Second law of thermodynamics and entropy

1-1 Introduction

1. It has been observed that energy can flow from a system in the form of heat or work.

2. first law of thermodynamics deals with quantity of energy.

second law of thermodynamics deals with quantity and quality of energy.
 first law not limit the direction of energy, but the second law limit this direction from high temperature to lower temperature but not in opposite direction without assistance





1-2 The Second Law of Thermodynamics: 1-2-1 Kelvin–Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.

The impossibility of having a 100% efficient heat engine is not due to friction or other dissipative effects. It is a limitation that applies to both the idealized and the actual heat engines

1-2-2 Clausius Statement

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lowertemperature body to a higher-temperature body.

In other word, heat of, itself, cannot flow from a colder to a hotter body.



FIGURE 6–18 A heat engine that violates the Kelvin– Planck statement of the second



FIGURE 6–28 A refrigerator that violates the Clausius statement of the second

1-2 PERPETUAL-MOTION MACHINES

1. The first law of thermodynamics states the principle of the conservation of energy. Energy is neither created nor destroyed, but only gets transformed from one form to another. *There can be no machine which would continuously supply mechanical work without some form of energy disappearing simultaneously* (Fig.6.27). Such a untrue machine is called a *perpetual motion machine of the first kind*, or in brief, **PMM 1**. A PMM1 is thus impossible.



FIGURE 6–27 A perpetual-motion machine that violates the first law of thermodynamics (PMM1)

2. The converse of the above statement is also true, i.e, there can be no machine which would continuously consume work without some other form energy appearing simultaneously (Fig6.28).



FIGURE 6–28 A perpetual-motion machine that violates the second law of thermodynamics (PMM2).

1-4Definitions.

Heat reservoir: a body which has large enough temperature and does not change when heat is added or removed is a heat reservoir. Examples oceans, lakes, and rivers as well as atmospheric air.

A reservoir that supplies energy in the form of heat is called a **source**, and one that absorbs energy in the form of heat is called a **sink** (Fig. 6–7).

Heat engine: a heat engine is a device that operates in a cycle and produces net positive work while heat transfer occurs across the boundaries of the device.

All heat engines can be characterized by the following (Fig.1.4)

- 1. They receive heat from a high-temperature source (solar energy, oil furnace, nuclear reactor, etc.).
- 2. They convert part of this heat to work (usually in the form of a rotating shaft).
- 3. They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.).
- **4.** They operate on a cycle.



1.5 Cycle Efficiency of a heat engine or thermal efficiency

The cycle efficiency of a heat engine is defined as the ratio of net work done to heat supplied. This is also known as thermal efficiency.

thermal efficiency =
$$\frac{\text{net work}}{\text{heat recevied}}$$
 $\eta_{th} = \frac{W_{net work}}{Q_{in}}$ $\eta_{th} = 1 - \frac{Q_{out}}{Q_{in}}$

Where

 $W_{net,out} = Q_{in} - Q_{out}$

 $Q_{\rm in}$ = amount of heat supplied from source (a high-temperature)

 Q_{out} = amount of heat rejected from source to (a low temperature sink)

 W_{out} = amount of work delivered by steam as it expands in turbine

 $W_{\rm in}$ = amount of work required to compress water to boiler pressure

 Q_H = magnitude of heat transfer between the cyclic device and the high temperature medium at temperature *TH*

 Q_L = magnitude of heat transfer between the cyclic device and the low temperature medium at temperature TL



6–6 **REVERSIBLE AND IRREVERSIBLE PROCESSES**

A reversible process is defined as a *process that can be reversed without leaving any trace on the surroundings* (Fig. 6–29).

Processes that are not reversible are called **irreversible processes**.



- All the processes occurring in nature are irreversible.
- Why are we interested in reversible processes?
- (1) they are easy to analyze and (2) they serve as idealized models (theoretical limits) to which actual processes can be compared.
- Some processes are more irreversible than others.
- We try to approximate reversible processes. Why?
- Reversible processes deliver the most and consume the least work.

- The factors that cause a process to be irreversible are called irreversibilities.
- They include friction, unrestrained expansion, mixing of two fluids, heat transfer across a finite temperature difference, electric resistance, inelastic deformation of solids, and chemical reactions.



• The presence of any of these effects renders a process irreversible

THE CARNOT CYCLE

The theoretical heat engine that operates on the Carnot cycle is called the Carnot heat engine.

