes we are concerned with the *changes* in enthalpy Δh , which is independent of the reference point selected.

water vapor in air behaves as if it existed alone and obeys the ideal-gas relation Pv = RT. Then the atmospheric air can be treated as an ideal-gas mixture whose pressure is the sum of the partial pressure of dry air* P_a and that of water vapor P_v :

$$P = P_a + P_v \qquad \text{(kPa)}$$

$$P = P_a + P_v \quad \text{(kPa)}$$

 P_a the sum of the partial pressure of dry air P_v water vapor

The partial pressure of water vapor is usually referred to as the **vapor pressure**. It is the pressure water vapor would exert if it existed alone

at the temperature and volume of atmospheric air.

DRY AIR		
<i>−T</i> , °C	$-c_p$, kJ/kg · °C	
-10	1.0038	
0	1.0041	
10	1.0045	
20	1.0049	
	1.0054	
40	1.0059	
50	1.0065	

The c_p of air can be assumed to be constant at 1.005 kJ/kg \cdot °C in the temperature range 10 to 50°C with an error under 0.2 %.

It certainly would be very convenient to also treat the water vapor in the air as an ideal gas and you would probably be willing to sacrifice some accuracy for such convenience. Well, it turns out that we can have the convenience without much sacrifice. At 50°C, the saturation pressure of water is 12.3 kPa. At pressures below this value, water vapor can be treated as an ideal gas with negligible error (under 0.2 %), even when it is a saturated vapor. For water: $h_g = 2500.9 \text{ kJ/kg} \text{ at } 0^{\circ}\text{C}$ $c_{p,avg} = 1.82 \text{ kJ/kg} \cdot ^{\circ}\text{C} \text{ at } -10 \text{ to } 50^{\circ}\text{C} \text{ range}$

$$h_g(T) \cong 2500.9 + 1.82T$$
 (kJ/kg) $T \text{ in }^\circ\text{C}$

Since water vapor is an ideal gas, the enthalpy of water vapor is a function of temperature only, that is, h = h(T).

Therefore, the enthalpy of water vapor in air can be taken to be equal to the enthalpy of saturated vapor at the same temperature. That is,

 $h_v(T, \text{low } P) \cong h_g(T)$



0 WATER VAPOR h_g , kJ/kg Difference. kJ/kg *T*, °C Eq. 14-4 Table A-4 -102482.1 2482.7 -0.62500.9 0.00 2500.92519.2 2519.1 100.120 2537.4 2537.3 0.130 2555.6 2555.5 0.1-0.240 2573.5 2573.72591.3 2591.9 50 -0.6

At temperatures below 50°C, the h = constant lines coincide with the *T*=constant lines in the superheated vapor region of water. In the temperature range 10 to 50°C, the h_g of water can be determined from $(h_g(T) \cong 2500.9 + 1.82 T)$ with negligible error.

SPECIFIC AND RELATIVE HUMIDITY OF AIR

Absolute or Specific humidity (humidity ratio): The amount of water vapor in the air can be specified in various ways. Probably the most logical way is to specify directly the mass of water vapor present in a unit mass of dry air. This is called **absolute** or **specific humidity** (also called *humidity ratio*) and is denoted by v:

$$\omega = \frac{m_v}{m_a} = \frac{P_v V/R_v T}{P_a V/R_a T} = \frac{P_v /R_v}{P_a /R_a} = 0.622 \frac{P_v}{P_a}$$

The specific humidity can also be expressed as

$$\omega = \frac{m_v}{m_a} \qquad (\text{kg water vapor/kg dry air})$$

where *P* is the total pressure:
$$\omega = \frac{0.622P_v}{P - P_v} \qquad (\text{kg water vapor/kg dry air})$$

Saturated air: The air is said to be saturated with moisture.

Relative humidity (ϕ) : The comfort level depends more on the amount of moisture the air holds (m_v) relative to the maximum amount of moisture the air can hold at the same temperature (m_a). The ratio of these two quantities is called the **relative humidity**.

$$\phi = \frac{m_v}{m_g} = \frac{P_v V/R_v T}{P_g V/R_v T} = \frac{P_v}{P_g}$$

$$P_g = P_{\operatorname{doy} \underline{@} T}$$



For staturated air, the vapor pressure is equal to the saturation pressure of water.

The amount of moisture in the air has a definite effect on how comfortable we feel in an environment.

However, the comfort level depends more on the amount of moisture the air holds (m_v) relative to the maximum amount of moisture the air can hold at the same temperature (m_a) . The ratio of these two quantities is called the **relative humidity** ϕ



Specific humidity is the actual amount of water vapor in 1 kg of dry air, whereas relative humidity is the ratio of the actual amount of moisture in the air to the maximum amount of moisture air can hold at the temperature.

$$\phi = \frac{\omega P}{(0.622 + \omega)P_g} \quad \text{and} \quad \omega = \frac{0.622\phi P_g}{P - \phi P_g}$$

The relative humidity ranges from 0 for dry air to 1 for saturated air. Note that the amount of moisture air can hold depends on its temperature. Therefore, the relative humidity of air changes with temperature even when its specific humidity remains constant.

Atmospheric air is a mixture of dry air and water vapor, and thus the enthalpy of air is expressed in terms of the enthalpies of the dry air and the water vapor. In most practical applications, the amount of dry air in the air–water-vapor mixture remains constant, but the amount of water vapor changes.

Therefore, the enthalpy of atmospheric air is expressed *per unit mass of dry air* instead of per unit mass of the air–water-vapor mixture.

$$H = H_a + H_v = m_a h_a + m_v h_v$$

$$h = \frac{H}{m_a} = h_a + \frac{m_v}{m_a} h_v = h_a + \omega h_v$$

$$h = h_a + \omega h_g \quad (kJ/kg dry air)$$

$$h_v \simeq h_g$$

Dry-bulb temperature: The ordinary temperature of atmospheric air is frequently referred to as the **dry-bulb temperature** to differentiate it from other forms of temperatures.



The enthalpy of moist (atmospheric) air is expressed per unit mass of dry air, not per unit mass of moist air.

Example 14–1

A 5-m 5-m 3-m room contains air at 25°C and 100 kPa at a relative humidity of 75%. Determine (a) the partial pressure of dry air, (b) the specific humidity, (c) the enthalpy per unit mass of the dry air, and (d) the masses of the dry air and water vapor in the room.

(a) the partial pressure of dry air

$$P_a = P - P_v$$

ROOM

$$5 \text{ m} \times 5 \text{ m} \times 3 \text{ m}$$

 $T = 25^{\circ}\text{C}$
 $P = 100 \text{ kPa}$
 $\phi = 75\%$

$$P_v = \phi P_g = \phi P_{\text{sat @ 25^{\circ}C}} = (0.75)(3.1698 \text{ kPa}) = 2.38 \text{ kPa}$$

$$P_a = (100 - 2.38) \text{ kPa} = 97.62 \text{ kPa}$$

(b) the specific humidity

$$\omega = \frac{0.622P_v}{P - P_v} = \frac{(0.622)(2.38 \text{ kPa})}{(100 - 2.38) \text{ kPa}} = 0.0152 \text{ kg H}_2\text{O/kg dry air}$$

(c) the enthalpy per unit mass of the dry air

$$h = h_a + \omega h_v \cong c_p T + \omega h_g$$

= (1.005 kJ/kg · °C)(25°C) + (0.0152)(2546.5 kJ/kg)
= 63.8 kJ/kg dry air

The enthalpy of water vapor (2546.5 kJ/kg) could also be determined from the approximation given $(h_g(T) \cong 2500.9 + 1.82T)$

$$h_{g@25^{\circ}C} \cong 2500.9 + 1.82(25) = 2546.4 \text{ kJ/kg}$$

(d) Both the dry air and the water vapor fill the entire room completely. Therefore, the volume of each gas is equal to the volume of the room:

$$V_a = V_v = V_{\text{room}} = (5)(5)(3) = 75 \text{ m}^3$$

$$m_{a} = \frac{P_{a}V_{a}}{R_{a}T} = \frac{(97.62 \text{ kPa})(75 \text{ m}^{3})}{(0.287 \text{ kPa} \cdot \text{m}^{3}/\text{kg} \cdot \text{K})(298 \text{ K})} = 85.61 \text{ kg}$$
$$m_{v} = \frac{P_{v}V_{v}}{R_{v}T} = \frac{(2.38 \text{ kPa})(75 \text{ m}^{3})}{(0.4615 \text{ kPa} \cdot \text{m}^{3}/\text{kg} \cdot \text{K})(298 \text{ K})} = 1.3 \text{ kg}$$

The mass of the water vapor in the air could also be determined from $\omega = rac{m_v}{m_a}$

$$m_v = \omega m_a = (0.0152)(85.61 \text{ kg}) = 1.30 \text{ kg}$$

DEW-POINT TEMPERATURE

Dew-point temperature T_{dp} : T_{dp} is defined as the temperature at which condensation begins when the air is cooled at constant pressure.



Constant-presssure cooling of moist air and the dew-point temperature on the *T*-*s* diagram of water. The vapor in the air (state 1) undergoes a constant-pressure cooling process until it strikes the saturated vapor line (state 2).

The temperature at this point is T_{dp} , and if the temperature drops any further, some vapor condenses out.

As a result, the amount of vapor in the air decreases, which results in a decrease in P_v . The air remains saturated during the condensation process and thus follows a path of 100 % relative humidity (the saturated vapor line). The ordinary temperature and the dew-point temperature of saturated air are identical.



When the temperature of a cold drink is below the dewpoint temperature of the surrounding air, it "sweats."

You have probably noticed that when you buy a cold canned drink from a vending machine on a hot and humid day, dew forms on the can.

The formation of dew on the can indicates that the temperature of the drink is below the dew-point temperature of the surrounding air .

Example 14-2

In cold weather, condensation frequently occurs on the inner surfaces of the windows due to the lower air temperatures near the window surface. Consider a house that contains air at 20°C and 75 percent relative humidity. At what window temperature will the moisture in the air start condensing on the inner surfaces of the windows?

The saturation pressure of water at 20°C is P_{sat} = 2.3392 kPa

The temperature distribution in a house, in general, is not uniform. When the outdoor temperature drops in winter, so does the indoor temperature near the walls and the windows. Therefore, the air near the walls and the windows remains at a lower temperature than at the inner parts of a house even though the total pressure and the vapor pressure remain constant throughout the house. As a result, the air near the walls and the windows will undergo a P_v constant cooling process until the moisture in the air starts condensing. This will happen when the air reaches its dew-point temperature T_{dp} . The dew point is determined from;



 $T_{dp} = T_{sat @ P_{v}} \qquad P_{v} = \phi P_{g @ 20^{\circ}C} = (0.75)(2.3392 \text{ kPa}) = 1.754 \text{ kPa}$ $T_{dp} = T_{sat @ 1.754 \text{ kPa}} = \mathbf{15.4 ^{\circ}C}$

Therefore, the inner surface of the window should be maintained above 15.4°C if condensation on the window surfaces is to be avoided.

ADIABATIC SATURATION AND WET-BULB TEMPERATURES

Relative humidity and specific humidity are frequently used in engineering and atmospheric sciences, and it is desirable to relate them to easily measurable quantities such as temperature and pressure.

One way of determining the relative humidity is to determine the dew-point temperature of air, as discussed in the last section. Knowing the dew-point temperature, we can determine the vapor pressure P_v and thus the relative humidity. This approach is simple, but not quite practical.

Mass balance:		
	$\dot{m}_{a_1} = \dot{m}_{a_2} = \dot{m}_a$	(The mass flow rate of dry air remains constant)
	$\dot{m}_{w_1} + \dot{m}_f = \dot{m}_{w_2}$	(The mass flow rate of vapor in the air increases by an amount equal to the rate of evaporation \dot{m}_f)

$$\dot{m}_a \omega_1 + \dot{m}_f = \dot{m}_a \omega_2$$

$$\dot{m}_f = \dot{m}_a(\omega_2 - \omega_1)$$



Another way of determining the absolute or relative humidity is related to an *adiabatic saturation process*, shown schematically and on a *T-s* diagram in Figure.

The system consists of a long insulated channel that contains a pool of water. A steady stream of unsaturated air that has a specific humidity of ω_1 (unknown) and a temperature of T_1 is passed through this channel.

As the air flows over the water, some water will evaporate and mix with the airstream. The moisture content of air will increase during this process, and its temperature will decrease, since part of the latent heat of vaporization of the water that evaporates will come from the air. If the channel is long enough, the airstream will exit as saturated air (ϕ = 100 percent) at temperature T_2 , which is called the **adiabatic saturation temperature**.



The adiabatic saturation process discussed above provides a means of determining the absolute or relative humidity of air, but it requires a long channel or a spray mechanism to achieve saturation conditions at the exit.

A more practical approach is to use a thermometer whose bulb is covered with a cotton wick saturated with water and to blow air over the wick, as shown in Figure. The temperature measured in this manner is called the **wetbulb temperature** T_{wb} , and it is commonly used in airconditioning applications.

The basic principle involved is similar to that in adiabatic saturation. When unsaturated air passes over the wet wick, some of the water in the wick evaporates. As a result, the temperature of the water drops, creating a temperature difference (which is the driving force for heat transfer) between the air and the. After a while, the heat loss from the water by evaporation equals the heat gain from the air, and the water temperature stabilizes. The thermometer reading at this point is the wet-bulb temperature.



A simple arrangement to measure the wet-bulb temperature.

The wet bulb temperature can also be measured by placing the wet-wicked thermometer in a holder attached to a handle and rotating the holder rapidly that is, by moving the thermometer instead of the air. that is, by moving the thermometer instead of the air. Advances in electronics made it possible to measure humidity directly in a fast and reliable way. It appears that sling psychrometers and wet-wicked thermometers are about to become things of the past.

Today, hand-held electronic humidity measurement devices based on the capacitance change in a thin polymer film as it absorbs water vapor are capable of sensing and digitally displaying the relative humidity within 1 percent accuracy in a matter of seconds.



Example 14-3

The dry- and the wet-bulb temperatures of atmospheric air at 1 atm (101.325-kPa) pressure are measured with a sling psychrometer and determined to be 25 and 15°C, respectively. Determine (*a*) the specific humidity, (*b*) the relative humidity, and (*c*) the enthalpy of the air.

(a) the specific humidity ω_1 $\omega_1 = \frac{c_p(T_2 - T_1) + \omega_2 h_{fg_2}}{h_{g_1} - h_{f_2}} = \frac{0.622 P_{g_2}}{P_2 - P_{g_2}} = \frac{(0.622)(1.7057 \text{ kPa})}{(101.325 - 1.7057) \text{ kPa}}$ $= 0.01065 \text{ kg H}_2\text{O/kg dry air}$

$$P_{1} = \frac{(1.005 \text{ kJ/kg} \cdot {}^{\circ}\text{C})[(15 - 25){}^{\circ}\text{C}] + (0.01065)(2465.4 \text{ kJ/kg})}{(2546.5 - 62.982) \text{ kJ/kg}}$$

 $= 0.00653 \text{ kg H}_2\text{O/kg dry air}$

(b) the relative humidity ϕ_1

 $(\mathbf{0})$

 $\phi_1 = \frac{\omega_1 P_2}{(0.622 + \omega_1) P_{g_1}} = \frac{(0.00653)(101.325 \text{ kPa})}{(0.622 + 0.00653)(3.1698 \text{ kPa})} = 0.332 \text{ or } 33.2\%$

(c) the enthalpy of the air

$$h_{1} = h_{a_{1}} + \omega_{1}h_{\nu_{1}} \cong c_{p}T_{1} + \omega_{1}h_{g_{1}}$$

= (1.005 kJ/kg · °C)(25°C) + (0.00653)(2546.5 kJ/kg)
= **41.8 kJ/kg dry air**
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THE PSYCHROMETRIC CHART

The state of the atmospheric air at a specified pressure is completely specified by two independent intensive properties. The rest of the properties can be calculated easily from the relations above. The sizing of a typical air conditioning system involves numerous such calculations, which may eventually get on the nerves of even the most patient engineers. Therefore, there is clear motivation to computerize calculations or to do these calculations once and to present the data in the form of easily readable charts. Such charts are called **psychrometric charts**, and they are used extensively in air-conditioning applications.



Example 14-4

Consider a room that contains air at 1 atm, 35° C, and 40 percent relative humidity. Using the psychrometric chart, determine (*a*) the specific humidity, (*b*) the enthalpy, (*c*) the wet-bulb temperature, (*d*) the dew-point temperature, and (*e*) the specific volume of the air.

(a) The specific humidity is determined by drawing a horizontal line from the specified state to the right until it intersects with the ω axis;

 $\omega = 0.0142 \text{ kg H}_2\text{O/kg dry air}$

b) The enthalpy of air per unit mass of dry air is determined by drawing a line parallel to the h=constant lines from the specific state until it intersects the enthalpy scale;

h = 71.5 kJ/kg dry air

(c) The wet-bulb temperature is determined by drawing a line parallel to the T_{wb} =cnst lines from the specified state until it intersects the saturation line.

$$T_{\rm wb} = 24^{\circ}{\rm C}$$

(d) The dew-point temperature is determined by drawing a horizontal line from the specified state to the left until it intersects the saturation line.

(e) The specific volume per unit mass of dry air is determined by noting the distances between the specified state and the v constant lines on both sides of the point.,



 $T_{\rm dp} = 19.4^{\circ}{\rm C}$

$$v = 0.893 \text{ m}^3/\text{kg} \text{ dry air}$$

ASH RAE Psyc hrome trie Chart No. 1 Normal Temperature Barometric Pres sure: 101.325 kPa



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HUMAN COMFORT AND AIR-CONDITIONING

Human beings have an inherent weakness—they want to feel comfortable. They want to live in an environment that is neither hot nor cold, neither humid nor dry. However, comfort does not come easily since the desires of the human body and the weather usually are not quite compatible.

Achieving comfort requires a constant struggle against the factors that cause discomfort, such as high or low temperatures and high or low humidity. As engineers, it is our duty to help people feel comfortable.



The human body can be viewed as a heat engine whose energy input is food. As with any other heat engine, the human body generates waste heat that must be rejected to the environment if the body is to continue operating. The rate of heat generation depends on the level of the activity. For an average adult male, it is about 87 W when sleeping, 115 W when resting or doing office work, 230 W when bowling, and 440 W when doing heavy physical work.



A body feels comfortable when it can freely dissipate its waste heat, and no more..

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In hot environments, we have the opposite problem—we do not seem to be dissipating enough heat from our bodies, and we feel as if we are going to burst. We dress lightly to make it easier for heat to get away from our bodies, and we reduce the level of activity to minimize the rate of waste heat generation in the body.

We also turn on the fan to continuously replace the warmer air layer that forms around our bodies as a result of body heat by the cooler air in other parts of the room.

The corresponding numbers for an adult female are about 15 percent less. (This difference is due to the body size, not the body temperature. The deep-body temperature of a healthy person is maintained constant at 37°C.)

A body will feel comfortable in environments in which it can dissipate this waste heat comfortably.

The comfort of the human body depends primarily on three factors: The (dry-bulb) temperature, relative humidity, and air motion.

The temperature of the environment is the single most important index of comfort. Most people feel comfortable when the environment temperature is between 22-27°C.

The relative humidity also has a considerable effect on comfort since it affects the amount of heat a body can dissipate through evaporation.

Relative humidity is a measure of air's ability to absorb more moisture.

High relative humidity slows down heat rejection by evaporation, and low relative humidity speeds it up.

Most people prefer a relative humidity of 40 to 60 percent.

AIR-CONDITIONING PROCESSES

Maintaining a living space or an industrial facility at the desired temperature and humidity requires some processes called air-conditioning processes. These processes include

simple heating (raising the temperature), simple cooling (lowering the temperature), humidifying (adding moisture), and dehumidifying (removing moisture).

Sometimes two or more of these processes are needed to bring the air to a desired temperature and humidity level.



Various air-conditioning processes are illustrated on the psychrometric chart. Notice that simple heating and cooling processes appear as horizontal lines on this chart since the moisture content of the air remains constant ($\omega = \text{constant}$) during these processes. Air is commonly heated and humidified in winter and cooled and dehumidified in summer.

Notice how these processes appear on the psychrometric chart.

Most air-conditioning processes can be modeled as steady-flow processes, and thus the *mass balance* relation an be expressed for *dry air* and *water* as;

Mass balance

$$\dot{m}_{\rm in} = \dot{m}_{\rm out}$$



where the subscripts *i* and *e* denote the inlet and the exit states, respectively. Disregarding the kinetic and potential energy changes, the *steady-flow energy balance* relation can be expressed in this case as;

$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{Q}_{\rm in} + \dot{W}_{\rm in} + \sum \dot{m}_i h_i = \dot{Q}_{\rm out} + \dot{W}_{\rm out} + \sum \dot{m}_e h_e$$

The work term usually consists of the *fan work input,* which is small relative to the other terms in the energy balance relation.

Simple Heating and Cooling (ω = constant)

Many residential heating systems consist of a stove, a heat pump, or an electric resistance heater. The air in these systems is heated by circulating it through a duct that contains the tubing for the hot gases or the electric resistance wires.