1. The Carnot cycle is a hypothetical cycle developed by Carnot for either engine or a reversed heat engine (Refrigerators, Heat pumps)

2. The Carnot cycle is a reversible cycle because it consists of two isothermal and two adiabatic processes

3. All the processes involved in the cycle are reversible, thereby providing the best possible device that one could construct

4. Results from the cycle analysis can be used to determine the maximum efficiency of performance possible for either a heat engine or reversed heat engine. The following assumptions will be used for the derivation of the efficiency of a Carnot cycle applied to a non-flow cycle, i.e one carried out in a closed system, example cylinder-frictionless piston .



Notes:

(a) A hot source , is a heat reservoir of infinite capacity at the maximum constant temperature T1 or TH

(b) A cold sink, is a heat reservoir of infinite capacity at the minimum constant temperature T2 or TL $\,$



FIGURE 6–36 Execution of the Carnot cycle in a closed system.

Reversible Isothermal Expansion (process 1-2, *TH* 5 constant).

$Q_{12} = mRT_1 ln \frac{V_1}{V_2}$	(1)
Reversible Adiabatic Expansion (process 2-3, temperature drops from <i>TH</i> to <i>TL</i>).	
$Q_{23} = 0$	(2)
Reversible Isothermal Compression (process 3-4, TL 5 constant).	
$Q_{34} = mRT_2 ln \frac{v_3}{v_4}$	(3)
Reversible Adiabatic Compression (process 4-1, temperature rises from <i>TL</i> to <i>TH</i>).	
$Q_{41} = 0$	(4)

From the adiabatic expansion 2-3 and compression 4-1

$$\frac{v_2}{v_1} = \frac{v_3}{v_4}$$
 sub Eq (3)
$$Q_{34} = mRT_2 ln \frac{v_2}{v_4}$$

Applied the first law to the cycle, we note that

$$\oint \boldsymbol{Q} = \oint \boldsymbol{W} \qquad \text{or} \qquad \qquad \boldsymbol{Q}_{12} - \boldsymbol{Q}_{34} = \boldsymbol{W}_{net}$$

The efficiency of Carnot cycle is

$$\eta = \frac{\text{net work}}{\text{heat recevied}} \qquad \eta = \frac{W_{\text{net}}}{Q_{12}} \qquad \eta = \frac{Q_{12} - Q_{34}}{Q_{12}}$$
$$\eta = \frac{mRT_1 \ln \frac{V_1}{V_2} - mRT_2 \ln \frac{V_2}{V_1}}{mRT_1 \ln \frac{V_1}{V_2}} \qquad \eta_{carnot} = \frac{T_1 - T_2}{T_1} \qquad \eta_{carnot} = 1$$

 $-\frac{T_2}{T_1}$

The Reversed Carnot Cycle

The Carnot heat-engine cycle is a totally reversible cycle. Therefore, all the processes that comprise it can be *reversed*, in which case it becomes the **Carnot refrigeration cycle**.

6-8 THE CARNOT PRINCIPLES

1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.

2. The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.



Example(2): A heat engine operating between two reservoirs receives energy Q1=2100 KJ by heat transfer from a hot reservoir (source) at T1= 2000 K and rejects energy Q2=500 KJ by heat transfer to a cold reservoir(sink) at T2= 400 K. Determine the reversible and irreversible efficiencies of heat engine.

SOL:

$$\eta_{rev} = \eta_{carnot} = 1 - \frac{T_2}{T_1} = 1 - \frac{400}{2000} = 0.8 = 80\%$$

$$\eta_{Irev} = \eta_{actual} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{500}{2100} = 0.762 = 76.2\%$$

 $\eta_{rev} > \eta_{Irev}$

6–9 THE THERMODYNAMIC TEMPERATURE SCALE

A temperature scale that is independent of the properties of the substances that are used to measure temperature is called a **thermodynamic temperature scale**. Such a temperature scale offers great conveniences in thermodynamic calculations, and its derivation is given below using some reversible heat engines.



6-10 THE CARNOT HEAT ENGINE



Any heat engine $\eta_{th} = 1 - \frac{Q_L}{Q_H}$ Carnot heat engine $\eta_{th,rev} = 1 - \frac{T_2}{T}$

 $\eta_{th} \begin{cases} < & \eta_{th,rev} \text{ ireversible heat engine} \\ = & \eta_{th,rev} \text{ reversible heat engine} \\ > & \eta_{th,rev} \text{ impossible heat engine} \end{cases}$

EXAMPLE 6–5 Analysis of a Carnot Heat Engine

A Carnot heat engine, shown in Fig. 6–47, receives 500 kJ of heat per cycle from a high-temperature source at 652°C and rejects heat to a low-temperature sink at 30°C. Determine (*a*) the thermal efficiency of this Carnot engine and (*b*) the amount of heat rejected to the sink per cycle.