The amount of moisture in the air remains constant during this process since no moisture is added to or removed from the air. That is, the specific humidity of the air remains constant (ω = constant) during a heating (or cooling) process with no humidification or dehumidification. Such a heating process will proceed in the direction of increasing dry-bulb temperature following a line of constant specific humidity on the psychrometric chart, which appears as a horizontal line.

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Notice that the relative humidity of air decreases during a heating process even if the specific humidity v remains constant. This is because the relative humidity is the ratio of the moisture content to the moisture capacity of air at the same temperature, and moisture capacity increases with temperature. Therefore, the relative humidity of heated air may be well below comfortable levels, causing dry skin, respiratory difficulties, and an increase in static electricity.

The conservation of mass equations for a heating or cooling process that involves no humidification or dehumidification reduce to;

for dry air

$$\dot{m}_{a_1} = \dot{m}_{a_2} = \dot{m}a$$
for water

$$\omega_1 = \omega_2$$
Energy balance
 $\dot{Q} = \dot{m}_a(h_2 - h_1)$ or $q = h_2 - h_1$

The conservation of mass equations for a heating or cooling process that involves no humidification or dehumidification reduce to $\dot{m}_{a1} = \dot{m}_{a2} = \dot{m}_a$ for dry air and v1 v2 for water. Neglecting any fan work that may be present, the conservation of energy equation in this case reduces to Q veya q ;

$$\dot{Q} = \dot{m}_a(h_2 - h_1)$$
 or $q = h_2 - h_1$

where h_1 and h_2 are enthalpies per unit mass of dry air at the inlet and the exit of the heating or cooling section, respectively.



During simple cooling, specific humidity remains constant, but relative humidity increases.
Heating with Humidification



The location of state 3 depends on how the humidification is accomplished.

If steam is introduced in the humidification section, this will result in humidification with additional heating $(T_3 > T_2)$. If humidification is accomplished by spraying water into the airstream instead, part of the latent heat of vaporization will come from the air, which will result in the cooling of the heated airstream $(T_3 < T_2)$. Air should be heated to a higher temperature in the heating section in this case to make up for the cooling effect during the humidification process.

Example 14-5

An air-conditioning system is to take in outdoor air at 10°C and 30 percent relative humidity at a steady rate of 45 m3/min and to condition it to 25°C and 60 percent relative humidity. The outdoor air is first heated to 22°C in the heating section and then humidified by the injection of hot steam in the humidifying section. Assuming the entire process takes place at a pressure of 100 kPa, determine (a) the rate of heat supply in the heating section and (b) the mass flow rate of the steam required in the humidifying section.



$$P_{v_{1}} = \phi_{1}P_{g_{1}} = \phi P_{\text{sat }@\ 10^{\circ}\text{C}} = (0.3)(1.2281 \text{ kPa}) = 0.368 \text{ kPa}$$

$$P_{a_{1}} = P_{1} - P_{v_{1}} = (100 - 0.368) \text{ kPa} = 99.632 \text{ kPa}$$

$$v_{1} = \frac{R_{a}T_{1}}{P_{a}} = \frac{(0.287 \text{ kPa} \cdot \text{m}^{3}/\text{kg} \cdot \text{K})(283 \text{ K})}{99.632 \text{ kPa}} = 0.815 \text{ m}^{3}/\text{kg} \text{ dry air}$$

$$\dot{m}_{a} = \frac{\dot{V}_{1}}{v_{1}} = \frac{45 \text{ m}^{3}/\text{min}}{0.815 \text{ m}^{3}/\text{kg}} = 55.2 \text{ kg/min}$$

$$I_{1} = \frac{0.622P_{v_{1}}}{P_{1} - P_{v_{1}}} = \frac{0.622(0.368 \text{ kPa})}{(100 - 0.368) \text{ kPa}} = 0.0023 \text{ kg H}_{2}\text{O/kg dry air}$$

$$I_{1} = c_{p}T_{1} + \omega_{1}h_{g_{1}} = (1.005 \text{ kJ/kg} \cdot ^{\circ}\text{C})(10^{\circ}\text{C}) + (0.0023)(2519.2 \text{ kJ/kg})$$

$$= 15.8 \text{ kJ/kg dry air}$$

 $h_2 = c_p T_2 + \omega_2 h_{g_2} = (1.005 \text{ kJ/kg} \cdot ^\circ\text{C})(22^\circ\text{C}) + (0.0023)(2541.0 \text{ kJ/kg})$ = 28.0 kJ/kg dry air

= 28.0 kJ/kg dry air

ω

h

since $\omega_2 = \omega_1$. Then the rate of heat transfer to air in the heating section becomes

$$\dot{Q}_{in} = \dot{m}_a (h_2 - h_1) = (55.2 \text{ kg/min})[(28.0 - 15.8) \text{ kJ/kg}]$$

= 673 kJ/min

(b) The mass balance for water in the humidifying section

$$\dot{m}_{a_2}\omega_2 + \dot{m}_w = \dot{m}_{a_3}\omega_3 \qquad \qquad \dot{m}_w = \dot{m}_a(\omega_3 - \omega_2)$$

$$\omega_3 = \frac{0.622\phi_3 P_{g_3}}{P_3 - \phi_3 P_{g_3}} = \frac{0.622(0.60)(3.1698 \text{ kPa})}{[100 - (0.60)(3.1698)] \text{ kPa}}$$
$$= 0.01206 \text{ kg H}_2\text{O/kg dry air}$$

$$\dot{m}_w = (55.2 \text{ kg/min})(0.01206 - 0.0023)$$

= 0.539 kg/min

Cooling with Dehumidification

The specific humidity of air remains constant during a simple cooling process, but its relative humidity increases. If the relative humidity reaches undesirably high levels, it may be necessary to remove some moisture from the air, that is, to dehumidify it. This requires cooling the air below its dewpoint temperature.



Example 14-6 Air enters a window air conditioner at 1 atm, 30°C, and 80 percent relative humidity at a rate of 10 m3/min, and it leaves as saturated air at 14°C. Part of the moisture in the air that condenses during the process is also removed at 14°C. Determine the rates of heat and moisture removal from the air.





The enthalpy of saturated liquid water at 14°C is 58.8 kJ/kg (Table A–4). Also, the inlet and the exit states of the air are completely specified, and the total pressure is 1 atm. Therefore, we can determine the properties of the air at both states from the psychrometric chart to be

 $h_1 = 85.4 \text{ kJ/kg dry air} \qquad h_2 = 39.3 \text{ kJ/kg dry air}$ $\omega_1 = 0.0216 \text{ kg H}_2\text{O/kg dry air} \quad \text{and} \quad \omega_2 = 0.0100 \text{ kg H}_2\text{O/kg dry air}$ $v_1 = 0.889 \text{ m}^3\text{/kg dry air}$

Dry air mass balance: $\dot{m}_{a_1} = \dot{m}_{a_2} = \dot{m}_a$
Water mass balance: $\dot{m}_{a_1}\omega_1 = \dot{m}_{a_2}\omega_2 + \dot{m}_w \rightarrow \dot{m}_w = \dot{m}_a(\omega_1 - \omega_2)$
Energy balance: $\sum \dot{m}_i h_i = \dot{Q}_{out} + \sum \dot{m}_e h_e \rightarrow$
$\dot{Q}_{\rm out} = \dot{m}(h_1 - h_2) - \dot{m}_w h_w$
$h_w = h_{f@~14^\circ C} = 58.8 \text{ kJ/kg}$
$\dot{m}_a = \frac{\dot{V}_1}{V_1} = \frac{10 \text{ m}^3/\text{min}}{0.889 \text{ m}^3/\text{kg dry air}} = 11.25 \text{ kg/min}$
$\dot{m}_w = (11.25 \text{ kg/min})(0.0216 - 0.0100) = 0.131 \text{ kg/min}$
$\dot{Q}_{out} = (11.25 \text{ kg/min})[(85.4 - 39.3) \text{ kJ/kg}] - (0.131 \text{ kg/min})(58.8 \text{ kJ/kg})$
= 511 kJ/min

Therefore, this air-conditioning unit removes moisture and heat from the air at rates of 0.131 kg/min and 511 kJ/min, respectively.

Evaporative Cooling

In desert (hot and dry) climates, we can avoid the high cost of cooling by using evaporative coolers, also known as swamp coolers.

Evaporative cooling is based on a simple principle:

As water evaporates, the latent heat of vaporization is absorbed from the water body and the surrounding air. As a result, both the water and the air are cooled during the process.

This approach has been used for thousands of years to cool water. A porous jug or pitcher filled with water is left in an open, shaded area. A small amount of water leaks out through the porous holes, and the pitcher "sweats." In a dry environment, this water evaporates and cools the remaining water in the pitcher.





Water in a porous jug left in an open, breezy area cools as a result of evaporative cooling.

Adiabatic Mixing of Airstreams

Many air-conditioning applications require the mixing of two airstreams. This is particularly true for large buildings, most production and process plants, and hospitals, which require that the conditioned air be mixed with a certain fraction of fresh outside air before it is routed into the living space. The mixing is accomplished by simply merging the two airstreams.

The heat transfer with the surroundings is usually small, and thus the mixing processes can be assumed to be adiabatic. Mixing processes normally involve no work interactions, and the changes in kinetic and potential energies, if any, are negligible.

$$\frac{\dot{m}_{a_1}}{\dot{m}_{a_2}} = \frac{\omega_2 - \omega_3}{\omega_3 - \omega_1} = \frac{h_2 - h_3}{h_3 - h_1}$$

Mass of dry air: $\dot{m}_{a_1} + \dot{m}_{a_2} = \dot{m}_{a_3}$ Mass of water vapor: $\omega_1 \dot{m}_{a_1} + \omega_2 \dot{m}_{a_2} = \omega_3 \dot{m}_{a_3}$ Energy: $\dot{m}_{a_1}h_1 + \dot{m}_{a_2}h_2 = \dot{m}_{a_3}h_3$

when two airstreams at two different states (states 1 and 2) are mixed adiabatically, the state of the mixture (state 3) will lie on the straight line connecting states 1 and 2 on the psychrometric chart, and the ratio of the distances 2-3 and 3-1 is equal to the ratio of mass flow rates \dot{m}_{a1} and \dot{m}_{a2} .



The concave nature of the saturation curve and the conclusion above lead to an interesting possibility. When states 1 and 2 are located close to the saturation curve, the straight line connecting the two states will cross the saturation curve, and state 3 may lie to the left of the saturation curve. In this case, some water will inevitably condense during the mixing process.

Example 14-8

Saturated air leaving the cooling section of an air-conditioning system at 14°C at a rate of 50 m³/min is mixed adiabatically with the outside air at 32°C and 60 percent relative humidity at a rate of 20 m³/min. Assuming that the mixing process occurs at a pressure of 1 atm, determine the specific humidity, the relative humidity, the dry-bulb temperature, and the volume flow rate of the mixture.

The properties of each inlet stream are determined from the psychrometric chart to be

$h_1 = 39.4 \text{ kJ/kg}$ dry air	$h_2 = 79.0 \text{ kJ/kg dry air}$
$\omega_1 = 0.010 \text{ kg H}_2\text{O/kg dry air}$	$\omega_2 = 0.0182 \text{ kg H}_2\text{O/kg dry air}$
$v_1 = 0.826 \text{ m}^3/\text{kg}$ dry air	$v_2 = 0.889 \text{ m}^3/\text{kg}$ dry air

The mass flow rates of dry air in each stream are

$$\dot{m}_{a_1} = \frac{\dot{V}_1}{v_1} = \frac{50 \text{ m}^3/\text{min}}{0.826 \text{ m}^3/\text{kg dry air}} = 60.5 \text{ kg/min}$$
$$\dot{m}_{a_2} = \frac{\dot{V}_2}{v_2} = \frac{20 \text{ m}^3/\text{min}}{0.889 \text{ m}^3/\text{kg dry air}} = 22.5 \text{ kg/min}$$

From the mass balance of dry air,

$$\dot{m}_{a_3} = \dot{m}_{a_1} + \dot{m}_{a_2} = (60.5 + 22.5) \text{ kg/min} = 83 \text{ kg/min}$$

$$\frac{\dot{m}_{a_1}}{\dot{m}_{a_2}} = \frac{\omega_2 - \omega_3}{\omega_3 - \omega_1} = \frac{h_2 - h_3}{h_3 - h_1}$$

$$\frac{60.5}{22.5} = \frac{0.0182 - \omega_3}{\omega_3 - 0.010} = \frac{79.0 - h_3}{h_3 - 39.4}$$

$$\omega_3 = 0.0122 \text{ kg H}_2\text{O/kg dry air}$$

 $h_3 = 50.1 \text{ kJ/kg dry air}$

These two properties fix the state of the mixture. Other properties of the mixture are determined from the psychrometric chart:

$$T_3 = 19.0^{\circ} \text{C}$$

 $\phi_3 = 89\%$
 $v_3 = 0.844 \text{ m}^3/\text{kg dry air}$

$$\dot{V}_3 = \dot{m}_{a_3} v_3 = (83 \text{ kg/min})(0.844 \text{ m}^3/\text{kg}) = 70.1 \text{ m}^3/\text{min}$$

Notice that the volume flow rate of the mixture is approximately equal to the sum of the volume flow rates of the two incoming streams. This is typical in air-conditioning applications.

Wet Cooling Towers

Power plants, large air-conditioning systems, and some industries generate large quantities of waste heat that is often rejected to cooling water from nearby lakes or rivers. In some cases, however, the water supply is limited or thermal pollution is a serious concern. In such cases, the waste heat must be rejected to the atmosphere, with cooling water recirculating and serving as a transport medium for heat transfer between the source and the sink (the atmosphere). One way of achieving this is through the use of wet cooling towers.

A **wet cooling tower** is essentially a semienclosed evaporative cooler.



An induced-draft counterflow cooling tower.

Another popular type of cooling tower is the **natural-draft cooling tower**, which looks like a large chimney and works like an ordinary chimney. The air in the tower has a high water-vapor content, and thus it is lighter than the outside air. Consequently, the light air in the tower rises, and the heavier outside air fills the vacant space, creating an airflow from the bottom of the tower to the top. The flow rate of air is controlled by the conditions of the atmospheric air. Natural-draft cooling towers do not require any external power to induce the air, but they cost a lot more to build than forced-draft cooling towers. The natural-draft cooling towers are hyperbolic in profile, and some are over 100 m high. The hyperbolic profile is for greater structural strength, not for any thermodynamic reason.



Example 14-9

Cooling water leaves the condenser of a power plant and enters a wet cooling tower at 35°C at a rate of 100 kg/s. The water is cooled to 22°C in the cooling tower by air that enters the tower at 1 atm, 20°C, and 60 percent relative humidity and leaves saturated at 30°C. Neglecting the power input to the fan, determine (a) the volume flow rate of air into the cooling tower and (b) the mass flow rate of the required makeup water.

 $h_1 = 42.2 \text{ kJ/kg dry air}$ $h_2 = 100.0 \text{ kJ/kg dry air}$ (4)100 kg/s $\omega_1 = 0.0087 \text{ kg H}_2\text{O/kg dry air}$ and $\omega_2 = 0.0273 \text{ kg H}_2\text{O/kg dry air}$ SERİN SU 22°C $v_1 = 0.842 \text{ m}^3/\text{kg} \text{ dry air}$ Tamamlama suyu (a) Applying the mass and energy balances on the cooling tower gives $\dot{m}_{a_1} = \dot{m}_{a_2} = \dot{m}_a$ Dry air mass balance: $\dot{m}_3 + \dot{m}_{a_1}\omega_1 = \dot{m}_4 + \dot{m}_{a_2}\omega_2$ Water mass balance: $\dot{m}_{3} - \dot{m}_{4} = \dot{m}_{a}(\omega_{2} - \omega_{1}) = \dot{m}_{makeup}$ or Energy balance: $\sum \dot{m}_i h_i = \sum \dot{m}_e h_e \rightarrow \dot{m}_{a_1} h_1 + \dot{m}_3 h_3 = \dot{m}_{a_2} h_2 + \dot{m}_4 h_4$

or

$$\dot{m}_3 h_3 = \dot{m}_a (h_2 - h_1) + (\dot{m}_3 - \dot{m}_{\text{makeup}}) h_4$$

30°C

(2) $\phi_2 = \%100$

ΛΛΛΛΛ

(1)HAVA

 $\phi_1 = \%60$

1 atm

20°C

Ŭ1

ILIK

SU 35°C

100 kg/s

Sistem

sınırı

(3)

Solving for \dot{m}_a gives

$$\dot{m}_{a} = \frac{\dot{m}_{3}(h_{3} - h_{4})}{(h_{2} - h_{1}) - (\omega_{2} - \omega_{1})h_{4}}$$

$$h_{3} \approx h_{f@\ 35^{\circ}C} = 146.64 \text{ kJ/kg H}_{2}O$$

$$h_{4} \approx h_{f@\ 22^{\circ}C} = 92.28 \text{ kJ/kg H}_{2}O$$

$$\frac{(100 \text{ kg/s})[(146.64 - 92.28) \text{ kJ/kg}]}{[(100.0 - 42.2) \text{ kJ/kg}] - [(0.0273 - 0.0087)(92.28) \text{ kJ/kg}]} = 96.9 \text{ kg/s}$$

Then the volume flow rate of air into the cooling tower becomes

$$\dot{V}_1 = \dot{m}_a V_1 = (96.9 \text{ kg/s})(0.842 \text{ m}^3/\text{kg}) = 81.6 \text{ m}^3/\text{s}$$

(b) The mass flow rate of the required makeup water is determined from

$$\dot{m}_{\text{makeup}} = \dot{m}_a(\omega_2 - \omega_1) = (96.9 \text{ kg/s})(0.0273 - 0.0087) = 1.80 \text{ kg/s}$$

Note that over 98 percent of the cooling water is saved and recirculated in this case.

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 $\dot{m}_a =$

SUMMARY

- In this chapter we discussed the air—water-vapor mixture, which is the most commonly encountered gas—vapor mixture in practice.
- The air in the atmosphere normally contains some water vapor, and it is referred to as atmospheric air.
- By contrast, air that contains no water vapor is called dry air.
- The needs of the human body and the conditions of the environment are not quite compatible. Therefore, it often becomes necessary to change the conditions of a living space to make it more comfortable.
- During a simple heating or cooling process, the specific humidity remains constant, but the temperature and the relative humidity change.

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CHEMICAL REACTIONS

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CHEMICAL REACTIONS

15-1 Fuels and Combustion
15-2 Theoretical and Actual Combustion Processes
15-3 Enthalpy of Formation and Enthalpy of Combustion
15-4 First-Law Analysis of Reacting Systems
Steady-Flow Systems
Closed Systems
15-5 Adiabatic Flame Temperature
15-6 Entropy Change of Reacting Systems

15-7 Second-Law Analysis of Reacting Systems

Objectives

- Introduce the concepts of fuels and combustion.
- Apply the conservation of mass to reacting systems to determine balanced reaction equations.
- Define the parameters used in combustion analysis, such as air-fuel ratio, percent theoretical air, and dew-point temperature.
- Apply energy balances to reacting systems for both steady flow control volumes and fixed mass systems.
- Calculate the enthalpy of reaction, enthalpy of combustion, and the heating values of fuels.
- Determine the adiabatic flame temperature for reacting mixtures.
- Evaluate the entropy change of reacting systems.
- Analyze reacting systems from the second-law perspective.

FUELS AND COMBUSTION

Any material that can be burned to release thermal energy is called a fuel. Most familiar fuels consist primarily of hydrogen and carbon. They are called hydrocarbon fuels and are denoted by the general formula C_nH_m .

Hydrocarbon fuels exist in all phases, some examples being coal, gasoline, and natural gas.



A comparison of some alternative fuels to the traditional petroleum-based fuels used in transportation

Fuel	Energy content kJ/L	Gasoline equivalence,* L/L-gasoline
Gasoline	31.850	1
Light diesel	33,170	0.96
Heavy diesel	35,800	0.89
LPG (Liquefied petroleum gas,		
primarily propane)	23,410	1.36
Ethanol (or ethyl alcohol)	29,420	1.08
Methanol (or methyl alcohol)	18,210	1.75
CNG (Compressed natural gas, primarily methane, at 200 atm)	8,080	3.94
LNG (Liquefied natural gas, primarily methane)	20,490	1.55

On a mole or a volume basis, dry air is composed of 20.9 % oxygen, 78.1 % nitrogen, 0.9 % argon, and small amounts of carbon dioxide, helium, neon, and hydrogen. In the analysis of combustion processes, the argon in the air is treated as nitrogen, and the gases that exist in trace amounts are disregarded.

Then dry air can be approximated as 21 % oxygen and 79 % nitrogen by mole numbers. Therefore, each mole of oxygen entering a combustion chamber will be accompanied by 0.79/0.21 = 3.76 mol of nitrogen.



Each kmol of O_2 in air is accompanied by 3.76 kmol of N_2



Combustion is a chemical reaction during which a fuel is oxidized and a large quantity of energy is released.

$1 \text{ kmol O}_2 + 3.76 \text{ kmol N}_2 = 4.76 \text{ kmol air}$

We should also mention that bringing a fuel into intimate contact with oxygen is not sufficient to start a combustion process. The fuel must be brought above its ignition temperature to start the combustion. The minimum ignition temperatures of various substances in atmospheric air are approximately 260°C for gasoline, 400°C for carbon, 580°C for hydrogen, 610°C for carbon monoxide, and 630°C for methane. Moreover, the proportions of the fuel and air must be in the proper range for combustion to begin. For example, natural gas will not burn in air in concentrations less than 5 % or greater than about 15%.



In a steady-flow combustion process, the components that enter the reaction chamber are called reactants and the components that exit are called products.



The mass (and number of atoms) of each element is conserved during a chemical reaction. A frequently used quantity in the analysis of combustion processes to quantify the amounts of fuel and air is the air-fuel ratio AF.

It is usually expressed on a mass basis and is defined as the ratio of the mass of air to the mass of fuel for a combustion process.

The air-fuel ratio can also be expressed on a mole basis as the ratio of the mole numbers of air to the mole numbers of fuel. But we will use the former definition. The reciprocal of air-fuel ratio is called the fuel-air ratio.



Example 15–1 One kmol of octane (C_8H_{18}) is burned with air that contains 20 kmol of O Assuming the products contain

only CO_2 , H_2O , O_2 , and N_2 , determine the mole number of each gas in the products and the air–fuel ratio for this combustion process.



$$C_{8}H_{18} + 20(O_{2} + 3.76N_{2}) \rightarrow xCO_{2} + yH_{2}O + zO_{2} + wN_{2}$$

$$C: \qquad 8 = x \rightarrow x = 8$$

$$H: \qquad 18 = 2y \rightarrow y = 9$$

$$O: \qquad 20 \times 2 = 2x + y + 2z \rightarrow z = 7.5$$

$$N_{2}: \qquad (20)(3.76) = w \rightarrow w = 75.2$$

$$C_{8}H_{18} + 20(O_{2} + 3.76N_{2}) \rightarrow 8CO_{2} + 9H_{2}O + 7.5O_{2} + 75.2N_{2}$$

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{(NM)_{air}}{(NM)_{C} + (NM)_{H_{2}}}$$

$$= \frac{(20 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(8 \text{ kmol})(12 \text{ kg/kmol}) + (9 \text{ kmol})(2 \text{ kg/kmol})}$$

$$= 24.2 \text{ kg air/kg fuel}$$
That is, 24.2 kg of air is used to burn each kilogram of fuel during this combustion process.

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THEORETICAL AND ACTUAL COMBUSTION PROCESSES

It is often instructive to study the combustion of a fuel by assuming that the combustion is complete.

A combustion process is complete if all the carbon in the fuel burns to CO_2 , all the hydrogen burns to H_2O , and all the sulfur (if any) burns to SO_2 . That is, all the combustible components of a fuel are burned to completion during a complete combustion process.

Conversely, the combustion process is incomplete if the combustion products contain any unburned fuel or components such as C, H₂, CO, or OH.

Insufficient oxygen is an obvious reason for incomplete combustion, but it is not the only one. Incomplete combustion occurs even when more oxygen is present in the combustion chamber than is needed for complete combustion.

This may be attributed to insufficient mixing in the combustion chamber during the limited time that the fuel and the oxygen are in contact.

Another cause of incomplete combustion is dissociation, which becomes important at high temperatures.



A combustion process is complete if all the combustible components of the fuel are burned to completion. **Stoichiometric or theoretical air:** The minimum amount of air needed for the complete combustion of a fuel.

Stoichiometric or theoretical combustion: The ideal combustion process during which a fuel is burned completely with theoretical air.

Excess air: In actual combustion processes, it is common practice to use more air than the stoichiometric amount to increase the chances of complete combustion or to control the temperature of the combustion chamber. The amount of air in excess of the stoichiometric amount is called excess air.

Deficiency of air: Amounts of air less than the stoichiometric amount.

Equivalence ratio: he amount of air used in combustion processes is also expressed in terms of the equivalence ratio, which is the ratio of the actual fuel—air ratio to the stoichiometric fuel—air ratio.

50 % excess air = 150 % theoretical air 200 % excess air = 150 % theoretical air 90 % theoretical air = 10 % deficiency air	The complete combustion process with no free oxygen in the products is called theoretical combustion.	$CH_4 + 2(O_2 + 3.76N_2) \rightarrow$ $CO_2 + 2H_2O + 7.52N_2$ • no unburned fuel • no free oxygen in products

Predicting the composition of the products is relatively easy when the combustion process is assumed to be complete and the exact amounts of the fuel and air used are known.

All one needs to do in this case is simply apply the mass balance to each element that appears in the combustion equation, without needing to take any measurements.



However, when one is dealing with actual combustion processes. For one thing, actual combustion processes are hardly ever complete, even in the presence of excess air.

Therefore, it is impossible to predict the composition of the products on the basis of the mass balance alone. Then the only alternative we have is to measure the amount of each component in the products directly.

Commonly used device to analyze the composition of combustion gases is the **Orsat gas analyzer**.

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Example 15-2 Ethane (C_2H_6) is burned with 20 percent excess air during a combustion process. Assuming complete combustion and a total pressure of 100 kPa, determine (a) the air–fuel ratio and (b) the dew-point temperature of the products.



 $C_2H_6 + 1.2a_k(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O + 0.2a_kO_2 + (1.2 \times 3.76)a_kN_2$

$$O_2:$$
 1.2 $a_k = 2 + 1.5 + 0.2a_k \rightarrow a_k = 3.5$

 $C_2H_6 + 4.2(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O + 0.7O_2 + 15.79N_2$

(a) The air-fuel ratio is determined by taking the ratio of the mass of the air to the mass of the fuel,

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{(4.2 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(2 \text{ kmol})(12 \text{ kg/kmol}) + (3 \text{ kmol})(2 \text{ kg/kmol})}$$

= 19.3 kg air/kg fuel

(b) the dew-point temperature of the products

$$P_{v} = \left(\frac{N_{v}}{N_{\text{prod}}}\right) (P_{\text{prod}}) = \left(\frac{3 \text{ kmol}}{21.49 \text{ kmol}}\right) (100 \text{ kPa}) = 13.96 \text{ kPa}$$
$$T_{\text{dp}} = T_{\text{sat @ 13.96 kPa}} = 52.3^{\circ}\text{C} \qquad \text{(Table A-5)}$$

Example A certain CH ₄ , 9 % burned w combusti Assumin determin	e 15-3 natural gas ha b H ₂ , 14 % N ₂ , with the stoichic ion chamber at g complete cor e the dew-poir onsidering 1	as the following volumetri 2 % O ₂ , and 3 % CO ₂ . The ometric amount of air that 20°C, 1 atm, and 80 % in mbustion and a total present t temperature of the procession kmol. of fuel	c analysis: 7 his gas is no t enters the relative hum sure of 1 at ducts.	72 % w iidity. m,	FUEL $CH_4, O_2, H_2,$ N_2, CO_2 AIR $20^{\circ}C, \phi = 80\%$	Combustion chamber 1 atm	CO ₂ H ₂ O N ₂
(0.7	$72CH_4 + 0.09$	$\frac{\text{fuel}}{9\text{H}_2 + 0.14\text{N}_2 + 0.020}$	$O_2 + 0.030$	CO ₂)	$\frac{dry a}{a_{th}(O_2 + xCO_2 + yH)}$	$\frac{\text{ir}}{3.76\text{N}_2} - \frac{1}{2}\text{O} + z\text{N}_2$	<i>></i>
	C: H: O ₂ : N ₂ :	$0.72 + 0.000 \times 0.72 \times 4 + 0.000 \times 0.002 + 0.003 + a_k$ 0.14 + 3.7	$0.03 = x$ $2 = 2y$ $x + \frac{y}{2}$ $6a_{k} = z$	\rightarrow \rightarrow \rightarrow \rightarrow	x = 0.75 y = 1.53 $a_k = 1.465$ z = 5.648		
4.7	$P_{v, air}$	(1.465) = 6.97 kmol = $\phi_{air} P_{sat @ 20^{\circ}C} = (0.$ Prof. Dr. Ali PINARBAŞI	of dry air. 80)(2.3392	2 kPa)	= 1.871 kPa Chapter :	L L5 CHEMICAL RE	ACTIONS

$$N_{\nu, \text{ air}} = \left(\frac{P_{\nu, \text{ air}}}{P_{\text{total}}}\right) N_{\text{total}} = \left(\frac{1.871 \text{ kPa}}{101.325 \text{ kPa}}\right) (6.97 + N_{\nu, \text{ air}}) \qquad N_{\nu, \text{ air}} = 0.131 \text{ kmol}$$

$$\overbrace{(0.72CH_4 + 0.09H_2 + 0.14N_2 + 0.02O_2 + 0.03CO_2)}^{\text{fuel}} + \overbrace{1.465(O_2 + 3.76N_2)}^{\text{dry air}}$$

$$\xrightarrow{\text{moisture}}_{+ 0.131H_2O} \rightarrow 0.75CO_2 + \overbrace{1.661H_2O}^{\text{dry air}} + 5.648N_2$$

$$P_{\nu, \text{prod}} = \left(\frac{N_{\nu, \text{prod}}}{N_{\text{prod}}}\right) P_{\text{prod}} = \left(\frac{1.661 \text{ kmol}}{8.059 \text{ kmol}}\right) (101.325 \text{ kPa}) = 20.88 \text{ kPa}$$

$$T_{\rm dp} = T_{\rm sat @ 20.88 kPa} = 60.9^{\circ}{\rm C}$$

Discussion If the combustion process were achieved with dry air instead of moist air, the products would contain less moisture, and the dew-point temperature in this case would be 59.5°C.

Example 15-4

Octane (C_8H_{18}) is burned with dry air. The volumetric analysis of the products on a dry basis is given below. Determine (a) the air–fuel ratio, (b) the percentage of theoretical air used, and (c) the amount of H_2O that condenses as the products are cooled to 25°C at 100 kPa.



 $xC_8H_{18} + a(O_2 + 3.76N_2) \rightarrow 10.02CO_2 + 0.88CO + 5.62O_2 + 83.48N_2 + bH_2O$

	N ₂ :	3.76a = 83.48	\rightarrow	a = 22.20	
	C:	8x = 10.02 + 0.88	\rightarrow	x = 1.36	
	H:	18x = 2b	\rightarrow	b = 12.24	
	O ₂ :	$a = 10.02 + 0.44 + 5.62 + \frac{b}{2}$	\rightarrow	22.20 = 22.20	
1.36C ₈	$H_{18} + 22$	$2.2(O_2 + 3.76N_2) \rightarrow$			
		$10.02 \text{CO}_2 + 0.88 \text{CO} + 5.0$	620_2 -1	+ 83.48N ₂ + 12.24	$4H_2O$

 $C_8H_{18} + 16.32(O_2 + 3.76N_2) \rightarrow$

 $7.37 \text{CO}_2 + 0.65 \text{CO} + 4.13 \text{O}_2 + 61.38 \text{N}_2 + 9 \text{H}_2 \text{O}$

(a) The air-fuel ratio is determined by taking the ratio of the mass of the air to the mass of the fuel

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{(16.32 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(8 \text{ kmol})(12 \text{ kg/kmol}) + (9 \text{ kmol})(2 \text{ kg/kmol})}$$
$$= 19.76 \text{ kg air/kg fuel}$$

(b) To find the percentage of theoretical air used, we need to know the theoretical amount of air, which is determined from the theoretical combustion equation of the fuel,

 $C_8H_{18} + a_k(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 3.76a_kN_2$

$$O_2:$$
 $a_k = 8 + 4.5 \rightarrow a_k = 12.5$

Percentage of theoretical air
$$= \frac{m_{\text{air, act}}}{m_{\text{air, th}}} = \frac{N_{\text{air, act}}}{N_{\text{air, th}}}$$
$$= \frac{(16.32)(4.76) \text{ kmol}}{(12.50)(4.76) \text{ kmol}}$$
$$= 131\%$$

That is, 31 percent excess air was used during this combustion process. Notice that some carbon formed carbon monoxide even though there was considerably more oxygen than needed for complete combustion.

(c) For each kmol of fuel burned, 7.37 + 0.65 + 4.13 + 61.38 + 9 = 82.53 kmol of products are formed, including 9 kmol of H₂O. Assuming that the dew-point temperature of the products is above 25°C, some of the water vapor will condense as the products are cooled to 25°C.

$$\frac{N_v}{N_{\text{prod, gas}}} = \frac{P_v}{P_{\text{prod}}}$$
$$\frac{9 - N_w}{82.53 - N_w} = \frac{3.1698 \text{ kPa}}{100 \text{ kPa}}$$
$$N_w = 6.59 \text{ kmol}$$

ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

During a chemical reaction, some chemical bonds that bind the atoms into molecules are broken, and new ones are formed. The chemical energy associated with these bonds, in general, is different for the reactants and the products. Therefore, a process that involves chemical reactions will involve changes in chemical energies, which must be accounted for in an energy balance.


Enthalpy of reaction, h_R : The difference between the enthalpy of the products at a specified state and the enthalpy of the reactants at the same state for a complete reaction.

Enthalpy of combustion, h_c : The amount of heat released during a steady-flow combustion process when 1 kmol (or 1 kg) of fuel is burned completely at a specified temperature and pressure.

Enthalpy of formation, h_f : The enthalpy of a substance at a specified state due to its chemical composition.

To establish a starting point, we assign the enthalpy of formation of all stable elements (such as O_2 , N_2 , H_2 , and C) a value of zero at the standard reference state of 25°C and 1 atm. That is, $h^o_f = 0$ for all stable elements.

$$Q = H_{\text{prod}} - H_{\text{react}} = -393,520 \text{ kJ/kmol}$$

 $h_R = h_C = H_{\text{prod}} - H_{\text{react}}$

$$\overline{h}_{f, CO_2}^{\circ} = -393,520 \text{ kJ/kmol}$$



The formation of CO₂ during a steady flow combustion process at 25C and 1 atm.

Heating value: The amount of heat released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants.

Higher heating value (HHV): The heating value depends on the phase of the H_2O in the products The heating value is called the higher heating value (HHV) when the H_2O in the products is in the liquid form.

Lower heating value (LHV): when the H₂O in the products is in the vapor

Heating value = $|h_C|$ (kJ/kg fuel)

$$HHV = LHV + (mh_{fg})_{H_2O} \qquad (kJ/kg \text{ fuel})$$



$$HHV = LHV + (mh_{fg})_{H_2O}$$

The higher heating value of a fuel is equal to the sum of the lower heating value of the fuel and the latent heat of vaporization of the H_2O in the products.

where m is the mass of H_2O in the products per unit mass of fuel and h_{fg} is the enthalpy of vaporization of water at the specified temperature.

Example 15–5 Determine the enthalpy of combustion of liquid octane (C_8H_{18}) at 25°C and 1 atm, using enthalpy-of-formation data from Table A–26. Assume the water in the products is in the liquid form..



 $C_8H_{18} + a_k(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O(\ell) + 3.76a_kN_2$

$$\overline{h}_{C} = H_{\text{prod}} - H_{\text{react}}$$
$$= \sum N_{p} \overline{h}_{f, p}^{\circ} - \sum N_{r} \overline{h}_{f, r}^{\circ} = (N \overline{h}_{f}^{\circ})_{\text{CO}_{2}} + (N \overline{h}_{f}^{\circ})_{\text{H}_{2}\text{O}} - (N \overline{h}_{f}^{\circ})_{\text{C}_{8}\text{H}_{18}}$$

$$\overline{h}_{C} = (8 \text{ kmol})(-393,520 \text{ kJ/kmol}) + (9 \text{ kmol})(-285,830 \text{ kJ/kmol})$$
$$- (1 \text{ kmol})(-249,950 \text{ kJ/kmol})$$
$$= -5,471,000 \text{ kJ/kmol} C_{8}H_{18} = -47,891 \text{ kJ/kg} C_{8}H_{18}$$

It can be shown that the result for gaseous octane is -5,512,200 kJ/kmol or -48,255 kJ/kg.

FIRST-LAW ANALYSIS OF REACTING SYSTEMS

The energy balance (or the first-law) relations developed in Chaps. 4 and 5 are applicable to both reacting and nonreacting systems. However, chemically reacting systems involve changes in their chemical energy, and thus it is more convenient to rewrite the energy balance relations so that the changes in chemical energies are explicitly expressed. We do this first for steady-flow systems and then for closed systems.

Steady-Flow Systems

Enthalpy =
$$\overline{h}_{f}^{\circ} + (\overline{h} - \overline{h}^{\circ})$$
 (kJ/kmol)

where the term in the parentheses represents the sensible enthalpy relative to the standard reference state, which is the difference between \overline{h} (the sensible enthalpy at the specified state) and \overline{h}_o (the sensible enthalpy at the standard reference state of 25°C and 1 atm).

This definition enables us to use enthalpy values from tables regardless of the reference state used in their construction.



The enthalpy of a chemical component at a specified state is the sum of the enthalpy of the component at 25C, 1 atm (h_f°) , and the sensible enthalpy of the component relative to 25C, 1 atm.

$$\dot{E}_{\rm in} = \dot{E}_{\rm out}$$

$$\underline{\dot{Q}_{\text{in}} + \dot{W}_{\text{in}} + \sum \dot{n}_r (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_r}_{\text{Rate of net energy transfer in}} = \underbrace{\dot{Q}_{\text{out}} + \dot{W}_{\text{out}} + \sum \dot{n}_p (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_p}_{\text{Rate of net energy transfer out}}$$

Rate of net energy transfer in by heat, work, and mass

Rate of net energy transfer out by heat, work, and mass

$$\underbrace{\dot{Q}_{\text{in}} + \dot{W}_{\text{in}} + \sum N_r (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_r}_{\text{Energy transfer in per mole of fuel}} = \underbrace{\dot{Q}_{\text{out}} + \dot{W}_{\text{out}} + \sum N_p (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_p}_{\text{Energy transfer out per mole of fuel}}$$

Taking heat transfer to the system and work done by the system to be positive quantities, the energy balance relation above can be expressed more compactly as

$$Q - W = \sum N_p (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_p = \sum N_r (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_r$$

$$Q - W = H_{\text{prod}} - H_{\text{react}} \quad (\text{kJ/kmol fuel})$$

$$H_{\text{prod}} = \sum N_p (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_p = \quad (\text{kJ/kmol fuel})$$

$$H_{\text{react}} = \sum N_r (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_r = \quad (\text{kJ/kmol fuel})$$

If the enthalpy of combustion $\overline{h^o}_c$ for a particular reaction is available, the steady-flow energy equation per mole of fuel can be expressed as

$$Q - W = \overline{h}_{C}^{\circ} + \sum N_{p}(\overline{h} - \overline{h}^{\circ})_{p} - \sum N_{r}(\overline{h} - \overline{h}^{\circ})_{r} \qquad (\text{kJ/kmol})$$

A combustion chamber normally involves heat output but no heat input. Then the energy balance for a *typical steady-flow combustion process* becomes

$$Q_{\text{out}} = \sum N_r (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_r - \sum N_p (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_p$$

Energy in by mass per mole of fuel Energy out by mass per mole of fuel

Closed Systems

The general closed-system energy balance relation E_{in} - $E_{out} = \Delta E_{system}$ can be expressed for a stationary chemically reacting closed system as

$$(Q_{\rm in} - Q_{\rm out}) + (W_{\rm in} - W_{\rm out}) = U_{\rm prod} - U_{\rm react} \qquad (kJ/kmol fuel)$$

the internal energy of formation

$$Q - W = \sum N_p (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ - P\overline{\nu})_p - \sum N_r (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ - P\overline{\nu})_r$$

we need to know whether the fuel is a solid, a liquid, or a gas since the enthalpy of formation h_f^{o} of a fuel depends on the phase of the fuel. We also need to know the state of the fuel when it enters the combustion chamber in order to determine its enthalpy.

$$\begin{split} U &= H - PV \\ &= N(\bar{h}_{f}^{\circ} + \bar{h} - \bar{h}^{\circ}) - PV \\ &= N(\bar{h}_{f}^{\circ} + \bar{h} - \bar{h}^{\circ} - P\bar{v}) \end{split}$$

An expression for the internal energy of a chemical component in terms of the enthalpy..