SOLUTION The heat supplied to a Carnot heat engine is given. The thermal efficiency and the heat rejected are to be determined.

Analysis (a) The Carnot heat engine is a reversible heat engine, and so its efficiency can be determined from Eq. 6-18 to be

$$\eta_{\text{th,rev}} = 1 - \frac{T_L}{T_H} = 1 - \frac{(30 + 273) \text{ K}}{(652 + 273) \text{ K}} = 0.672$$

That is, this Carnot heat engine converts 67.2 percent of the heat it receives to work.

(b) The amount of heat rejected Q_L by this reversible heat engine is easily determined from Eq. 6–16 to be

$$Q_{L,\text{rev}} = \frac{T_L}{T_H} Q_{H,\text{rev}} = \frac{(30 + 273) \text{ K}}{(652 + 273) \text{ K}} (500 \text{ kJ}) = 164 \text{ kJ}$$

6-11 THE CARNOT REFRIGERATOR AND HEAT PUMP

A refrigerator or a heat pump that operates on the reversed Carnot cycle is called a **Carnot refrigerator**, or a **Carnot heat pump**. The coefficient of performance of any refrigerator or heat pump, reversible or irreversible, is given by Eqs.

$$COP = \frac{Desired energy result}{work input}$$
$$COP_{R} = \frac{1}{\frac{Q_{H}}{Q_{L}} - 1}$$
$$COP_{HP} = \frac{1}{1 - \frac{Q_{L}}{Q_{H}}}$$

Any refrigerator or heat pump

Carnot refrigerator or heat pump $COP_{R,rev} = \frac{1}{\frac{T_H}{T_L} - 1}$ $COP_{HP,rev} = \frac{1}{1 - \frac{T_L}{T_H}}$ $COP_R \begin{cases} < COP_{R,rev} \ ireversible \ refrigerator \\ = \ COP_{R,rev} \ reversible \ refrigerator \\ > \ COP_{R,rev} \ impossible \ refrigerator \end{cases}$



FIGURE 6–50 No refrigerator can have a higher COP than a reversible refrigerator operating between the same temperature limits.



EXAMPLE 6–7 Heating a House by a Carnot Heat Pump

A heat pump is to be used to heat a house during the winter, as shown in Fig. 6–52. The house is to be maintained at 21°C at all times. The house is estimated to be losing heat at a rate of 135,000 kJ/h when the outside temperature drops to -5° C. Determine the minimum power required to drive this heat pump.

SOLUTION A heat pump maintains a house at a constant temperature. The required minimum power input to the heat pump is to be determined. *Assumptions* Steady operating conditions exist.

Analysis The heat pump must supply heat to the house at a rate of $\dot{Q}_{H} = 135,000 \text{ kJ/h} = 37.5 \text{ kW}$. The power requirements are minimum when a reversible heat pump is used to do the job. The COP of a reversible heat pump operating between the house and the outside air is

$$\text{COP}_{\text{HP,rev}} = \frac{1}{1 - T_L/T_H} = \frac{1}{1 - (-5 + 273 \text{ K})/(21 + 273 \text{ K})} = 11.3$$

Then, the required power input to this reversible heat pump becomes

$$\dot{W}_{\text{net,in}} = \frac{\dot{Q}_H}{\text{COP}_{\text{HP}}} = \frac{37.5 \text{ kW}}{11.3} = 3.32 \text{ kW}$$

Discussion This reversible heat pump can meet the heating requirements of this house by consuming electric power at a rate of 3.32 kW only. If this

FIGURE 6–52 Schematic for Example 6–7.

Example 4 :

A power cycle operating between two reservoirs receives energy Q1 by heat transfer from a hot reservoir at T1= 2000K and rejects energy Q2 by heat transfer to a cold reservoir at T2=400K. For each of the following cases, determine whether the cycle operates reversibly, irreversibly, or is impossible.