Example 15-6

Liquid propane (C_3H_8) enters a combustion chamber at 25°C at a rate of 0.05 kg/min where it is mixed and burned with 50 % excess air that enters the combustion chamber at 7°C. An analysis of the combustion gases reveals that all the hydrogen in the fuel burns to H_2O but only 90 % of the carbon burns to CO_2 , with the remaining 10 percent forming CO. If the exit temperature of the combustion gases is 1500 K, determine (*a*) the mass flow rate of air and (*b*) the rate of heat transfer from the combustion chamber.



$$C_{3}H_{8}(\ell) + a_{th}(O_{2} + 3.76N_{2}) \rightarrow 3CO_{2} + 4H_{2}O + 3.76a_{th}N_{2}$$

$$O_2$$
 balance: $a_{th} = 3 + 2 = 5$

$$C_{3}H_{8}(s) + 7.5(O_{2} + 3.76N_{2}) \rightarrow 2.7CO_{2} + 0.3CO + 4H_{2}O + 2.65O_{2} + 28.2N_{2}$$

(a) The air-fuel ratio for this combustion process is

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{(7.5 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(3 \text{ kmol})(12 \text{ kg/kmol}) + (4 \text{ kmol})(2 \text{ kg/kmol})}$$
$$= 25.53 \text{ kg air/kg fuel}$$

$$\dot{m}_{air} = (AF)(\dot{m}_{fuel})$$

= (23.53 kg air/kg fuel)(0.05 kg fuel/min)

= 1.18 kg air/min

29

(b) The heat transfer for this steady-flow combustion process is determined from the steady -flow energy balance $E_{out}=E_{in}$ applied on the combustion chamber per unit mole of the fuel,

$$Q_{\text{out}} + \sum N_p (\overline{h}_f^{\circ} + \overline{h} - \overline{h}^{\circ})_p = \sum N_r (\overline{h}_f^{\circ} + \overline{h} - \overline{h}^{\circ})_r$$

$$Q_{\text{out}} = \sum N_r (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_r - \sum N_p (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_p$$

Prof. Dr. Ali PINARBAŞI			Cha	pter 15 CHEMICAL REACTI	IONS
CO	-110,530	—	8669	47,517	
CO ₂	-393,520	—	9364	71,078	
H ₂ O(<i>g</i>)	-241,820	—	9904	57,999	
N ₂	0	8141	8669	47,073	
02	0	8150	8682	49,292	
C ₃ H ₈ (ℓ)	-118,910			_	
Substance	kJ/kmol	kJ/kmol	kJ/kmol	kJ/kmol	
	\overline{h}_{f}°	$ar{h}_{ m 280~K}$	${ar h}_{ m 298}$ к	<i></i> $\overline{h}_{1500 \ { m K}}$	

 $Q_{\text{out}} = (1 \text{ kmol } \text{C}_3\text{H}_8)[(-118,910 + h_{298} - h_{298}) \text{ kJ/kmol } \text{C}_3\text{H}_8]$

- + $(7.5 \text{ kmol O}_2)[(0 + 8150 8682) \text{ kJ/kmol O}_2]$
- + $(28.2 \text{ kmol } N_2)[(0 + 8141 8669) \text{ kJ/kmol } N_2]$
- $-(2.7 \text{ kmol CO}_2)[(-393,520 + 71,078 9364) \text{ kJ/kmol CO}_2]$
- -(0.3 kmol CO)[(-110,530 + 47,517 8669) kJ/kmol CO]
- $(4 \text{ kmol } \text{H}_2\text{O})[(-241,820 + 57,999 9904) \text{ kJ/kmol } \text{H}_2\text{O}]$
- $-(2.65 \text{ kmol O}_2)[(0 + 49,292 8682) \text{ kJ/kmol O}_2]$
- $-(28.2 \text{ kmol } N_2)[(0 + 47,073 8669) \text{ kJ/kmol } N_2]$

= 363,880 kJ/kmol of C₃H₈

Thus 363,880 kJ of heat is transferred from the combustion chamber for each kmol (44 kg) of propane. This corresponds to 363,880/44 = 8270 kJ of heat loss per kilogram of propane. Then the rate of heat transfer for a mass flow rate of 0.05 kg/min for the propane becomes.

 $\dot{Q}_{out} = \dot{m}q_{out} = (0.05 \text{ kg/min})(8270 \text{ kJ/kg}) = 413.5 \text{ kJ/min} = 6.89 \text{ kW}$

ADIABATIC FLAME TEMPERATURE

In the absence of any work interactions and any changes in kinetic or potential energies, the chemical energy released during a combustion process either is lost as heat to the surroundings or is used internally to raise the temperature of the combustion products. The smaller the heat loss, the larger the temperature rise. In the limiting case of no heat loss to the surroundings (Q= 0), the temperature of the products will reach a maximum, which is called the **adiabatic flame** or **adiabatic combustion temperature** of the reaction

$$\sum N_p (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_p = \sum N_r (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_r$$



 $H_{\rm prod} = H_{\rm react}$

Note that the adiabatic flame temperature of a fuel is not unique.

Its value depends on

- (1) the state of the reactants,
- (2) the degree of completion of the reaction, and
- (3) the amount of air used.

For a specified fuel at a specified state burned with air at a specified state, the adiabatic flame temperature attains its maximum value when complete combustion occurs with the theoretical amount of air.



The maximum temperature encountered in a combustion chamber is lower than the theoretical adiabatic flame temperature.

ENTROPY CHANGE OF REACTING SYSTEMS

The entropy balance relations developed in Chap. 7 are equally applicable to both reacting and nonreacting systems provided that the entropies of individual constituents are evaluated properly using a common basis. The **entropy balance** for *any system* (including reacting systems) undergoing *any process* can be expressed as



Using quantities per unit mole of fuel and taking the positive direction of heat transfer to be *to* the system, the entropy balance relation can be expressed more explicitly for a *closed* or *steady-flow* reacting system a

$$\sum_{T_k}^{Q_k} + S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}} \qquad (\text{kJ/K})$$

where *Tk* is temperature at the boundary where Q_k crosses it. For an *adiabatic process* (*Q* = 0), the entropy transfer term drops out and Eq. 15–19 reduces to

$$S_{\text{gen, adiabatic}} = S_{\text{prod}} - S_{\text{react}} \ge 0$$



The total entropy generated during a process can be determined by applying the entropy balance to an *extended system* that includes the system itself and its immediate surroundings where external irreversibilities might be occurring. When evaluating the entropy transfer between an extended system and the surroundings, the boundary temperature of the extended system is simply taken to be the *environment temperature*.

The determination of the entropy change associated with a chemical reaction seems to be straightforward, except for one thing: The entropy relations for the reactants and the products involve the *entropies* of the components, *not entropy changes*, which was the case for nonreacting systems. Thus we are faced with the problem of finding a common base for the entropy of all substances, as we did with enthalpy. The search for such a common base led to the establishment of the **third law of thermodynamics** in the early part of this century.

The third law was expressed as: *The entropy of a pure crystalline substance at absolute zero temperature is zero*.



At a specified temperature, the absolute entropy of an ideal gas at pressures other than $P_0=1$ atm can be determined by subtracting $R \ln (P/P_0)$ from the tabulated value at 1 atm.

SECOND-LAW ANALYSIS OF REACTING SYSTEMS

Once the total entropy change or the entropy generation is evaluated, the **exergy** destroyed $X_{destroyed}$ associated with a chemical reaction can be determined from

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} \qquad (\text{kJ})$$

$$W_{\rm rev} = \sum N_r (\overline{h}_f^{\circ} + \overline{h} - \overline{h}^{\circ} - T_0 \overline{s})_r - \sum N_p (\overline{h}_f^{\circ} + \overline{h} - \overline{h}^{\circ} - T_0 \overline{s})_p$$

In the absence of any changes in kinetic and potential energies, the reversible work relation for a steady-flow combustion process that involves heat transfer only with the surroundings at T_0 can be obtained by replacing the enthalpy terms by , $\bar{h}_f{}^o + \bar{h} - \bar{h}^o$ yielding

$$\overline{h} - \overline{T}_0 \overline{s} = (\overline{h} - \overline{T}_0 \overline{s})_{T_0} = \overline{g}_0$$
 Gibbs function.

$$W_{\rm rev} = \sum N_r \overline{g}_{0,r} - \sum N_p \overline{g}_{0,p}$$

where , $\bar{g}_{f}{}^{o}$ is the Gibbs function of formation

$$W_{\text{rev}} = \sum N_r (\overline{g}_f^\circ + \overline{g}_{T_0} - \overline{g}^\circ)_r - \sum N_p (\overline{g}_f^\circ + \overline{g}_{T_0} - \overline{g}^\circ)_p$$





The negative of the Gibbs function of formation of a compound at 25C, 1 atm represents the reversible work associated with the formation of that compound from its stable elements at 25C, 1 atm in an environment that is at 25C, 1 atm..

SUMMARY

- Any material that can be burned to release energy is called a *fuel*, and a chemical reaction during which a fuel is oxidized and a large quantity of energy is released is called *combustion*.
- The ratio of the mass of air to the mass of fuel during a combustion process is called the *air-fuel ratio* AF.
- The minimum amount of air needed for the complete combustion of a fuel is called the *stoichiometric* or *theoretical air*.
- For combustion processes, the enthalpy of reaction is usually referred to as the *enthalpy of combustion* h_c
- The enthalpy of a substance at a specified state due to its chemical composition is called the *enthalpy of formation* h_f
- The heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel
- In the absence of any heat loss to the surroundings (*Q*= 0), the temperature of the products will reach a maximum, which is called the *adiabatic flame temperature* of the reaction.

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CHEMICAL AND PHASE EQUILIBRIUM

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EXERGY: A MEASURE OF WORK POTENTIAL

16-1 Criterion for Chemical Equilibrium
16-2 The Equilibrium Constant for Ideal-Gas Mixtures
16-3 Some Remarks about the KP of Ideal-Gas Mixtures
16-4 Chemical Equilibrium for Simultaneous Reactions
16-5 Variation of KP with Temperature
16-6 Phase Equilibrium
Phase Equilibrium for a Single-Component System
The Phase Rule
Phase Equilibrium for a Multicomponent System

Objectives

• Develop the equilibrium criterion for reacting systems based on the second law of thermodynamics; more specifically, the increase of entropy principle.

• Develop a general criterion for chemical equilibrium applicable to any reacting system based on minimizing the Gibbs function for the system.

- Define and evaluate the chemical equilibrium constant.
- Apply the general criterion for chemical equilibrium analysis to reacting ideal-gas mixtures.
- Apply the general criterion for chemical equilibrium analysis to simultaneous reactions.
- Relate the chemical equilibrium constant to the enthalpy of reaction.

• Establish the phase equilibrium for nonreacting systems in terms of the specific Gibbs function of the phases of a pure substance.

• Apply the Gibbs phase rule to determine the number of independent variables associated with a multicomponent, multiphase system.

• Identify Henry's law and Raoult's law for gases dissolved in liquids.

CRITERION FOR CHEMICAL EQUILIBRIUM

Consider a reaction chamber that contains a mixture of CO, O_2 , and CO_2 at a specified temperature and pressure. Let us try to predict what will happen in this chamber.

 $CO + \frac{1}{2}O_2 \rightarrow CO_2$

This reaction is certainly a possibility, but it is not the only possibility. It is also possible that some CO_2 in the combustion chamber dissociated into CO and O_2 .

Yet a third possibility would be to have no reactions among the three components at all, that is, for the system to be in chemical equilibrium.

It appears that although we know the temperature, pressure, and composition (thus the state) of the system, we are unable to predict whether the system is in chemical equilibrium.



A reaction chamber that contains a mixture of CO_2 , CO_2 , and O_2 at a specified temperature and pressure.

Assume that the CO, O_2 , and CO_2 mixture mentioned above is in chemical equilibrium at the specified temperature and pressure. The chemical composition of this mixture will not change unless the temperature or the pressure of the mixture is changed.

$$dS_{\rm sys} \ge \frac{\delta Q}{T}$$

A system and its surroundings form an adiabatic system, and for such systems it reduces to $dS_{sys} \ge 0$.

That is, a chemical reaction in an adiabatic chamber proceeds in the direction of increasing entropy.

When the entropy reaches a maximum, the reaction stops.

Therefore, entropy is a very useful property in the analysis of reacting adiabatic systems.



Equilibrium criteria for a chemical reaction that takes place adiabatically..

Consider a reacting (or nonreacting) simple compressible system of fixed mass with only quasi-equilibrium work modes at a specified temperature *T* and pressure *P*

$$\left. \begin{array}{l} \delta Q - P \, dV = dU \\ dS \ge \frac{\delta Q}{T} \end{array} \right\} \quad dU + P \, dV - T \, ds \le 0$$

The differential of the Gibbs function at constant T and P

$$(G = H - TS)$$

REACTION
CHAMBER
Control
mass
$$T, P$$

 δQ

A control mass undergoing a chemical reaction at a specified temperature and pressure.

$$(dG)_{T,P} = dH - T dS - S dT$$
$$= (dU + P dV + V dP) - T dS - S dT$$
$$= dU + P dV - T dS$$

$$(dG)_{T,P} \leq 0$$

A chemical reaction at a specified temperature and pressure will proceed in the direction of a decreasing Gibbs function. The reaction will stop and chemical equilibrium will be established when the Gibbs function attains a minimum value. Therefore, the criterion for chemical equilibrium can be expressed as

$$(dG)_{T,P}=0$$

A chemical reaction at a specified temperature and pressure cannot proceed in the direction of the increasing Gibbs function since this will be a violation of the second law of thermodynamics.

Notice that if the temperature or the pressure is changed, the reacting system will assume a different equilibrium state, which is the state of the minimum Gibbs function at the new temperature or pressure.



Criteria for chemical equilibrium for a fixed mass at a specified temperature and pressure.

$$dN_AA + dN_BB \longrightarrow dN_CC + dN_DD$$

$$(dG)_{T,P} = \sum (dG_i)_{T,P} = \sum (\overline{g}_i \cdot dN_i)_{T,P} = 0$$

REACTION	
CHAMBER	
Т, Р	
N_A moles of A	
N_B moles of B	
N_C moles of C	
N_D moles of D	

 $dN_AA + dN_BB \rightarrow dN_CC + dN_DD$

An infinitesimal reaction in a chamber at constant temperature and pressure.

$$H_2 \rightarrow 2H$$

$$0.1H_2 \rightarrow 0.2H$$

$$0.01H_2 \rightarrow 0.02H$$

$$0.001H_2 \rightarrow 0.002H$$

$$V_{H_2} = 1$$

$$V_{H} = 2$$

The changes in the number of moles of the components during a chemical reaction are proportional to the stoichiometric coefficients regardless of the extent of the reaction.

$$\overline{g}_{C} dN_{C} + \overline{g}_{D} dN_{D} + \overline{g}_{A} dN_{A} + \overline{g}_{B} dN_{B} = 0$$

$$\nu_A A + \nu_B B \Longrightarrow \nu_C C + \nu_D D$$

$$dN_A = -\varepsilon \nu_A \qquad dN_C = \varepsilon \nu_C$$

$$dN_B = -\varepsilon \nu_B \qquad dN_D = \varepsilon \nu_D$$

For example, if the reactants are C_2H_6 and O_2 and the products are CO_2 and H_2O , the reaction of 1 μ mol (10⁻⁶ mol) of C_2H_6 will result in a 2- μ mol increase in CO_2 , a 3- μ mol increase in H_2O , and a 3.5- μ mol decrease in O_2 in accordance with the stoichiometric equation.

$$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$$

That is, the change in the number of moles of a component is one-millionth ($\varepsilon = 10^{-6}$) of the stoichiometric coefficient of that component in this case, canceling ε , we obtain;

$$\nu_C \overline{g}_C + \nu_D \overline{g}_D - \nu_A \overline{g}_A - \nu_B \overline{g}_B = 0$$

This equation involves the stoichiometric coefficients and the molar Gibbs functions of the reactants and the products, and it is known as the **criterion for chemical equilibrium.** It is valid for any chemical reaction regardless of the phases involved.

THE EQUILIBRIUM CONSTANT FOR IDEAL-GAS MIXTURES

Consider a mixture of ideal gases that exists in equilibrium at a specified temperature and pressure. Like entropy, the Gibbs function of an ideal gas depends on both the temperature and the pressure. The Gibbs function values are usually listed versus temperature at a fixed reference pressure P_0 , which is taken to be 1 atm. The variation of the Gibbs function of an ideal gas with pressure at a fixed temperature is determined by using the definition of the Gibbs function and the entropy-change relation for isothermal processes

$$\bar{g} = \bar{h} - T\bar{s}$$
 $\Delta \bar{s} = -R_u \ln \left(\frac{P_2}{P_1}\right)$

$$(\Delta \overline{g})_T = \Delta \overline{h} - T(\Delta \overline{s})_T = -T(\Delta \overline{s})_T = R_u T \ln \frac{P_2}{P_1}$$

Thus the Gibbs function of component *i* of an ideal-gas mixture at its partial pressure *P*_i and mixture temperature *T* can be expressed as

$$\overline{g}_i(T, P_i) = \overline{g}_i^*(T) + R_u T \ln P_i$$

 $\nu_C[\overline{g}_C^*(T) + R_u T \ln P_C] + \nu_D[\overline{g}_D^*(T) + R_u T \ln P_D]$

 $-\nu_A \left[\overline{g}_A^*(T) + R_u T \ln P_A \right] - \nu_B \left[\overline{g}_B^*(T) + R_u T \ln P_B \right] = 0$

For convenience, we define the **standard-state Gibbs function change** as

$$\Delta G^*(T) = \nu_C \overline{g}_C^*(T) + \nu_D \overline{g}_D^*(T) - \nu_A \overline{g}_A^*(T) - \nu_B \overline{g}_B^*(T)$$
$$\Delta G^*(T) = -R_u T (\nu_C \ln P_C + \nu_D \ln P_D - \nu_A \ln P_A - \nu_B \ln P_B) = -R_u T \ln \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}}$$

(1) In terms of partial pressures

$$K_P = \frac{P_C^{\vee_C} P_D^{\vee_D}}{P_A^{\vee_A} P_B^{\vee_B}}$$

(2) In terms of
$$\Delta G^*(T)$$

 $K_{a} = e^{-\Delta G^*(T)/R_{u}T}$

$$K_P = e^{-\Delta G^*(T)/R_l}$$

(3) In terms of the equilibrium composition

$$K_{P} = \frac{N_{C}^{\nu_{C}} N_{D}^{\nu_{D}}}{N_{A}^{\nu_{A}} N_{B}^{\nu_{B}}} \left(\frac{P}{N_{\text{total}}}\right)^{\Delta \nu}$$

Three equivalent K_P relations for reacting ideal-gas mixtures

the equilibrium constant K_P

$$K_{P} = \frac{P_{C}^{\nu_{C}} P_{D}^{\nu_{D}}}{P_{A}^{\nu_{A}} P_{B}^{\nu_{B}}}$$

$$K_P = e^{-\Delta G^*(T)/R_u T}$$

$$P_i = y_i P = \frac{N_i}{N_{\text{total}}} P$$

$$K_P = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{P}{N_{\text{total}}}\right)^{\Delta \nu}$$

$$\Delta \nu = \nu_C + \nu_D - \nu_A - \nu_B$$

Example 16-1

Using below equation and the Gibbs function data, determine the equilibrium constant *KP* for the dissociation process N2 \rightarrow 2N at 25°C. Compare your result to the *K*_P value listed in Table A–28.

 $K_P = e^{-\Delta G^*(T)/R_u T}$

$$\Delta G^*(T) = \nu_N \overline{g}_N^*(T) - \nu_{N_2} \overline{g}_{N_2}^*(T)$$

= (2)(455510 kJ/kmol) - 0
= 911020 kJ/kmol
$$\ln K_P = -\frac{911020 \text{ kJ/kmol}}{(8.314 \text{ kJ/kmol} \cdot \text{K})(298.15 \text{ K})}$$

= -367.5

 $K_P \cong \mathbf{2} \times \mathbf{10}^{-160}$

Note that this reaction involves one product (N) and one reactant (N₂), and the stoichiometric coefficients for this reaction are $v_N = 2$ and $v_{N2} = 1$. Also note that the Gibbs function of all stable elements (such as N₂) is assigned a value of zero at the standard reference state of 25°C and 1 atm. The Gibbs function values at other temperatures can be calculated from the enthalpy and absolute entropy data by using the definition of the Gibbs function,

$$\bar{g}^{*}(T) = \bar{h}(T) - T \bar{s}^{*}(T), \ \bar{h}(T) = \bar{h}_{f}^{*} + \bar{h}_{T} - \bar{h}_{298 \text{ K}}$$



We conclude that 10 % of H_2 will dissociate into H when the temperature is raised to 3535 K. If the temperature is increased further, the percentage of H_2 that dissociates into H will also increase.

SOME REMARKS ABOUT THE Kp OF IDEAL-GAS MIXTURES

1. The K_p of a reaction depends on temperature only. It is independent of the pressure of the equilibrium mixture and is not affected by the presence of inert gases. This is because K_p depends on $\Delta G^*(T)$, which depends on temperature only, and the $\Delta G^*(T)$ of inert gases is zero. Thus, at a specified temperature the following four reactions have the same K_p value:

$H_2 + \frac{1}{2}O_2 \Longrightarrow H_2O$	1 atm
$H_2 + \frac{1}{2}O_2 \Longrightarrow H_2O$	5 atm
$H_2 + \frac{1}{2}O_2 + 3N_2 \Longrightarrow H_2O + 3N_2$	3 atm
$H_2 + 2O_2 + 5N_2 \Longrightarrow H_2O + 1.5O_2 + 5N_2$	2 atm

2. The K_p of the reverse reaction is $1/K_p$. For reverse reactions, the products and reactants switch places, and thus the terms in the numerator move to the denominator and vice versa. Consequently, the equilibrium constant of the reverse reaction becomes $1/K_p$.

$$K_P = 0.1147 \times 10^{11} \qquad \text{for} \quad \text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O} \qquad \text{at 1000 K}$$
$$K_P = 8.718 \times 10^{-11} \qquad \text{for} \qquad \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2 \qquad \text{at 1000 K}$$

0				
<u> </u>		$H_2 \rightarrow 2H$		
0		P = 1 atm		_
	Т, К	K _P	% mol H	
	1000	5.17×10^{-18}	0.00	
	2000	2.65×10^{-6}	0.16	
	3000	0.025	14.63	_
	4000	2.545	76.80	
~	5000	41.47	97.70	
0	6000	267.7	99.63	_

The larger the *K_P*, the more complete the reaction.