(a)
$$Q1 = 1000 \text{KJ}$$
, $W = 850 \text{KJ}$ (b) $Q1 = 2000 \text{KJ}$, $Q2 = 400 \text{KJ}$ (c) $W = 1600 \text{KJ}$, $Q2 = 500 \text{KJ}$ (d) $Q1 = 1000 \text{KJ}$, $\eta = 30\%$

SOL

Given : T1 = 2000K Temperature of source

T2 = 400K Temperature of sink

$$\eta_{rev} = \eta_{carnot} = 1 - \frac{T_2}{T} = 1 - \frac{400}{2000} = 0.8 = 80\%$$

a) $\eta_{irev} = \frac{W_{net \, work}}{Q_{in}} = \frac{850}{1000} = 0.85 = 85\%$

 $\eta_{irev} > \eta_{rev}$ Impossible cycle for this case

b)
$$\eta_{irev} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{400}{2000} = 80\%$$

 $\eta_{irev} = \eta_{rev}$ reversible cycle for this case

C)
$$W_{net,out} = Q_{in} - Q_{out}$$
 1600=Q₁-500

$$\eta_{irev} = 1 - \frac{q_{out}}{q_{in}} = 1 - \frac{500}{2100} = 76.2\%$$

 $\eta_{irev} < \eta_{rev}$ irreversible cycle for this case

d) $\eta_{irev} < \eta_{rev}$ irreversible cycle for this case

Example 5:

A refrigerator cycle operating between two reservoirs receives energy Q2 from a cold reservoir at T2 = 250K and rejects energy Q1 to a hot reservoir at T1 = 300K. For each of the following cases determine whether the cycle operates reversibly, irreversibly or is impossible.

(a)
$$Q2 = 1000KJ$$
, $W = 400KJ$
(b) $Q2 = 2000KJ$, $Q1 = 2200KJ$
(c) $Q1 = 3000KJ$, $W = 500KJ$
(d) $W = 400 KJ$, $COP = 6$

Sol

Given $T1 = 300K = 27^{\circ}C$

T2 = 250 K = -23 °C

Q₁=2100 KJ

a) $COP_{R,rev} = \frac{1}{\frac{T_H}{T_L} - 1}$	$COP_{R,rev} = \frac{1}{\frac{300}{250} - 1} = 5$	
400=Q ₁ -1000	Q ₁ =1400 KJ	
$COP_R = \frac{1}{\frac{Q_H}{Q_L} - 1}$	$COP_R = \frac{1}{\frac{1000}{1400} - 1} = 2.5$	
$\text{COP}_{R,irev} < \text{COP}_{R,rev}$	ireversible refrigerator	
b) $COP_R = \frac{1}{\frac{Q_H}{Q_L} - 1}$	$COP_R = \frac{1}{\frac{3200}{2000} - 1} = 10$	
$COP_{R,irev} > COP_{R,rev}$	impossible refrigerator	
<i>c)</i> 500=3000 – Q ₂	Q2=2500 KJ	
$COP_R = \frac{1}{\frac{Q_H}{Q_L} - 1}$	$COP_R = \frac{1}{\frac{3000}{2500} - 1} = 5$	
$COP_{R,irev} = COP_{R,rev}$	reversible refrigerator	

Example(3): A refrigeration cycle operating between two reservoirs receives energy Q2=1000 KJ from a cold reservoir at T2 =250 K and rejects energy Q1 = 1400 KJ to a cold reservoir at T1 = 300K. Determine the coefficient of performance of refrigerator when operates reversibly and irreversibly.

Solution :

Given : Q2 = 1000 KJ , Q1 = 1400 KJ

T2=250 K, T1=300 K

$$COP_{R,rev} = \frac{1}{\frac{300}{250} - 1} = 5$$

$$COP_{R} = \frac{1}{\frac{Q_{H}}{Q_{L}} - 1}$$

$$COP_{R} = \frac{1}{\frac{1400}{1000} - 1} = 2.5$$

ENTROPY

2.1 Introduction

It may be noted that all heat is not equally valuable for converting into work. Heat that supplied to a substance (system) at high temperature has a greater possibility of conversion into work than heat supplied to a substance at a lower temperature.