The presence of inert gases does not affect the equilibrium constant, but it does affect the equilibrium composition..

4. The mixture pressure affects the equilibrium composition (although it does not affect the equilibrium constant K_p).

5. *The presence of inert gases affects the equilibrium composition* (although it does not affect the equilibrium constant *KP*).

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6. When the stoichiometric coefficients are doubled, the value of K_p is squared.

$$H_{2} + \frac{1}{2}O_{2} \iff H_{2}O \qquad K_{P_{1}} = \frac{P_{H_{2}O}}{P_{H_{2}}P_{O_{2}}^{1/2}}$$
$$2H_{2} + O_{2} \iff 2H_{2}O \qquad K_{P_{2}} = \frac{P_{H_{2}O}^{2}}{P_{H_{2}}^{2}P_{O_{2}}} = (K_{P_{1}})^{2}$$

7. Free electrons in the equilibrium composition can be treated as an ideal gas.

$$\mathbf{H} \rightleftharpoons \mathbf{H}^+ + e^-$$



Equilibrium-constant relation for the ionization reaction of hydrogen.

8. Equilibrium calculations provide information on the equilibrium composition of a reaction, not on the reaction rate.

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Example 16–3 A mixture of 2 kmo a pressure of 304 k assuming the mixtu	l of CO and 3 kmol Pa. Determine the re consists of CO ₂	of O ₂ is heated to 2 equilibrium compos , CO, and O ₂ .	2600 K at sition,	Initial composition 2 kmol CO 3 kmol O ₂	-	Equilibrium composition at 2600 K, 304 kPa $x CO_2$ y CO $z O_2$
Stoichiome Actual:	etric: $CO + \frac{1}{2}O_2$ $2CO + 3O_2$	$c \rightleftharpoons CO_2$ (thu $\longrightarrow xCO_2 + yO_2$ products	s $V_{CO_2} =$ CO + zO reactants (leftover)	$1, v_{\rm CO} = 1, an$	d V _o	$D_2 = \frac{1}{2}$
	C balance: O balance:	2 = x + y $8 = 2x + y + y$	or 2z or	$y = 2 - x$ $z = 3 - \frac{x}{2}$		

Total number of moles: $N_{\text{total}} = x + y + z = 5 - \frac{x}{2}$ Pressure:P = 304 kPa = 3.0 atm

Assuming ideal-gas behavior for all components, the equilibrium constant relation

$$K_P = \frac{N_{\rm CO_2}^{\nu_{\rm CO_2}}}{N_{\rm CO}^{\nu_{\rm CO}} N_{\rm O_2}^{\nu_{\rm O_2}}} \left(\frac{P}{N_{\rm total}}\right)^{\nu_{\rm CO_2} - \nu_{\rm CO} - \nu_{\rm O_2}}$$
$$16.461 = \frac{x}{(2-x)(3-x/2)^{1/2}} \left(\frac{3}{5-x/2}\right)^{-1/2}$$
$$x = 1.906$$
$$y = 2 - x = 0.094$$
$$z = 3 - \frac{x}{2} = 2.047$$

 $1.906CO_2 + 0.094CO + 2.074O_2$

In solving this problem, we disregarded the dissociation of O_2 into O according to the reaction $O_2 \rightarrow 2O$, which is a real possibility at high temperatures. This is because $\ln K_p = 7.521$ at 2600 K for this reaction, which indicates that the amount of O_2 that dissociates into O in this case is negligible.

Example 1 A mixture of heated to 26 equilibrium	l 6-4 3 kmol of CO, 500 K at a pres composition of	2.5 kmol of O ₂ , sure of 5 atm. [the mixture.	and 8 kmol of N ₂ is Determine the	Initial composition 3 kmol CO 2.5 kmol O ₂ 8 kmol N ₂	-	Equilibrium composition at 2600 K, 5 atm $x CO_2$ y CO $z O_2$ $8 N_2$
Stor Act	ichiometric: ual:	$CO + \frac{1}{2}O_2 = 3CO + 2.5$	$\implies CO_2 \text{ (thus } V_{CO_2} = O_2 + 8N_2 \longrightarrow xCO_2$	$= 1, V_{CO} = 1, an$ $D_2 + yCO + zO$ $= 1, an$ $D_2 + yCO + zO$ $= 1, an$ $= 1, v_{CO} + zO$	nd V_{c}	$\sum_{D_2} = \frac{1}{2}$ $(8N_2)$ inert
	C balance: O balance: Total numbe	r of moles:	$3 = x + y$ $8 = 2x + y + 2$ $N_{\text{total}} = x + y + z$	or $y = 3$ ez or $z = 2$. + $8 = 13.5 - 100$	-x $5-\frac{x}{2}$	$\frac{x}{2}$

Assuming ideal-gas behavior for all components, the equilibrium constant relation

$$K_{P} = \frac{N_{CO_{2}}^{\nu_{CO_{2}}}}{N_{CO}^{\nu_{CO}}N_{O_{2}}^{\nu_{O_{2}}}} \left(\frac{P}{N_{\text{total}}}\right)^{\nu_{CO_{2}}-\nu_{CO}-\nu_{O_{2}}}$$

$$16.461 = \frac{x}{(3-x)(2.5-x/2)^{1/2}} \left(\frac{5}{13.5-x/2}\right)^{-1/2}$$
$$x = 2.754 \qquad y = 3 - x = 0.246 \qquad z = 2.5 - \frac{x}{2} = 1.123$$

 $2.754CO_2 + 0.246CO + 1.123O_2 + 8N_2$

Note that the inert gases do not affect the K_p value or the K_p relation for a reaction, but they do affect the equilibrium composition.

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CHEMICAL EQUILIBRIUM FOR SIMULTANEOUS REACTIONS

Most practical chemical reactions involve two or more reactions that occur simultaneously, which makes them more difficult to deal with. In such cases, it becomes necessary to apply the equilibrium criterion to all possible reactions that may occur in the reaction chamber. When a chemical species appears in more than one reaction, the application of the equilibrium criterion, together with the mass balance for each chemical species, results in a system of simultaneous equations from which the equilibrium composition can be determined.

The number of K_P relations needed to determine the equilibrium composition of a reacting mixture is equal to the number of chemical species minus the number of elements present in equilibrium.

Composition: CO ₂ , CO, O ₂ , O
No. of components: 4 No. of elements: 2 No. of K_p relations needed: $4-2=2$

The number of *KP* relations needed to determine the equilibrium composition of a reacting mixture is the difference between the number of species and the number of elements.

Örnek 16-5 Initial A mixture of 1 kmol of H_2O and 2 kmol of O_2 is heated to 4000 K at a pressure of 1 atm. Determine the equilibrium composition of this mixture assuming that only H_2O , OH, O_2 and H_2 are present. $H_2O + 2O_2 \longrightarrow xH_2O + yH_2 + zO_2 + wOH$ H balance: 2 = 2x + 2y + w5 = x + 2z + wO balance: $H_2O \iff H_2 + \frac{1}{2}O_2$ (reaction 1) $H_2O \implies \frac{1}{2}H_2 + OH$ (reaction 2) $\ln K_{P_1} = -0.542 \longrightarrow K_{P_1} = 0.5816$ $\ln K_{P_2} = -0.044 \longrightarrow K_{P_2} = 0.9570$ $K_{P_1} = \frac{N_{H_2}^{\nu_{H_2}} N_{O_2}^{\nu_{O_2}}}{N_{H_2O}^{\nu_{H_2O}}} \left(\frac{P}{N_{total}}\right)^{\nu_{H_2} + \nu_{O_2} - \nu_{H_2O}}$ $K_{P_2} = \frac{N_{H_2}^{\nu_{H_2}} N_{OH}^{\nu_{OH}}}{N_{H_2O}^{\nu_{H_2O}}} \left(\frac{P}{N_{H_2O}}\right)^{\nu_{H_2} + \nu_{OH} - \nu_{H_2O}}$ $N_{\text{total}} = N_{\text{H}_2\text{O}} + N_{\text{H}_2} + N_{\text{O}_2} + N_{\text{OH}} = x + y + z + w$



$$0.5816 = \frac{(y)(z)^{1/2}}{x} \left(\frac{1}{x+y+z+w}\right)^{1/2}$$
$$0.9570 = \frac{(w)(y)^{1/2}}{x} \left(\frac{1}{x+y+z+w}\right)^{1/2}$$

$$x = 0.271$$
 $y = 0.213$
 $z = 1.849$ $w = 1.032$

 $0.271H_2O + 0.213H_2 + 1.849O_2 + 1.032OH$

We could also solve this problem by using the K_p relation for the stoichiometric reaction $O_2 \rightleftharpoons 2O$ as one of the two equations.

VARIATION OF K_P WITH TEMPERATURE

$$\ln K_{P} = -\frac{\Delta G^{*}(T)}{R_{u}T}$$

$$\frac{d(\ln K_{p})}{dT} = \frac{\Delta H^{*}(T)}{R_{u}T^{2}} - \frac{d[\Delta H^{*}(T)]}{R_{u}T dT} + \frac{d[\Delta S^{*}(T)]}{R_{u} dT}$$

$$\frac{d(\ln K_{p})}{dT} = \frac{\Delta H^{*}(T)}{R_{u}T^{2}} = \frac{\bar{h}_{R}(T)}{R_{u}T^{2}}$$
Van't Hoff equation
$$\frac{Reaction: C + O_{2} \rightarrow CO_{2}}{T, K} - \frac{K_{P}}{1000 - 4.78 \times 10^{20}}$$

$$\ln \frac{K_{P_{2}}}{K_{P_{1}}} \approx \frac{\bar{h}_{R}}{R_{u}} \left(\frac{1}{T_{1}} - \frac{1}{T_{2}}\right)$$

$$\ln \frac{K_{P_{2}}}{K_{P_{1}}} \approx \frac{\bar{h}_{R}}{R_{u}} \left(\frac{1}{T_{1}} - \frac{1}{T_{2}}\right)$$

Exothermic reactions are less complete at higher temperatures.

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Example 16-6

Estimate the enthalpy of reaction \bar{h}_R for the combustion process of hydrogen H₂ + 0.5O₂ \rightarrow H₂O at 2000 K, using (*a*) enthalpy data and (*b*) K_P data.

(a) The \bar{h}_R of the combustion process of H₂ at 2000 K is the amount of energy released as 1 kmol of H₂ is burned in a steady-flow combustion chamber at a temperature of 2000 K.

$$\begin{split} \overline{h}_{R} &= \sum_{N_{H_{2}O}} N_{ii} (\overline{h}_{ol}^{\circ} + \overline{h} - \overline{h}^{\circ})_{ii} - \sum_{N_{g}} N_{g} (\overline{h}_{ol}^{\circ} + \overline{h} - \overline{h}^{\circ})_{g} \\ &= N_{H_{2}O} (\overline{h}_{ol}^{\circ} + \overline{h}_{2000 \text{ K}} - \overline{h}_{298 \text{ K}})_{H_{2}O} - N_{H_{2}} (\overline{h}_{ol}^{\circ} + \overline{h}_{2000 \text{ K}} - \overline{h}_{298 \text{ K}})_{H_{2}} \\ &- N_{O_{2}} (\overline{h}_{ol}^{\circ} + h_{2000 \text{ K}} - h_{298 \text{ K}})_{O_{2}} \\ &= (1 \text{ kmol } \text{H}_{2}\text{O}) [(-241820 + 82593 - 9904) \text{ kJ/kmol } \text{H}_{2}\text{O}] \\ &- (1 \text{ kmol } \text{H}_{2}) [(0 + 61400 - 8468) \text{ kJ/kmol } \text{H}_{2}] \\ &- (0.5 \text{ kmol } \text{O}_{2}) [(0 + 67881 - 8682) \text{ kJ/kmol } \text{O}_{2}] \\ &= -251663 \text{ kJ/kmol} \\ \end{split}$$
(b) From K_{p} data
$$\ln \frac{869.6}{18,509} \approx \frac{\overline{h}_{R}}{8.314 \text{ kJ/kmol} \cdot \text{K}} \left(\frac{1}{1800 \text{ K}} - \frac{1}{2200 \text{ K}}\right) \\ \overline{h}_{R} \approx -251,698 \text{ kJ/kmol} \\ \end{cases}$$
Despite the large temperature difference between T_{1} and T2 (400 \text{ K}), the two results are

almost identical.

PHASE EQUILIBRIUM

We know from experience that a wet T-shirt hanging in an open area eventually dries, a small amount of water left in a glass evaporates, and the aftershave in an open bottle quickly disappears.

There is a driving force between the two phases of a substance that forces the mass to transform from one phase to another. The magnitude of this force depends, among other things, on the relative concentrations of the two phases.



A wet T-shirt will dry much quicker in dry air than it would in humid air..

In fact, it will not dry at all if the relative humidity of the environment is 100 percent.

In this case, there will be no transformation from the liquid phase to the vapor phase, and the two phases will be in phase equilibrium.

The conditions of phase equilibrium will change, however, if the temperature or the pressure is changed.

Therefore, we examine phase equilibrium at a specified temperature and pressure.

Phase Equilibrium for a Single-Component System

The equilibrium criterion for two phases of a pure substance such as water is easily developed by considering a mixture of saturated liquid and saturated vapor in equilibrium at a specified temperature and pressure. The total Gibbs function of this mixture is

$$G = m_s g_s + m_g g_g$$

$$(dG)_{T,P} = g_s dm_s + g_g dm_g$$
Also from the conservation of mass, dmg=-dmf
$$(dG)_{T,P} = (g_s - g_g) dm_s$$

$$(dG)_{T,P} = 0$$
Which must be equal to zero at equilibrium. It yields
$$g_s = g_g$$
Also from the constant temperature and pressure

The two phases of a pure substance are in equilibrium when each phase has the same value of specific Gibbs function. Also, at the triple point (the state at which all three phases coexist in equilibrium), the specific Gibbs function of each one of the three phases is equal.

What happens if $g_s > g_g$?

Obviously the two phases will not be in equilibrium at that moment.

The second law requires that $(dG)_{T,P} = (g_s - g_g) dm_s \le 0$.

Thus, dm_f must be negative, which means that some liquid must vaporize until $g_f = g_g$.

Therefore, the Gibbs function difference is the driving force for phase change, just as the temperature difference is the driving force for heat transfer

Example 16-7

Show that a mixture of saturated liquid water and saturated water vapor at 120°C satisfies the criterion for phase equilibrium.

Using the definition of Gibbs function together with the enthalpy and entropy data, we have

$$g_f = h_f - Ts_f = 503.81 \text{ kJ/kg} - (393.15 \text{ K})(1.5279 \text{ kJ/kg} \cdot \text{K})$$
$$= -96.9 \text{ kJ/kg}$$
$$g_g = h_g - Ts_g = 2706.0 \text{ kJ/kg} - (393.15 \text{ K})(7.1292 \text{ kJ/kg} \cdot \text{K})$$

$$= -96.8 \text{ kJ/kg}$$

The two results are in close agreement. They would match exactly if more accurate property data were used. Therefore, the criterion for phase equilibrium is satisfied.

The Phase Rule

Notice that a single-component two-phase system may exist in equilibrium at different temperatures (or pressures). However, once the temperature is fixed, the system will be locked into an equilibrium state and all intensive properties of each phase (except their relative amounts) will be fixed. Therefore, a single-component two-phase system has one independent property, which may be taken to be the temperature or the pressure.

Multiphase system is given by the Gibbs phase rule,

IV = C - PH + 2

- IV : the number of independent variables,
- C : the number of components,
- PH : the number of phases present in equilibrium.

Example: One independent intensive property needs to be specified, for the single-component (C =1) two-phase (PH=2) system discussed above, which is (IV = 1)

Two independent intensive properties need to be specified to fix the equilibrium state of a pure substance in a single phase.



According to the Gibbs phase rule, a single-component, twophase system can have only one independent variable.

Phase Equilibrium for a Multicomponent System

Many multiphase systems encountered in practice involve two or more components. A multicomponent multiphase system at a specified temperature and pressure will be in phase equilibrium when there is no driving force between the different phases of each component. Thus, for phase equilibrium, the specific Gibbs function of each component must be the same in all phases.

$g_{f,1} = g_{g,1} = g_{s,1}$	for component 1
$g_{f,2} = g_{g,2} = g_{s,2}$	for component 2
$g_{f,N} = g_{g,N} = g_{s,N}$	for component N

T, P
NH₃ + H₂O VAPOR
$$g_{f,NH_3} = g_{g,NH_3}$$

 $g_{f,H_2O} = g_{g,H_2O}$
LIQUID NH₃ + H₂O

A multicomponent multiphase system is in phase equilibrium when the specific Gibbs function of each component is the same in all phases. A two-component, two phase system has two independent variables, and such a system will not be in equilibrium unless two independent intensive properties are fixed.



Equilibrium diagram for the two-phase mixture of oxygen and nitrogen at 0.1 MPa.

Example: At 84 K, the mole fractions are 30 % nitrogen and 70 % oxygen in the liquid phase and 66 % nitrogen and 34 % oxygen in the vapor phase..

$$y_{s,N_2} + y_{s,O_2} = 0.30 + 0.70 = 1$$

 $y_{g,N_2} + y_{g,O_2} = 0.66 + 0.34 = 1$

Chapter 16 CHEMICAL AND PHASE EQUILIBRIUM

It is interesting to note that temperature is a *continuous* function, but mole fraction (which is a dimensionless concentration) in general, is not.

Example: The water and air temperatures at the free surface of a lake, are always the same. The mole fractions of air on the two sides of a water–air interface, however, are obviously very different (in fact, the mole fraction of air in water is close to zero).

Likewise, the mole fractions of water on the two sides of a water—air interface are also different even when air is saturated. Therefore, when specifying mole fractions in two-phase mixtures, we need to clearly specify the intended phase.



Unlike temperature, the mole fraction of species on the two sides of a liquid–gas (or solid–gas or solid–liquid) interface are usually not the same. Many processes involve the absorption of a gas into a liquid. Most gases are weakly soluble in liquids (such as air in water), and for such dilute solutions the mole fractions of a species *i* in the gas and liquid phases at the interface are observed to be proportional to each other. That is, $y_{i,gas side} \propto y_{i,liquid side}$ or $P_{i,gas side} \propto P_{yi,liquid side}$ since $y_i = P_i / P$ for ideal-gas mixtures. This is known as the **Henry's law** and is expressed as

$$y_{i, \text{ liquid side}} = \frac{P_{i, \text{ gas side}}}{H}$$

where *H* is the **Henry's constant**, which is the product of the total pressure of the gas mixture and the proportionality constant. Solubility of two inorganic compounds in water at various temperatures, in kg (in 100 kg of water)

(from Handbook of Chemistry, McGraw-Hill, 1961)

	Solute			
Tempera- ture, K	Salt NaCl	Calcium bicarbonate Ca(HCO ₃) ₂		
273.15	35.7	16.15		
280	35.8	16.30		
290	35.9	16.53		
300	36.2	16.75		
310	36.5	16.98		
320	36.9	17.20		
330	37.2	17.43		
340	37.6	17.65		
350	38.2	17.88		
360	38.8	18.10		
370	39.5	18.33		
373.15	39.8	18.40		





 $P_{A, \text{ gas side}} = H y_{A, \text{ liquid side}}$

Dissolved gases in a liquid can be driven off by heating the liquid. We mentioned earlier that the use of Henry's law is limited to dilute gas—liquid solutions, that is, liquids with a small amount of gas dissolved in them.

Then the question that arises naturally is, what do we do when the gas is highly soluble in the liquid (or solid), such as ammonia in water? In this case, the linear relationship of Henry's law does not apply, and the mole fraction of a gas dissolved in the liquid (or solid) is usually expressed as a function of the partial pressure of the gas in the gas phase and the temperature.

An approximate relation in this case for the *mole fractions* of a species on the *liquid* and *gas sides* of the interface is given by **Raoult's law** as

$$P_{i,\text{gas side}} = y_{i,\text{gas side}} P_{\text{total}} = y_{i,\text{liquid side}} P_{i,\text{sat}}(T)$$

Henry's constant *H* (in bars) for selected gases in water at low to moderate pressures (for gas *i*, $H = P_{i,\text{gas side}}/y_{i,\text{water side}}$) (from Mills, Ref. 6, Table A.21, p. 874)

Solute	290 K	300 K	310 K	320 K	330 K	340 K
H ₂ S	440	560	700	830	980	1140
$C\bar{O}_2$	1,280	1,710	2,170	2,720	3,220	_
02	38,000	45,000	52,000	57,000	61,000	65,000
H_2	67,000	72,000	75,000	76,000	77,000	76,000
CŌ	51,000	60,000	67,000	74,000	80,000	84,000
Air	62,000	74,000	84,000	92,000	99,000	104,000
N ₂	76,000	89,000	101,000	110,000	118,000	124,000

From this table and Henry equation above we make the following observations:

1. The concentration of a gas dissolved in a liquid is inversely proportional to the Henry's constant. Therefore, the larger the Henry's constant, the smaller the concentration of dissolved gases in the liquid.

2. The Henry's constant increases with increasing temperature. Therefore, the dissolved gases in a liquid can be driven off by heating the liquid.

3. The concentration of a gas dissolved in a liquid is proportional to the partial pressure of the gas. Therefore, the amount of gas dissolved in a liquid can be increased by increasing the pressure of the gas. This can be used to advantage in the carbonation of soft drinks with CO_2 gas.

Example 16-8

Determine the mole fraction of the water vapor at the surface of a lake whose temperature is 15°C, and compare it to the mole fraction of water in the lake. Take the atmospheric pressure at lake level to be 92 kPa.

$$P_{v} = P_{\text{sat } @ 15^{\circ}\text{C}} = 1.7057 \text{ kPa}$$

$$y_{v} = \frac{P_{v}}{P} = \frac{1.7057 \text{ kPa}}{92 \text{ kPa}} = 0.0185 \text{ or } 1.85 \text{ percent}$$

$$y_{H_{2}O, \text{ air side}} = 0.0185$$

$$y_{H_{2}O, \text{ liquid side}} \cong 1.0 \text{ or } 100 \text{ percent}$$

$$y_{H_{2}O, \text{ liquid side}} \cong 1.0$$

Note that the concentration of water on a molar basis is 100 % just beneath the air–water interface and less than 2 % just above it even though the air is assumed to be saturated (so this is the highest value at 15°C). Therefore, large discontinuities can occur in the concentrations of a species across phase boundaries.

A *

Example 16-9

Determine the mole fraction of air at the surface of a lake whose temperature is 17°C. Take the atmospheric pressure at lake level to be 92 kPa



This value is very small, as expected. Therefore, the concentration of air in water just below the air–water interface is 1.45 moles per 100,000 moles. But obviously this is enough oxygen for fish and other creatures in the lake. Note that the amount of air dissolved in water will decrease with increasing depth unless phase equilibrium exists throughout the entire lake. Thermodynamics: An Engineering Approach, 5th Edition Yunus A. Cengel, Michael A. Boles McGraw-Hill, 2008

COMPRESSIBLE FLOW

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COMPRESSIBLE FLOW

17-1 Stagnation Properties 17-2 Speed of Sound and Mach Number 17-3 One-Dimensional Isentropic Flow Variation of Fluid Velocity with Flow Area Property Relations for Isentropic Flow of Ideal Gases 17-4 Isentropic Flow through Nozzles **Converging Nozzles Converging-Diverging Nozzles** 17–5 Shock Waves and Expansion Waves Normal Shocks **Oblique Shocks Prandtl-Meyer Expansion Waves** 17-6 Duct Flow with Heat Transfer and Negligible Friction (Rayleigh Flow) **Property Relations for Rayleigh Flow Choked Rayleigh Flow** 17-7 Steam Nozzles

Objectives

• Develop the general relations for the thermodynamics of high-speed gas flow.

• Introduce the concepts of *stagnation state, velocity of sound,* and *Mach number* for a compressible fluid.

• Develop the relationships between the static and stagnation fluid properties for isentropic flows of ideal gases.

• Derive the relationships between the static and stagnation fluid properties as functions of specific-heat ratios and Mach number.

• Derive the effects of area changes for one-dimensional isentropic subsonic and supersonic flows.

- Solve problems of isentropic flow through converging and converging–diverging nozzles.
- Develop the concept of the normal shock wave and the variation of flow properties across the shock wave.

• Develop the concept of duct flow with heat transfer and negligible friction known as *Rayleigh flow*.

STAGNATION PROPERTIES

When analyzing control volumes, we find it very convenient to combine the *internal energy* and the *flow energy* of a fluid into a single term, *enthalpy*, defined per unit mass as $h = u + P/\rho$.

Whenever the kinetic and potential energies of the fluid are negligible, as is often the case, the enthalpy represents the *total energy* of a fluid.

For high-speed flows, such as those encountered in jet engines, the potential energy of the fluid is still negligible, but the kinetic energy is not. In such cases, it is convenient to combine the enthalpy and the kinetic energy of the fluid into a single term called stagnation (or total) enthalpy h_0 , defined per unit mass as





$$h_0 = h + \frac{V^2}{2} \qquad (kJ/kg)$$

Aircraft and jet engines involve high speeds, and thus the kinetic energy term should always be considered when analyzing them. When the potential energy of the fluid is negligible, the stagnation enthalpy represents the *total energy of a flowing fluid stream* per unit mass. Thus it simplifies the thermodynamic analysis of high-speed flows.

Throughout this chapter the ordinary enthalpy *h* is referred to as the **static enthalpy**, whenever necessary, to distinguish it from the stagnation enthalpy. Notice that the stagnation enthalpy is a combination property of a fluid, just like the static enthalpy, and these two enthalpies become identical when the kinetic energy of the fluid is negligible.

Consider the steady flow of a fluid through a duct such as a nozzle, diffuser, or some other flow passage where the flow takes place adiabatically and with no shaft or electrical work. Assuming the fluid experiences little or no change in its elevation and its potential energy, the energy balance relation (\dot{E}_{in} = \dot{E}_{out}) for this single-stream steady-flow system reduces to

$$h_1 + \frac{V_1^2}{2} = h_2 + \frac{V_2^2}{2}$$
 $h_{01} = h_{02}$



through an adiabatic duct.

in the absence of any heat and work interactions and any changes in potential energy, the stagnation enthalpy of a fluid remains constant during a steady-flow process.

Flows through nozzles and diffusers usually satisfy these conditions, and any increase in fluid velocity in these devices creates an equivalent decrease in the static enthalpy of the fluid.

If the fluid were brought to a complete stop, then the velocity at state 2 would be zero and equation become

$$h_1 + \frac{V_1^2}{2} = h_2 = h_{02}$$

Thus the stagnation enthalpy represents the enthalpy of a fluid when it is brought to rest adiabatically.

During a stagnation process, the kinetic energy of a fluid is converted to enthalpy (internal energy+flow energy), which results in an increase in the fluid temperature and pressure.

The properties of a fluid at the stagnation state are called **stagnation properties** (stagnation temperature, stagnation pressure, stagnation density, etc.).

The stagnation state and the stagnation properties are indicated by the subscript 0.

The stagnation state is called the **isentropic stagnation state** when the stagnation process is reversible as well as adiabatic (i.e., isentropic).

Notice that the stagnation enthalpy of the fluid (and the stagnation temperature if the fluid is an ideal gas) is the same for both cases.

However, the actual stagnation pressure is lower than the isentropic stagnation pressure since entropy increases during the actual stagnation process as a result of fluid friction.

The stagnation processes are often approximated to be isentropic, and the isentropic stagnation properties are simply referred to as stagnation properties.



Kinetic energy is converted to enthalpy during a stagnation process.



The actual state, actual stagnation state, and isentropic stagnation state of a fluid on an *h-s* diagram.

When the fluid is approximated as an *ideal gas* with constant specific heats, its enthalpy can be replaced by $c_p T$.

$$c_p T_0 = c_p T + \frac{V^2}{2}$$

$$T_0 = T + \frac{V^2}{2c_p}$$

Here T_0 is called the **stagnation** (or **total**) **temperature**, and it represents *the temperature an ideal gas attains when it is brought to rest adiabatically.* The term $V^2/2c_p$ corresponds to the temperature rise during such a process and is called the **dynamic temperature**.

For example, the dynamic temperature of air flowing at 100 m/s is

 $(100 \text{ m/s})^2/(2 \text{ x}1.005 \text{ kJ/kg} \cdot \text{K}) = 5.0 \text{ K}.$

Therefore, when air at 300 K and 100 m/s is brought to rest adiabatically (at the tip of a temperature probe), its temperature rises to the stagnation value of 305 K.



The temperature of an ideal gas flowing at a velocity V rises by $V^2/2c_p$ when it is brought to a complete stop Note that for low-speed flows, the stagnation and static (or ordinary) temperatures are practically the same.

But for high-speed flows, the temperature measured by a stationary probe placed in the fluid (the stagnation temperature) may be significantly higher than the static temperature of the fluid.

The pressure a fluid attains when brought to rest isentropically is called the **stagnation pressure** P_0 . For ideal gases with constant specific heats, P_0 is related to the static pressure of the fluid by

$$\frac{P_0}{P} = \left(\frac{T_0}{T}\right)^{k/(k-1)}$$

By noting that $\rho = 1/v$ and using the isentropic relation $Pv^k = P_o v_o^k$, the ratio of the stagnation density to static density can be expressed as,

$$\frac{\rho_0}{\rho} = \left(\frac{T_0}{T}\right)^{1/(k-1)}$$

When stagnation enthalpies are used, there is no need to refer explicitly to kinetic energy. Then the energy balance for a single-stream, steady-flow device can be expressed as

$$q_{\rm in} + w_{\rm in} + (h_{01} + gz_1) = q_{\rm out} + w_{\rm out} + (h_{02} + gz_2)$$

where h_{01} and h_{02} are the stagnation enthalpies at states 1 and 2, respectively. When the fluid is an ideal gas with constant specific heats,

$$(q_{\rm in} - q_{\rm out}) + (w_{\rm in} - w_{\rm out}) = c_p(T_{02} - T_{01}) + g(z_2 - z_1)$$

where T_{01} and T_{02} are the stagnation temperatures.

Notice that kinetic energy terms do not explicitly appear in Eqs. 17–7 and 17–8, but the stagnation enthalpy terms account for their contribution.

Example 17-1 An aircraft is flying at a cruising speed of 250 m/s at an altitude of 5000 m where the atmospheric pressure is 54.05 kPa and the ambient air temperature is 255.7 K. The ambient air is first decelerated in a diffuser before it enters the compressor. Assuming both the diffuser and the compressor to be isentropic, determine (*a*) the stagnation pressure at the compressor inlet and (*b*) the required compressor work per unit mass if the stagnation pressure ratio of the compressor is 8.

The constant-pressure specific heat c_p and the specific heat ratio k of air at room temperature are



$$c_p = 1.005 \text{ kJ/kg} \cdot \text{K}$$
 ve $k = 1.4$

(a) İzantropik akış koşullarında, kompresör girişinde (veya yayıcı çıkışında) durma sıcaklığı ve basıncı,

$$T_{01} = T_1 + \frac{V_1^2}{2c_p} = 255.7 \text{ K} + \frac{(250 \text{ m/s})^2}{(2)(1.005 \text{ kJ/kg} \cdot \text{K})} \left(\frac{1 \text{ kJ/kg}}{1000 \text{ m}^2/\text{s}^2}\right)$$
$$= 286.8 \text{ K}$$

$$P_{01} = P_1 \left(\frac{T_{01}}{T_1}\right)^{k/(k-1)} = (54.05 \text{ kPa}) \left(\frac{286.8 \text{ K}}{255.7 \text{ K}}\right)^{1.4/(1.4-1)}$$
$$= 80.77 \text{ kPa}$$

Hava 250 m/s hızdan sıfır hıza yavaşlarken sıcaklığı 31.1°C, basıncı da 26.72 kPa artar. Havanın sıcaklık ve basıncındaki bu artışlar kinetik enerjinin entalpiye dönüşümünden kaynaklanmaktadır.

(b) To determine the compressor work, we need to know the stagnation temperature of air at the compressor exit T_{02} .

$$T_{02} = T_{01} \left(\frac{P_{02}}{P_{01}}\right)^{(k-1)/k} = (286.8 \text{ K})(8)^{(1.4-1)/1.4} = 519.5 \text{ K}$$

Disregarding potential energy changes and heat transfer, the compressor work per unit mass of air is

$$w_{in} = c_p (T_{02} - T_{01})$$

= (1.005 kJ/kg · K)(519.5 K - 286.8 K)
= 233.9 kJ/kg

Thus the work supplied to the compressor is 233.9 kJ/kg.

Notice that using stagnation properties automatically accounts for any changes in the kinetic energy of a fluid stream.

SPEED OF SOUND AND MACH NUMBER

An important parameter in the study of compressible flow is the **speed of sound** (or **the sonic speed**), which is the speed at which an infinitesimally small pressure wave travels through a medium.

The pressure wave may be caused by a small disturbance, which creates a slight rise in local pressure.

The wave front moves to the right through the fluid at the speed of sound *c* and separates the moving fluid adjacent to the piston from the fluid still at rest.

The fluid to the left of the wave front experiences an incremental change in its thermodynamic properties, while the fluid on the right of the wave front maintains its original thermodynamic properties



Propagation of a small pressure wave along a duct.


A second important parameter in the analysis of compressible fluid flow is the Mach number Ma, named after the Austrian physicist Ernst Mach (1838–1916).

Ma, It is the ratio of the actual velocity of the fluid (or an object in still air) to the speed of sound in the same fluid at the same state:

$$Ma = \frac{V}{c}$$



Example 17–2 Air enters a diffuser with a velocity of 200 m/s. Determine (*a*) the speed of sound and (*b*) the Mach number at the diffuser inlet when the air temperature is 30C.

(a) The speed of sound in air at 30C is determined from

$$c = \sqrt{kRT} = \sqrt{(1.4)(0.287 \text{ kJ/kg} \cdot \text{K})(303 \text{ K})\left(\frac{1000 \text{ m}^2/\text{s}^2}{1 \text{ kJ/kg}}\right)} = 349 \text{ m/s}$$

(b) Then the Mach number becomes

$$Ma = \frac{V}{c} = \frac{200 \text{ m/s}}{349 \text{ m/s}} = 0.573$$

The flow at the diffuser inlet is subsonic since Ma 1.

AIR

V = 200 m/s

 $T = 30^{\circ}C$

Diffuser

ONE-DIMENSIONAL ISENTROPIC FLOW

During fluid flow through many devices such as nozzles, diffusers, and turbine blade passages, flow quantities vary primarily in the flow direction only, and the flow can be approximated as one-dimensional isentropic flow with good accuracy.

Therefore, it merits special consideration. Before presenting a formal discussion of onedimensional isentropic flow, we illustrate some important aspects of it with an example.

Example 17–3

Carbon dioxide flows steadily through a varying cross-sectionalarea duct such as a nozzle at a mass flow rate of 3 kg/s. The carbon dioxide enters the duct at a pressure of 1400 kPa and 200C with a low velocity, and it expands in the nozzle to a pressure of 200 kPa. The duct is designed so that the flow can be approximated as isentropic. Determine the density, velocity, flow area, and Mach number at each location along the duct that corresponds to a pressure drop of 200 kPa.

$$T_0 \cong T_1 = 200^{\circ}\text{C} = 473 \text{ K}$$
 $P_0 \cong P_1 = 1400 \text{ kPa}$

$$T = T_0 \left(\frac{P}{P_0}\right)^{(k-1)/k} = (473 \text{ K}) \left(\frac{1200 \text{ kPa}}{1400 \text{ kPa}}\right)^{(1.289-1)/1.289} = 457 \text{ K}$$

$$V = \sqrt{2c_p(T_0 - T)}$$

= $\sqrt{2(0.846 \text{ kJ/kg} \cdot \text{K})(473 \text{ K} - 457 \text{ K})} \left(\frac{1000 \text{ m}^2/\text{s}^3}{1 \text{ kJ/kg}}\right)$

= 164.5 m/s

$$\rho = \frac{P}{RT} = \frac{1200 \text{ kPa}}{(0.1889 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(457 \text{ K})} = 13.9 \text{ kg/m}^3$$

Stagnation region:

1400 kPa

200°C

 CO_2

 $\dot{m} = -$

1400

1000

767

P. kPa

200

3.00 kg/s

$$A = \frac{\dot{m}}{\rho V} = \frac{3 \text{ kg/s}}{(13.9 \text{ kg/m}^3)(164.5 \text{ m/s})} = 13.1 \times 10^{-4} \text{ m}^2 = 13.1 \text{ cm}^2$$

$$c = \sqrt{kRT} = \sqrt{(1.289)(0.1889 \text{ kJ/kg} \cdot \text{K})(457 \text{ K})\left(\frac{1000 \text{ m}^2/\text{s}^2}{1 \text{ kJ/kg}}\right)} = 333.6 \text{ m/s}$$

$$Ma = \frac{V}{c} = \frac{164.5 \text{ m/s}}{333.6 \text{ m/s}} = 0.493$$

Note that as the pressure decreases, the temperature and speed of sound decrease while the fluid velocity and Mach number increase in the flow direction. The density decreases slowly at first and rapidly later as the fluid velocity increases.

variation of fidid properties in now direction in duct described in									
Example 17–3 for $\dot{m} = 3$ kg/s = constant									
<i>P</i> , kPa	<i>T</i> , K	V, m/s	ho, kg/m ³	<i>c</i> , m/s	A, cm ²	Ма			
1400	473	0	15.7	339.4	∞	0			
1200	457	164.5	13.9	333.6	13.1	0.493			
1000	439	240.7	12.1	326.9	10.3	0.736			
800	417	306.6	10.1	318.8	9.64	0.962			
767*	413	317.2	9.82	317.2	9.63	1.000			
600	391	371.4	8.12	308.7	10.0	1.203			
400	357	441.9	5.93	295.0	11.5	1.498			
200	306	530.9	3.46	272.9	16.3	1.946			

Variation of fluid properties in flow direction in duct described in

The flow area decreases with decreasing pressure up to a critical-pressure value where the Mach number is unity, and then it begins to increase with further reductions in pressure.

The Mach number is unity at the location of smallest flow area, called the throat. Note that the velocity of the fluid keeps increasing after passing the throat although the flow area increases rapidly in that region. This increase in velocity past the throat is due to the rapid decrease in the fluid density.

The flow area of the duct considered in this example first decreases and then increases. Such ducts are called **converging–diverging nozzles**.



Variation of normalized fluid properties and cross-sectional area along a duct as the pressure drops from 1400 to 200 kPa.

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Variation of Fluid Velocity with Flow Area



The cross section of a nozzle at the smallest flow area is called the *throat*.

$$\frac{d\rho}{\rho} + \frac{dA}{A} + \frac{dV}{V} = 0$$

$$\frac{dP}{\rho} + V \, dV = 0$$

$$\frac{dA}{A} = \frac{dP}{\rho} \left(\frac{1}{V^2} - \frac{d\rho}{dP} \right)$$

$$\frac{dA}{A} = \frac{dP}{\rho V^2} \left(1 - \mathrm{Ma}^2\right)$$

$$\frac{dA}{A} = -\frac{dV}{V}(1 - \mathrm{Ma}^2)$$

For subsonic flow (Ma < 1), $\frac{dA}{dV} < 0$ For supersonic flow (Ma > 1), $\frac{dA}{dV} > 0$ For sonic flow (Ma = 1), $\frac{dA}{dV} = 0$

CONSERVATION OF ENERGY (steady flow, w = 0, q = 0, $\Delta pe = 0$) $h_1 + \frac{V_1^2}{2} = h_2 + \frac{V_2^2}{2}$ $h + \frac{V^2}{2} = \text{constant}$ Differentiate, dh + V dV = 0Also, 0 (isentropic) T ds' = dh - v dP $dh = v dP = \frac{1}{\rho} dP$ Substitute, $\frac{dP}{Q} + V dV = 0$ 6

Derivation of the differential form of the energy equation for steady isentropic flow. Thus the proper shape of a nozzle depends on the highest velocity desired relative to the sonic velocity. To accelerate a fluid, we must use a converging nozzle at subsonic velocities and a diverging nozzle at supersonic velocities.

The velocities encountered in most familiar applications are well below the sonic velocity, and thus it is natural that we visualize a nozzle as a converging duct.

However, the highest velocity we can achieve by a converging nozzle is the sonic velocity, which occurs at the exit of the nozzle.

If we extend the converging nozzle by further decreasing the flow area, in hopes of accelerating the fluid to supersonic velocities, we are up for disappointment.

Now the sonic velocity will occur at the exit of the converging extension, instead of the exit of the original nozzle, and the mass flow rate through the nozzle will decrease because of the reduced exit area.



Yakınsak bir lüleye yakınsak bir bölüm ekleyerek sesüstü hızlar elde edilemez. Bu işlem sadece ses hızına ulaşılan bölümü akış yönüne doğru öteler ve kütlesel debiyi düşürür.



The opposite process occurs in the engine inlet of a supersonic aircraft. The fluid is decelerated by passing it first through a supersonic diffuser, which has a flow area that decreases in the flow direction. Ideally, the flow reaches a Mach number of unity at the diffuser throat. The fluid is further decelerated in a subsonic diffuser, which has a flow area that increases in the flow direction.



		8		
	Superheated steam, k = 1.3	Hot products of combustion, k = 1.33	Air, <i>k</i> = 1.4	Monatomic gases, k = 1.667
$\frac{P^*}{P_0}$	0.5457	0.5404	0.5283	0.4871
$\frac{T^*}{T_0}$	0.8696	0.8584	0.8333	0.7499
$\frac{\rho^*}{\rho_0}$	0.6276	0.6295	0.6340	0.6495

The critical-pressure, critical-temperature, and critical-density ratios for isentropic flow of some ideal gases

Example 17-4

Calculate the critical pressure and temperature of carbon dioxide for the flow conditions described in Example 17–3.

$$P_0 = 1.4 \text{ MPa}$$

 $T_0 = 473 \text{ K}$
 $P^*_{T^*}$

$$\frac{P^*}{P_0} = \left(\frac{2}{k+1}\right)^{k/(k-1)} = \left(\frac{2}{1.289+1}\right)^{1.289/(1.289-1)} = 0.5477$$

 $\frac{T^*}{T_0} = \frac{2}{k+1} = \frac{2}{1.289+1} = 0.8737$

$$T^* = 0.8737T_0 = (0.8737)(473 \text{ K}) = 413 \text{ K}$$

 $P^* = 0.5477P_0 = (0.5477)(1400 \text{ kPa}) = 767 \text{ kPa}$

Property values other than these at the throat would indicate that the flow is not critical, and the Mach number is not unity.