Entropy : is a function of a quantity of heat which shows the possibility of conversion of that heat into work .

$$\Delta s = \frac{Q}{T}$$
 Where Q = Heat, T = absolute temperature

$$\Delta S_{system} = S_2 - S_1 = \frac{Q}{T_{system}}$$

$$\Delta S_{surrounding} = \frac{Q}{T_{surrounding}}$$

Notes :

- 1. the increase in entropy is small when heat is added at a high temperature
- 2. the increase in entropy is high when heat is added at a low temperature.
- 3. heat supplied to system Q = + Ve
- 4. heat rejected(or loss) from the system Q = -Ve

EXAMPLE 7–1 Entropy Change during an Isothermal Process

A piston-cylinder device contains a liquid-vapor mixture of water at 300 K. During a constant-pressure process, 750 kJ of heat is transferred to the water. As a result, part of the liquid in the cylinder vaporizes. Determine the entropy change of the water during this process.

SOLUTION

$$\Delta S_{\text{sys,isothermal}} = \frac{Q}{T_{\text{sys}}} = \frac{750 \text{ kJ}}{300 \text{ K}} = 2.5 \text{ kJ/K}$$

EXAMPLE 7–2 Entropy Generation during Heat Transfer Processes

A heat source at 800 K loses 2000 kJ of heat to a sink at (a) 500 K and (b) 750 K. Determine which heat transfer process is more irreversible.



FIGURE 7–9 Schematic for Example 7–2. (a) For the heat transfer process to a sink at 500 K:

$$\Delta S_{\text{source}} = \frac{Q_{\text{source}}}{T_{\text{source}}} = \frac{-2000 \text{ kJ}}{800 \text{ K}} = -2.5 \text{ kJ/K}$$
$$\Delta S_{\text{sink}} = \frac{Q_{\text{sink}}}{T_{\text{sink}}} = \frac{2000 \text{ kJ}}{500 \text{ K}} = +4.0 \text{ kJ/K}$$

and

$$S_{\text{gen}} = \Delta S_{\text{total}} = \Delta S_{\text{source}} + \Delta S_{\text{sink}} = (-2.5 + 4.0) \text{ kJ/K} = 1.5 \text{ kJ/K}$$

Therefore, 1.5 kJ/K of entropy is generated during this process. Noting that both reservoirs have undergone internally reversible processes, the entire entropy generation took place in the partition.

(b) Repeating the calculations in part (a) for a sink temperature of 750 K, we obtain

$$\Delta S_{\text{source}} = -2.5 \text{ kJ/k}$$
$$\Delta S_{\text{sink}} = +2.7 \text{ kJ/K}$$

and

$$S_{\text{ren}} = \Delta S_{\text{total}} = (-2.5 + 2.7) \text{ kJ/K} = 0.2 \text{ kJ/K}$$

2.2 Inequality of Clausius

The inequality of Clausius is a relation between the heat transfers of a system with an arbitrary number of heat reservoirs and the absolute temperatures of these reservoirs when the system undergoes a cycle



The equality in the Clausius inequality holds for totally or just internally reversible cycles and the inequality for the irreversible ones.

7–3 ENTROPY CHANGE OF PURE SUBSTANCES

Entropy is a property, and thus the value of entropy of a system is fixed once the state of the system is fixed



EXAMPLE 7–3 Entropy Change of a Substance in a Tank

A rigid tank contains 5 kg of refrigerant-134a initially at 20°C and 140 kPa. The refrigerant is now cooled while being stirred until its pressure drops to 100 kPa. Determine the entropy change of the refrigerant during this process.

State 1

I:
$$T_1 = 20^{\circ}\text{C}$$
 $v_1 = 0.16544 \text{ m}^3/\text{kg}$

State 2:

$$v_{2} = 100 \text{ kPa}$$
 $v_{f} = 0.0007258 \text{ m}^{3}/\text{kg}$
 $v_{2} = v_{1}$ $v_{e} = 0.19255 \text{ m}^{3}/\text{kg}$

 $P_{\rm c} = 140 \, \text{kPa}$ $s_{\rm c} = 1.0625 \, \text{kJ/kg/K}$

The refrigerant is a saturated liquid-vapor mixture at the final state since $v_f < v_2 < v_g$ at 100 kPa pressure. Therefore, we need to determine the quality first:

$$x_2 = \frac{v_2 - v_f}{v_{fg}} = \frac{0.16544 - 0.0007258}{0.19255 - 0.0007258} = 0.859$$

Thus,

 $s_2 = s_f + x_2 s_{fg} = 0.07182 + (0.859)(0.88008) = 0.8278 \text{ kJ/kg·K}$

Then, the entropy change of the refrigerant during this process is

 $\Delta S = m(s_2 - s_1) = (5 \text{ kg})(0.8278 - 1.0625) \text{ kJ/kg·K}$ = -1.173 kJ/K

 $\Delta s = 0$

7–4 ISENTROPIC PROCESSES

A process during which the entropy remains constant is called an **isentropic process**. It is characterized by

or

Isentropic process:





FIGURE 7–14 During an internally reversible, adiabatic (isentropic) process, the entropy remains constant



FIGURE 7–17 The isentropic process appears as a vertical line segment on a *T-s* diagram.