ISENTROPIC FLOW THROUGH NOZZLES

Converging or converging–diverging nozzles are found in many engineering applications including steam and gas turbines, aircraft and spacecraft propulsion systems, and even industrial blasting nozzles and torch nozzles.

Converging Nozzles

The nozzle inlet is attached to a reservoir at pressure P_r and temperature T_r . The reservoir is sufficiently large so that the nozzle inlet velocity is negligible.

Since the fluid velocity in the reservoir is zero and the flow through the nozzle is approximated as isentropic, the stagnation pressure and stagnation temperature of the fluid at any cross section through the nozzle are equal to the reservoir pressure and temperature, respectively.

Reservoir

$$P_r = P_0$$

 $T_r = T_0$
 $V_r = 0$
 P/P_0
 The effect of back pressure on the pressure distribution along a converging nozzle.

$$\dot{m} = \rho AV = \left(\frac{P}{RT}\right)A(Ma\sqrt{kRT}) = PAMa\sqrt{\frac{k}{RT}}$$

$$\dot{m} = \frac{A \mathrm{Ma} P_0 \sqrt{k/(RT_0)}}{[1 + (k - 1) \mathrm{Ma}^2/2]^{(k+1)/[2(k-1)]}}$$

$$\dot{m}_{\text{max}} = A * P_0 \sqrt{\frac{k}{RT_0}} \left(\frac{2}{k+1}\right)^{(k+1)/[2(k-1)]}$$

$$P_e = \begin{cases} P_b & \text{ for } P_b \ge P * \\ P * & \text{ for } P_b < P * \end{cases}$$

A relation for the variation of flow area A through the nozzle relative to throat area A* can be obtained

$$\frac{A}{A^*} = \frac{1}{Ma} \left[\left(\frac{2}{k+1} \right) \left(1 + \frac{k-1}{2} Ma^2 \right) \right]^{(k+1)/[2(k-1)]}$$



The effect of back pressure P_b on the mass flow rate \dot{m} and the exit pressure P_e of a converging nozzle. An increase in P_0 (or a decrease in T_0) will increase the mass flow rate through the converging nozzle;

a decrease in P_0 (or an increase in T_0) will decrease it.



The variation of the mass flow rate through a nozzle with inlet stagnation properties.

Another parameter sometimes used in the analysis of 1-D isentropic flow of ideal gases is Ma^{*}, which is the ratio of the local velocity to the speed of sound at the throat:

$$Ma^{*} = \frac{V}{c^{*}} \qquad Ma^{*} = \frac{V}{c} \frac{c}{c^{*}} = \frac{Mac}{c^{*}} = \frac{Ma\sqrt{kRT}}{\sqrt{kRT^{*}}} = Ma\sqrt{\frac{T}{T^{*}}}$$
$$Ma^{*} = Ma\sqrt{\frac{k+1}{2+(k-1)Ma^{2}}}$$

Ma	Ma*	$\frac{A}{A^*}$	$\frac{P}{P_0}$	$\frac{\rho}{\rho_0}$	$\frac{T}{T_0}$
				•	•
:	:	:	:	:	:
0.90	0.9146	1.0089	0.5913	÷	:
1.00	1.0000	1.0000	0.5283	÷	÷
1.10	1.0812	1.0079	0.4684	÷	:
:	:	:	:	:	
•	•			:	:

Various property ratios for isentropic flow through nozzles and diffusers for k 1.4 for convenience.

Example 17–5 Air at 1 MPa and 600C enters a converging nozzle, with a velocity of 150 m/s. Determine the mass flow rate through the nozzle for a nozzle throat area of 50 cm² when the back pressure is (*a*) 0.7 Mpa and (*b*) 0.4 MPa..

AIR

$$P_i = 1$$
 MPa
 $T_i = 600^{\circ}$ C
 $V_i = 150$ m/s
 P_b
nozzle
 $A_t = 50$ cm²

$$T_{0i} = T_i + \frac{V_i^2}{2c_p} = 873 \text{ K} + \frac{(150 \text{ m/s})^2}{2(1.005 \text{ kJ/kg} \cdot \text{K})} \left(\frac{1 \text{ kJ/kg}}{1000 \text{ m}^2/\text{s}^2}\right) = 884 \text{ K}$$
$$P_{0i} = P_i \left(\frac{T_{0i}}{T_i}\right)^{k/(k-1)} = (1 \text{ MPa}) \left(\frac{884 \text{ K}}{873 \text{ K}}\right)^{1.4/(1.4-1)} = 1.045 \text{ MPa}$$

$$T_0 = T_{0i} = 884 \text{ K}$$
 ve $P_0 = P_{0i} = 1.045 \text{ MPa}$

from Table 17-2

 $P^*/P_0 = 0.5283$

(a) The back pressure ratio for this case is

$$\frac{P_b}{P_0} = \frac{0.7 \text{ MPa}}{1.045 \text{ MPa}} = 0.670$$

$$T_t = 0.892T_0 = 0.892(884 \text{ K}) = 788.5 \text{ K}$$

$$\rho_t = \frac{P_t}{RT_t} = \frac{700 \text{ kPa}}{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(788.5 \text{ K})} = 3.093 \text{ kg/m}^3$$

$$V_t = \text{Ma}_t c_t = \text{Ma}_t \sqrt{kRT_t}$$

$$= (0.778) \sqrt{(1.4)(0.287 \text{ kJ/kg} \cdot \text{K})(788.5 \text{ K}) \left(\frac{1000 \text{ m}^2/\text{s}^2}{1 \text{ kJ/kg}}\right)}$$

$$= 437.9 \text{ m/s}$$

 $\dot{m} = \rho_t A_t V_t = (3.093 \text{ kg/m}^3)(50 \times 10^{-4} \text{ m}^2)(437.9 \text{ m/s}) = 6.77 \text{ kg/s}$

(b) The back pressure ratio for the case of 0.4 Mpa

$$\frac{P_b}{P_0} = \frac{0.4 \text{ MPa}}{1.045 \text{ MPa}} = 0.383$$

$$\frac{m}{RT_0} = \frac{0.4 \text{ MPa}}{1.045 \text{ MPa}} = 0.383$$

$$= (50 \times 10^{-4} \text{ m}^2)(1045 \text{ kPa}) \times \sqrt{\frac{1.4}{(0.287 \text{ kJ/kg} \cdot \text{K})(884 \text{ K})}} \left(\frac{2}{1.4 + 1}\right)^{2.4/0.8}$$

= 7.10 kg/s

This is the maximum mass flow rate through the nozzle for the specified inlet conditions and nozzle throat area.

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Example 17–6

Nitrogen enters a duct with varying flow area at T_1 =400 K, P_1 =100 kPa, and Ma₁=0.3. Assuming steady isentropic flow, determine T_2 , P_2 , and Ma_2 at a location where the flow area has been reduced by 20 $\overline{\%}$.



For isentropic flow through a duct, the area ratio A/A^* (the flow area over the area of the throat where Ma=1). At the initial Mach number of Ma=0.3, we read

$$\frac{A_1}{A^*} = 2.0351 \qquad \frac{T_1}{T_0} = 0.9823 \qquad \frac{P_1}{P_0} = 0.9395$$
$$\frac{A_2}{A^*} = \frac{A_2}{A_1} \frac{A_1}{A^*} = (0.8)(2.0351) = 1.6281$$
$$\frac{T_2}{T_0} = 0.9701 \qquad \frac{P_2}{P_0} = 0.8993 \qquad \text{Ma}_2 = \textbf{0.391}$$
$$\frac{T_2}{T_1} = \frac{T_2/T_0}{T_1/T_0} \rightarrow T_2 = T_1 \left(\frac{T_2/T_0}{T_1/T_0}\right) = (400 \text{ K}) \left(\frac{0.9701}{0.9823}\right) = \textbf{395 K}$$
$$\frac{P_2}{P_1} = \frac{P_2/P_0}{P_1/P_0} \rightarrow P_2 = P_1 \left(\frac{P_2/P_0}{P_1/P_0}\right) = (100 \text{ kPa}) \left(\frac{0.8993}{0.9395}\right) = \textbf{95.7 kPa}$$

Note that the temperature and pressure drop as the fluid accelerates in a converging nozzle.

 $\frac{P_2}{P_1}$

Converging-Diverging Nozzles

When we think of nozzles, we ordinarily think of flow passages whose cross-sectional area decreases in the flow direction.

However, the highest velocity to which a fluid can be accelerated in a converging nozzle is limited to the sonic velocity (Ma = 1), which occurs at the exit plane (throat) of the nozzle. Accelerating a fluid to supersonic velocities (Ma>1) can be accomplished only by attaching a diverging flow section to the subsonic nozzle at the throat.



Converging–diverging nozzles are commonly used in rocket engines to provide high thrust.

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1. When $P_0 > P_b > P_c$, the flow remains subsonic throughout the nozzle, and the mass flow is less than that for choked flow. The fluid velocity increases in the first (converging) section and reaches a maximum at the throat (but Ma < 1). However, most of the gain in velocity is lost in the second (diverging) section of the nozzle, which acts as a diffuser.

The pressure decreases in the converging section, reaches a minimum at the throat, and increases at the expense of velocity in the diverging section.

2. When $P_b = P_c$, the throat pressure becomes P^* and the fluid achieves sonic velocity at the throat. But the diverging section of the nozzle still acts as a diffuser, slowing the fluid to subsonic velocities. The mass flow rate that was increasing with decreasing P_b also reaches its maximum value.



3. When $P_C > P_b > P_E$, the fluid that achieved a sonic velocity at the throat continues accelerating to supersonic velocities in the diverging section as the pressure decreases.

This acceleration comes to a sudden stop, however, as a **normal shock** develops at a section between the throat and the exit plane, which causes a sudden drop in velocity to subsonic levels and a sudden increase in pressure.

The normal shock moves downstream away from the throat as P_b is decreased, and it approaches the nozzle exit plane as P_b approaches P_F .

When $P_b = P_E$, the normal shock forms at the exit plane of the nozzle. The flow is supersonic through the entire diverging section in this case, and it can be approximated as isentropic.

However, the fluid velocity drops to subsonic levels just before leaving the nozzle as it crosses the normal shock.



4. When $P_E > P_b > 0$, the flow in the diverging section is supersonic, and the fluid expands to *PF* at the nozzle exit with no normal shock forming within the nozzle. Thus, the flow through the nozzle can be approximated as isentropic.

When $P_b = P_F$, no shocks occur within or outside the nozzle. When $P_b < P_F$, irreversible mixing and expansion waves occur downstream of the exit plane of the nozzle.

When $P_b > P_F$, however, the pressure of the fluid increases from P_F to P_b irreversibly in the wake of the nozzle exit, creating what are called **oblique shocks.**

Example 17-7

Air enters a converging–diverging nozzle, at 1.0 Mpa and 800 K with a negligible velocity. The flow is steady, one-dimensional, and isentropic with k= 1.4. For an exit Mach number of Ma= 2 and a throat area of 20 cm², determine (*a*) the throat conditions, (*b*) the exit plane conditions, including the exit area, and (*c*) the mass flow rate through the nozzle.



$$\rho_0 = \frac{P_0}{RT_0} = \frac{1000 \text{ kPa}}{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(800 \text{ K})} = 4.355 \text{ kg/m}^3$$

(a) At the throat of the nozzle Ma 1,

$$\frac{P^*}{P_0} = 0.5283 \quad ^{\circ}\frac{T^*}{T_0} = 0.8333 \quad ^{\circ}\frac{\rho^*}{\rho_0} = 0.6339$$

 $P^* = 0.5283P_0 = (0.5283)(1.0 \text{ MPa}) = 0.5283 \text{ MPa}$

 $T^* = 0.8333T_0 = (0.8333)(800 \text{ K}) = 666.6 \text{ K}$

 $\rho^* = 0.6339 \rho_0 = (0.6339)(4.355 \text{ kg/m}^3) = 2.761 \text{ kg/m}^3$

$$V^* = c^* = \sqrt{kRT^*} = \sqrt{(1.4)(0.287 \text{ kJ/kg} \cdot \text{K})(666.6 \text{ K}) \left(\frac{1000 \text{ m}^2/\text{s}^2}{1 \text{ kJ/kg}}\right)} = 517.5 \text{ m/s}$$

(b) Since the flow is isentropic, the properties at the exit plane can also be calculated by using data

$$\frac{P_e}{P_0} = 0.1278 \quad \frac{T_e}{T_0} = 0.5556 \quad \frac{\rho_e}{\rho_0} = 0.2300 \quad \text{Ma}_t^* = 1.6330 \quad \frac{A_e}{A^*} = 1.6875$$

$$P_e = 0.1278P_0 = (0.1278)(10 \text{ MPa}) = 0.1278 \text{ MPa}$$

$$T_e = 0.5556T_0 = (0.5556)(800 \text{ K}) = 444.5 \text{ K}$$

$$\rho_e = 0.2300\rho_0 = (0.2300)(4.355 \text{ kg/m}^3) = 1.002 \text{ kg/m}^3$$

$$A_e = 1.6875A^* = (1.6875)(20 \text{ cm}^2) = 33.75 \text{ cm}^2$$

$$V_e = \text{Ma}_e^* c^* = (1.6330)(517.5 \text{ m/s}) = 845.1 \text{ m/s}$$

$$V_e = \text{Ma}_e \sqrt{kRT_e} = 2\sqrt{(1.4)(0.287 \text{ kJ/kg} \cdot \text{K})(444.5 \text{ K})\left(\frac{1000 \text{ m}^2/\text{s}^2}{1 \text{ kJ/kg}}\right)}$$

$$= 845.2 \text{ m/s}$$

(c) Since the flow is steady, the mass flow rate of the fluid is the same at all sections of the nozzle.

$$\dot{m} = \rho^* A^* V^* = (2.761 \text{ kg/m}^3)(20 \times 10^{-4} \text{ m}^2)(517.5 \text{ m/s}) = 2.86 \text{ kg/s}$$

Note that this is the highest possible mass flow rate that can flow through this nozzle for the specified inlet conditions.

SHOCK WAVES AND EXPANSION WAVES

The flow process through the shock wave is highly irreversible and *cannot* be approximated as being isentropic.



We can combine the conservation of mass and energy relations into a single equation and plot it on an *h*-*s* diagram, using property relations. The resultant curve is called the Fanno line, and it is the locus of states that have the same value of stagnation enthalpy and mass flux (mass flow per unit flow area).

Likewise, combining the conservation of mass and momentum equations into a single equation and plotting it on the *h*-*s* diagram yield a curve called the **Rayleigh line**

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$$\frac{P_2}{P_1} = \frac{Ma_1\sqrt{1 + Ma_1^2(k-1)/2}}{Ma_2\sqrt{1 + Ma_2^2(k-1)/2}}$$
$$P_1 - P_2 = \frac{\dot{m}}{A} (V_2 - V_1) = \rho_2 V_2^2 - \rho_1 V_1^2$$
$$\rho V^2 = \left(\frac{P}{RT}\right) (Mac)^2 = \left(\frac{P}{RT}\right) (Ma\sqrt{kRT})^2 = PkMa^2$$

$$P_1(1 + kMa_1^2) = P_2(1 + kMa_2^2)$$

$$\frac{P_2}{P_1} = \frac{1 + k M a_1^2}{1 + k M a_2^2} \qquad Ma_2^2 = \frac{M a_1^2 + 2/(k-1)}{2M a_1^2 k/(k-1) - 1}$$

$$s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

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Schlieren image of the blast wave (expanding spherical normal shock) produced by the explosion of a firecracker detonated inside a metal can that sat on a stool. The shock expanded radially outward in all directions at a supersonic speed that decreased with radius from the center of the explosion. The microphone at the lower right sensed the sudden change in pressure of the passing shock wave and triggered the microsecond flashlamp that exposed the photograph.



Example 17-8

Show that the point of maximum entropy on the Fanno line (point *b* of Figure) for the adiabatic steady flow of a fluid in a duct corresponds to the sonic velocity, Ma=1.



Example 17-9

If the air flowing through the converging–diverging nozzle of Example 17–7 experiences a normal shock wave at the nozzle exit plane, determine the following after the shock: (*a*) the stagnation pressure, static pressure, static temperature, and static density; (*b*) the entropy change across the shock; (*c*) the exit velocity; and (*d*) the mass flow rate through the nozzle. Assume steady, 1-D, and isentropic flow with k=1.4 from the nozzle inlet to the shock location.



(*a*) The fluid properties at the exit of the nozzle just before the shock (denoted by subscript 1) are those evaluated

$$P_{01} = 1.0 \text{ MPa} \quad P_1 = 0.1278 \text{ MPa} \quad T_1 = 444.5 \text{ K} \quad \rho_1 = 1.002 \text{ kg/m}^3$$

$$Ma_2 = 0.5774 \quad \frac{P_{02}}{P_{01}} = 0.7209 \quad \frac{P_2}{P_1} = 4.5000 \quad \frac{T_2}{T_1} = 1.6875 \quad \frac{\rho_2}{\rho_1} = 2.6667$$

$$P_{02} = 0.7209P_{01} = (0.7209)(1.0 \text{ MPa}) = 0.721 \text{ MPa}$$

$$P_2 = 4.5000P_1 = (4.5000)(0.1278 \text{ MPa}) = 0.575 \text{ MPa}$$

$$T_2 = 1.6875T_1 = (1.6875)(444.5 \text{ K}) = 750 \text{ K}$$

$$\rho_2 = 2.6667\rho_1 = (2.6667)(1.002 \text{ kg/m}^3) = 2.67 \text{ kg/m}^3$$

(b) The entropy change across the shock is

$$\overline{F_2 - s_1} = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

= (1.005 kJ/kg·K)ln(1.6875) - (0.287 kJ/kg·K)ln(4.5000

 $= 0.0942 \text{ kJ/kg} \cdot \text{K}$

The entropy of the air increases as it experiences a normal shock, which is highly irreversible.

(c) The air velocity after the shock can be determined from V_2 =Ma₂ c_2 , where c_2 is the speed of sound at the exit conditions after the shock:

$$V_{2} = Ma_{2}c_{2} = Ma_{2}\sqrt{kRT_{2}} = (0.5774)\sqrt{(1.4)(0.287 \text{ kJ/kg} \cdot \text{K})(750 \text{ K})\left(\frac{1000 \text{ m}^{2}/\text{s}^{2}}{1 \text{ kJ/kg}}\right)}$$
$$= 317 \text{ m/s}$$

(*d*) The mass flow rate through a converging–diverging nozzle with sonic conditions at the throat is not affected by the presence of shock waves in the nozzle.

 $\dot{m} = 2.86 \text{ kg/s}$

This result can easily be verified by using property values at the nozzle exit after the shock at all Mach numbers significantly greater than unity.
Oblique Shocks

Not all shock waves are normal shocks (perpendicular to the flow direction). For example, when the space shuttle travels at supersonic speeds through the atmosphere, it produces a complicated shock pattern consisting of inclined shock waves called **oblique shocks**



Schlieren image of a small model of the space shuttle *Orbiter* being tested at Mach 3 in the supersonic wind tunnel of the Penn State Gas Dynamics Lab. Several *oblique shocks* are seen in the air surrounding the spacecraft.

First, we consider straight oblique shocks, like that produced when a uniform supersonic flow (Ma₁>1) impinges on a slender, 2-D wedge of half-angle δ . Since information about the wedge cannot travel upstream in a supersonic flow, the fluid "knows" nothing about the wedge until it hits the nose. At that point, since the fluid cannot flow *through* the wedge, it turns suddenly through an angle called the **turning angle** or **deflection angle** θ . The result is a straight oblique shock wave, aligned at **shock angle** or **wave angle** β , measured relative to the oncoming flow.



wedge of half-angle δ . The flow is turned by *deflection angle* θ downstream of the shock and the Mach number decreases When we apply conservation of momentum in the direction *normal* to the oblique shock, the only forces are pressure forces, and we get

$$P_1A - P_2A = \rho V_{2,n}AV_{2,n} - \rho V_{1,n}AV_{1,n} \rightarrow P_1 - P_2 = \rho_2 V_{2,n}^2 - \rho_1 V_{1,n}^2$$

since there is no work done by the control volume and no heat transfer into or out of the control volume, stagnation enthalpy does *not* change across an oblique shock, and conservation of energy yields

$$h_{01} = h_{02} = h_0 \quad \rightarrow \quad h_1 + \frac{1}{2}V_{1,n}^2 + \frac{1}{2}V_{1,t}^2 = h_2 + \frac{1}{2}V_{2,n}^2 + \frac{1}{2}V_{2,t}^2$$

$$h_1 + \frac{1}{2}V_{1,n}^2 = h_2 + \frac{1}{2}V_{2,n}^2$$

$$Ma_{1,n} = Ma_1 \sin\beta \quad \text{ve} \quad Ma_{2,n} = Ma_2 \sin(\beta - \theta)$$

All the equations, shock tables, etc., for normal shocks apply to oblique shocks as well, provided that we use only the **normal** components of the Mach number.

 $V_{2,n}$

 $V_{1,t}$

Ma

$$h_{01} = h_{02} \rightarrow T_{01} = T_{02}$$

$$Ma_{2,n} = \sqrt{\frac{(k-1)Ma_{1,n}^2 + 2}{2kMa_{1,n}^2 - k + 1}}$$

$$\frac{P_2}{P_1} = \frac{2k Ma_{1,n}^2 - k + 1}{k + 1}$$

$$\frac{\rho_2}{\rho_1} = \frac{V_{1,n}}{V_{2,n}} = \frac{(k+1)Ma_{1,n}^2}{2 + (k-1)Ma_{1,n}^2}$$

$$\frac{T_2}{T_1} = [2 + (k-1)Ma_{1,n}^2] \frac{2k Ma_{1,n}^2 - k + 1}{(k+1)^2 Ma_{1,n}^2}$$

$$\frac{P_{02}}{P_{01}} = \left[\frac{(k+1)Ma_{1,n}^2}{2 + (k-1)Ma_{1,n}^2}\right]^{k/(k-1)} \left[\frac{(k+1)}{2k Ma_{1,n}^2 - k + 1}\right]^{1/(k-1)}$$

Relationships across an oblique shock for an ideal gas in terms of the normal component of upstream Mach number $Ma_{1,n}$.

 $\frac{V_{2,n}}{V_{1,n}} = \frac{\tan(\beta - \theta)}{\tan\beta} = \frac{2 + (k - 1)\operatorname{Ma}_{1,n}^2}{(k + 1)\operatorname{Ma}_{1,n}^2} = \frac{2 + (k - 1)\operatorname{Ma}_1^2 \sin^2\beta}{(k + 1)\operatorname{Ma}_1^2 \sin^2\beta}$ $\cos 2\beta = \cos^2\beta - \sin^2\beta \quad \text{and} \quad \tan(\beta - \theta) = \frac{\tan\beta - \tan\theta}{1 + \tan\beta\tan\theta}$ $\frac{1}{1 + \tan\beta\tan\theta}$ $\frac{1}{1 + \tan\beta\tan\theta}$

A detached oblique shock occurs upstream of a two-dimensional wedge of half-angle δ when δ is greater than the maximum possible deflection angle θ . A shock of this kind is called a **bow wave** because of its resemblance to the water wave that forms at the bow of a ship.





The dependence of straight oblique shock deflection angle θ on shock angle β for several values of upstream Mach number Ma₁. Calculations are for an ideal gas with *k*=1.4. The dashed black line connects points of maximum deflection angle ($\theta = \theta_{max}$). Weak oblique shocks are to the left of this line, while strong oblique shocks are to the right of this line. The dashed gray line connects points where the downstream Mach number is sonic (Ma₂=1). Supersonic downstream flow (Ma₂> 1) is to the left of this line, while subsonic downstream flow (Ma₂<1) is to the right of this line.



Still frames from schlieren videography illustrating the detachment of an oblique shock from a cone with increasing cone half-angle δ in air at Mach=3. At (*a*) δ =20 and (*b*) δ =40, the oblique shock remains attached, but by (*c*) δ =60, the oblique shock has detached, forming a bow wave.

The shock angle for Mach waves is a unique function of the Mach number and is given the symbol μ , not to be confused with the coefficient of viscosity. Angle μ is called the Mach angle;

Mach angle: $\mu = \sin^{-1}(1/Ma_1)$



Shadowgram of a one-half-in diameter sphere in free flight through air at Ma=1.53. The flow is subsonic behind the part of the bow wave that is ahead of the sphere and over its surface back to about 45°. At about 90° the laminar boundary layer separates through an oblique shock wave and quickly becomes turbulent. The fluctuating wake generates a system of weak disturbances that merge into the second "recompression" shock wave.

Prandtl-Meyer Expansion Waves

We now address situations where supersonic flow is turned in the *opposite* direction, such as in the upper portion of a two-dimensional wedge at an angle of attack greater than its half-angle δ . We refer to this type of flow as an **expanding flow**, whereas a flow that produces an oblique shock may be called a **compressing flow**.

However, unlike a compressing flow, an expanding flow does *not* result in a shock wave. Rather, a continuous expanding region called an **expansion fan** appears, composed of an infinite number of Mach waves called **Prandtl–Meyer expansion waves**.



An expansion fan in the upper portion of the flow formed by a 2-D wedge at the angle of attack in a supersonic flow. The flow is turned by angle θ , and the Mach number increases across the expansion fan. Mach angles upstream and downstream of the expansion fan are indicated. Only three expansion waves are shown for simplicity, but in fact, there are an infinite number of them.

Turning angle across an expansion fan: $\theta = \nu(Ma_2) - \nu(Ma_1)$

where ν (Ma) is an angle called the **Prandtl–Meyer function** (not to be confused with the kinematic viscosity),

$$\nu(Ma) = \sqrt{\frac{k+1}{k-1}} \tan^{-1} \left[\sqrt{\frac{k-1}{k+1}} (Ma^2 - 1) \right] - \tan^{-1} \left(\sqrt{Ma^2 - 1} \right)$$

Prandtl–Meyer expansion fans also occur in axisymmetric supersonic flows, as in the corners and trailing edges of a cone-cylinder.



A cone-cylinder of 12.5° half-angle in a Mach number 1.84 flow. The boundary layer becomes turbulent shortly downstream of the nose, generating Mach waves that are visible in this shadowgraph. Expansion waves are seen at the corners and at the trailing edge of the cone.



The complex interactions between shock waves and expansion waves in an "overexpanded" supersonic jet. The flow is visualized by a schlierenlike differential interferogram.

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Example 17-10

Estimate the Mach number of the free-stream flow upstream of the space shuttle. Compare with the known value of Mach number provided in the figure caption.



Using a protractor, we measure the angle of the Mach lines in the free-stream flow: μ =19°. The Mach number is obtained from;

$$\mu = \sin^{-1} \left(\frac{1}{Ma_1} \right) \rightarrow Ma_1 = \frac{1}{\sin 19^\circ} \rightarrow Ma_1 = 3.07$$

Our estimated Mach number agrees with the experimental value of 3.0 ± 0.1 .

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Örnek 17-11

Supersonic air at Ma₁= 2.0 and 75.0 kPa impinges on a 2-D wedge of half-angle δ =10°. Calculate the two possible oblique shock angles, β_{weak} and β_{strong} , that could be formed by this wedge. For each case, calculate the pressure and Mach number downstream of the oblique shock, compare, and discuss.

we approximate the oblique shock deflection angle as equal to the wedge half-angle, i.e., $\theta \cong \delta = 10^{\circ}$. With $Ma_1 = 2.0$ and $\theta = 10^{\circ}$, we solve Eq. 17–46 for the two possible values of oblique shock angle $\beta_{weak} = 39.3^{\circ}$ and $\beta_{strong} = 83.7^{\circ}$. From these values, we use the first part of Eq. 17–44 to calculate the upstream normal Mach number $Ma_{1,n}$



The θ - β -Ma *relationship*:

$$\tan \theta = \frac{2 \cot \beta (\operatorname{Ma}_{1}^{2} \sin^{2} \beta - 1)}{\operatorname{Ma}_{1}^{2}(k + \cos 2\beta) + 2}$$

 $Ma_{1,n} = Ma_1 \sin \beta$ and $Ma_{2,n} = Ma_2 \sin(\beta - \theta)$ (17-44)

(17 - 46)

Weak shock:	$Ma_{1,n} = Ma_1 \sin \beta$ —	\rightarrow Ma _{1,n} =	$2.0 \sin 39.3^\circ = 1$.267
Strong shock:	$Ma_{1,n} = Ma_1 \sin \beta$ –	$\rightarrow Ma_{1,n} =$	$2.0 \sin 83.7^\circ =$	1.988

Weak shock:

$$\frac{P_2}{P_1} = \frac{2k\mathrm{Ma}_{1,n}^2 - k + 1}{k+1} \to P_2 = (75.0 \,\mathrm{kPa}) \frac{2(1.4)(1.267)^2 - 1.4 + 1}{1.4 + 1} = \mathbf{128} \,\mathrm{kPa}$$

Strong shock:

$$\frac{P_2}{P_1} = \frac{2k\mathrm{Ma}_{1,n}^2 - k + 1}{k+1} \to P_2 = (75.0 \,\mathrm{kPa}) \,\frac{2(1.4)(1.988)^2 - 1.4 + 1}{1.4 + 1} = 333 \,\mathrm{kPa}$$

Weak shock:

$$Ma_{2} = \frac{Ma_{2,n}}{\sin(\beta - \theta)} = \frac{0.8032}{\sin(39.3^{\circ} - 10^{\circ})} = 1.64$$
Strong shock:

$$Ma_{2} = \frac{Ma_{2,n}}{\sin(\beta - \theta)} = \frac{0.5794}{\sin(83.7^{\circ} - 10^{\circ})} = 0.604$$

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DUCT FLOW WITH HEAT TRANSFER AND NEGLIGIBLE FRICTION (RAYLEIGH FLOW)

Many compressible flow problems encountered in practice involve chemical reactions such as combustion, nuclear reactions, evaporation, and condensation as well as heat gain or heat loss through the duct wall.

Such problems are difficult to analyze exactly since they may involve significant changes in chemical composition during flow, and the conversion of latent, chemical, and nuclear energies to thermal energy



Consider steady one-dimensional flow of an ideal gas with constant specific heats through a constant-area duct with heat transfer, but with negligible friction. Such flows are referred to as Rayleigh flows after Lord Rayleigh (1842–1919).

Continuity equation

$$\rho_1 V_1 = \rho_2 V_2$$

x-Momentum equation

$$\sum \vec{F} = \sum_{g} \beta \dot{m} \vec{V} - \sum_{g} \beta \dot{m} \vec{V}$$

$$P_{1}A_{1} - P_{2}A_{2} = \dot{m}V_{2} - \dot{m}V_{1} \rightarrow P_{1} - P_{2} = (\rho_{2}V_{2})V_{2} - (\rho_{1}V_{1})V_{1}$$

$$\boxed{P_{1} + \rho_{1}V_{1}^{2} = P_{2} + \rho_{2}V_{2}^{2}}$$
gy equation
$$\dot{Q} + \dot{m}\left(h_{1} + \frac{V_{1}^{2}}{2}\right) = \dot{m}\left(h_{2} + \frac{V_{2}^{2}}{2}\right) \rightarrow q + h_{1} + \frac{V_{1}^{2}}{2} = h_{2} + \frac{V_{2}^{2}}{2}$$

$$\boxed{q = c_{p}(T_{2} - T_{1}) + \frac{V_{2}^{2} - V_{1}^{2}}{2}} \qquad q = h_{02} - h_{01} = c_{p}(T_{02} - T_{01})$$

Ż

 P_1, T_1, ρ_1

 V_1

 P_2, T_2, ρ_2

 V_2

Control volume

Control volume for flow in a

constant area duct with heat

transfer and negligible friction

Ener



The effects of heating and co	oling on the properties of Rayle	eigh flow		
	Heating		Cooling	
Property	Subsonic	Supersonic	Subsonic	Supersonic
Velocity, V	Increase	Decrease	Decrease	Increase
Mach number, Ma	Increase	Decrease	Decrease	Increase
Stagnation temperature, T_0	Increase	Increase	Decrease	Decrease
Temperature, T	Increase for Ma $< 1/k^{1/2}$ Decrease for Ma $> 1/k^{1/2}$	Increase	Decrease for Ma $< 1/k^{1/2}$ Increase for Ma $> 1/k^{1/2}$	Decrease
Density, ρ	Decrease	Increase	Increase	Decrease
Stagnation pressure, P_0	Decrease	Decrease	Increase	Increase
Pressure, P	Decrease	Increase	Increase	Decrease
Entropy, s	Increase	Increase	Decrease	Decrease

The effects of heating and cooling on the properties of Rayleigh flow

Property Relations for Rayleigh Flow

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$$\frac{T_0}{T_0^*} = \frac{(k+1)\mathrm{Ma}^2[2+(k-1)\mathrm{Ma}^2]}{(1+k\mathrm{Ma}^2)^2}$$

$$\frac{P_0}{P_0^*} = \frac{P_0}{P} \frac{P}{P^*} \frac{P}{P_0^*} = \left(1 + \frac{k-1}{2} \operatorname{Ma}^2\right)^{k/(k-1)} \left(\frac{1+k}{1+k\operatorname{Ma}^2}\right) \left(1 + \frac{k-1}{2}\right)^{-k/(k-1)}$$

$$\frac{P_0}{P_0^*} = \frac{k+1}{1+k\mathrm{Ma}^2} \left[\frac{2+(k-1)\mathrm{Ma}^2}{k+1}\right]^{k/(k-1)}$$

$$\begin{aligned} \frac{T_0}{T_0^*} &= \frac{(k+1)Ma^2[2+(k-1)Ma^2]}{(1+kMa^2)^2} \\ \frac{P_0}{P_0^*} &= \frac{k+1}{1+kMa^2} \left(\frac{2+(k-1)Ma^2}{k+1}\right)^{k/(k-1)} \\ \frac{T}{T^*} &= \left(\frac{Ma(1+k)}{1+kMa^2}\right)^2 \\ \frac{P}{P^*} &= \frac{1+k}{1+kMa^2} \\ \frac{P}{V^*} &= \frac{\rho^*}{\rho} = \frac{(1+k)Ma^2}{1+kMa^2} \end{aligned}$$

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Choked Rayleigh Flow

What happens if we continue to heat the fluid? Does the fluid continue to accelerate to supersonic velocities? An examination of the Rayleigh line indicates that the fluid at the critical state of Ma=1 cannot be accelerated to supersonic velocities by heating.

Therefore, the flow is choked. This is analogous to not being able to accelerate a fluid to supersonic velocities in a converging nozzle by simply extending the converging flow section. If we keep heating the fluid, we will simply move the critical state further downstream and reduce the flow rate since fluid density at the critical state will now be lower.



$$q_{\text{mak}} = h_0^* - h_{01} = c_p (T_0^* - T_{01})$$

For a given inlet state, the maximum possible heat transfer occurs when sonic conditions are reached at the exit state.

Further heat transfer causes choking and thus the inlet state to change (e.g., inlet velocity will decrease), and the flow no longer follows the same Rayleigh line. Cooling the subsonic Rayleigh flow reduces the velocity, and the Mach number approaches zero as the temperature approaches absolute zero.

STEAM NOZZLES

Water vapor at moderate or high pressures deviates considerably from ideal-gas behavior, and thus most of the relations developed in this chapter are not applicable to the flow of steam through the nozzles or blade passages encountered in steam turbines.

The steam properties such as enthalpy are functions of pressure as well as temperature and that no simple property relations exist, an accurate analysis of steam flow through the nozzles is no easy matter.

A further complication in the expansion of steam through nozzles occurs as the steam expands into the saturation region.

As the steam expands in the nozzle, its pressure and temperature drop, and ordinarily one would expect the steam to start condensing when it strikes the saturation line. However, this is not always the case.

Owing to the high velocities, the residence time of the steam in the nozzle is small, and there may not be sufficient time for the necessary heat transfer and the formation of liquid droplets. Consequently, the condensation of the steam may be delayed for a little while. This phenomenon is known as **supersaturation**, and the steam that exists in the wet region without containing any liquid is called **supersaturated steam**.

During the expansion process, the steam reaches a temperature lower than that normally required for the condensation process to begin. Once the temperature drops a sufficient amount below the saturation temperature corresponding to the local pressure, groups of steam moisture droplets of sufficient size are formed, and condensation occurs rapidly. The locus of points where condensation takes place regardless of the initial temperature and pressure at the nozzle entrance is called the Wilson line.



The critical-pressure ratio

$$\frac{P^*}{P_0} = \left(\frac{2}{k+1}\right)^{k/(k-1)} = 0.546$$

Chapter 17: COMPRESSIBLE FLOW

Example 17-16

Steam enters a converging–diverging nozzle at 2 MPa and 400°C with a negligible velocity and a mass flow rate of 2.5 kg/s, and it exits at a pressure of 300 kPa. The flow is isentropic between the nozzle entrance and throat, and the overall nozzle efficiency is 93 percent. Determine (*a*) the throat and exit areas and (*b*) the Mach number at the throat and the nozzle exit.



$$\frac{P_2}{P_{01}} = \frac{300 \text{ kPa}}{2000 \text{ kPa}} = 0.15$$

$$P_t = 0.546P_{01} = (0.546)(2 \text{ MPa}) = 1.09 \text{ MPa}$$

At the inlet,

$$\begin{array}{l} P_1 = P_{01} = 2 \text{ MPa} \\ T_1 = T_{01} = 400^{\circ}\text{C} \end{array} \right\} \qquad \begin{array}{l} h_1 = h_{01} = 3248.4 \text{ kJ/kg} \\ s_1 = s_t = s_{2s} = 7.1292 \text{ kJ/kg} \cdot \text{K} \end{array}$$

Also, at the throat,

$$\begin{array}{l} P_t = 1.09 \text{ MPa} \\ s_t = 7.1292 \text{ kJ/kg} \cdot \text{K} \end{array} \qquad \begin{array}{l} h_t = 3076.8 \text{ kJ/kg} \\ \nu_t = 0.24196 \text{ m}^3/\text{kg} \end{array}$$

Then the throat velocity is determined

$$V_t = \sqrt{2(h_{01} - h_t)} = \sqrt{\left[2(3248.4 - 3076.8) \text{ kJ/kg}\right] \left(\frac{1000 \text{ m}^2/\text{s}^2}{1 \text{ kJ/kg}}\right)} = 585.8 \text{ m/s}$$

The flow area at the throat is determined from the mass flow rate relation:

$$A_t = \frac{\dot{m}v_t}{V_t} = \frac{(2.5 \text{ kg/s})(0.2420 \text{ m}^3/\text{kg})}{585.8 \text{ m/s}} = 10.33 \times 10^{-4} \text{ m}^2 = 10.33 \text{ cm}^2$$

$$P_{2s} = P_2 = 300 \text{ kPa} \\ s_{2s} = s_1 = 7.1292 \text{ kJ/kg} \cdot \text{K}$$
 $h_{2s} = 2783.6 \text{ kJ/kg}$

The enthalpy of the steam at the actual exit state is

$$\eta_N = \frac{h_{01} - h_2}{h_{01} - h_{2s}}$$

$$0.93 = \frac{3248.4 - h_2}{3248.4 - 2783.6} \longrightarrow h_2 = 2816.1 \text{ kJ/kg}$$

$$P_{2} = 300 \text{ kPa} \\ h_{2} = 2816.1 \text{ kJ/kg}$$
 $v_{2} = 0.67723 \text{ m}^{3}/\text{kg} \\ s_{2} = 7.2019 \text{ kJ/kg} \cdot \text{K}$

Then the exit velocity and the exit area become

$$V_{2} = \sqrt{2(h_{01} - h_{2})} = \sqrt{\left[2(3248.4 - 2816.1) \text{ kJ/kg}\right] \left(\frac{1000 \text{ m}^{2}/\text{s}^{2}}{1 \text{ kJ/kg}}\right)} = 929.8 \text{ m/s}$$
$$A_{2} = \frac{\dot{m}v_{2}}{V_{2}} = \frac{(2.5 \text{ kg/s})(0.67723 \text{ m}^{3}/\text{kg})}{929.8 \text{ m/s}} = 18.21 \times 10^{-4} \text{ m}^{2} = 18.21 \text{ cm}^{2}$$

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(b) The velocity of sound and the Mach numbers at the throat and the exit of the nozzle are determined by replacing differential quantities with differences,

$$c = \left(\frac{\partial P}{\partial \rho}\right)_{s}^{1/2} \approx \left[\frac{\Delta P}{\Delta(1/\nu)}\right]_{s}^{1/2}$$

$$c = \sqrt{\frac{(1115 - 1065) \text{ kPa}}{(1/0.23776 - 1/0.24633) \text{ kg/m}^3} \left(\frac{1000 \text{ m}^2/\text{s}^2}{1 \text{ kPa} \cdot \text{m}^3/\text{kg}}\right)} = 584.6 \text{ m/s}$$

$$Ma = \frac{V}{c} = \frac{585.8 \text{ m/s}}{584.6 \text{ m/s}} = 1.002$$

The velocity of sound and the Mach number at the nozzle exit are determined by evaluating the specific volume at s_2 =7.2019 kJ/kg · K and at pressures of 325 and 275 kPa ($P_2 \mp 25$ kPa):

$$c = \sqrt{\frac{(325 - 275) \text{ kPa}}{(1/0.63596 - 1/0.72245) \text{ kg/m}^3} \left(\frac{1000 \text{ m}^2/\text{s}^2}{1 \text{ kPa} \cdot \text{m}^3/\text{kg}}\right)} = 515.4 \text{ m/s}$$

$$Ma = \frac{V}{c} = \frac{929.8 \text{ m/s}}{515.4 \text{ m/s}} = 1.804$$

Thus the flow of steam at the nozzle exit is supersonic.