FIGURE 7–12 Schematic and *T-s* diagram for Example 7–3.

Isentropic Expansion of Steam in a Turbine EXAMPLE 7–5

Steam enters an adiabatic turbine at 5 MPa and 450°C and leaves at a pressure of 1.4 MPa. Determine the work output of the turbine per unit mass of steam if the process is reversible.

SOLUTION

(since $\dot{Q} = 0$, ke \cong pe $\cong 0$)

$$W_{\rm out} = \dot{m}(h_1 - h_2)$$

State 1:

.

 $\begin{array}{l} P_1 = 5 \text{ MPa} \\ T_1 = 450^{\circ}\text{C} \end{array} \begin{array}{l} h_1 = 3317.2 \text{ kJ/kg} \\ s_1 = 6.8210 \text{ kJ/kg} \cdot \text{K} \end{array}$ - 1 4 MD-)

State 2:
$$P_2 = 1.4 \text{ MPa} \\ s_2 = s_1 \end{cases} h_2 = 2967.4 \text{ kJ/kg}$$

Then, the work output of the turbine per unit mass of the steam becomes

$$w_{\text{out}} = h_1 - h_2 = 3317.2 - 2967.4 = 349.8 \text{ kJ/kg}$$



7-8 ENTROPY CHANGE OF LIQUIDS AND SOLIDS

 $ds = \frac{du}{T} = \frac{CdT}{T}$

since cp = cv = c and du = c dT for incompressible substances. Then the entropy change during a process is determined by integration to be

Liquids , solids $S_1 - S_2 = 1$	$\int_{1}^{2} \mathcal{C}(T) \frac{dT}{T} \cong \mathcal{C}_{avg} \ln \frac{T_{2}}{T_{1}} \left(\frac{KJ}{Kg.K}\right)$
Isentropic $S_1 - S_1$	$S_2 = C_{avg} \ln \frac{T_2}{T_1} = 0$
$\delta Q - \delta w = dU$	first law of thermodynamics
But	
$\delta Q = T dS$	$\delta w = P dv$
Thus	
TdS=dU+PdV KJ	
h=u+pv	dh = du + pdv + vdp $Tds = du + pdv$ $Tds = dh - vdp$
du=CvdT	
P=RT/V	
Dividing equation (2) by T	, we get

 $ds = C_{v} \frac{dT}{T} + R \frac{dv}{v}$ $S_{1} - S_{2} = \int_{1}^{2} C_{V}(T) \frac{dT}{T} + R \ln \frac{V_{2}}{V_{1}} \qquad \left(\frac{KJ}{Kg.K}\right)$ $dh=C_{p}dt \text{ and } V=RT/P$ $S_{1} - S_{2} = \int_{1}^{2} C_{P}(T) \frac{dT}{T} - R \ln \frac{P_{2}}{P_{1}} \qquad \left(\frac{KJ}{Kg.K}\right)$ $S_{1} - S_{2} = C_{V} \ln \frac{T_{2}}{T_{1}} + R \ln \frac{V_{2}}{V_{1}} \qquad \left(\frac{KJ}{Kg.K}\right)$ $S_{1} - S_{2} = C_{P} \ln \frac{T_{2}}{T_{1}} - R \ln \frac{P_{2}}{P_{1}} \qquad \left(\frac{KJ}{Kg.K}\right)$ $S_{1} - S_{2} = C_{V} \ln \frac{P_{2}}{T_{1}} + C_{P} \ln \frac{V_{2}}{V_{1}} \qquad \left(\frac{KJ}{Kg.K}\right)$

Where R=C_P-C_V

Entropy changes can also be expressed on a unit-mole basis by multiplying these relations by molar mass:

$$\bar{s}_2 - \bar{s}_1 = \bar{c}_{v,avg} \ln \frac{T_2}{T_1} + R_u \ln \frac{V_2}{V_1} \quad (kJ/kmol \cdot K) \qquad \bar{s}_2 - \bar{s}_1 = \bar{c}_{p,avg} \ln \frac{T_2}{T_1} - R_u \ln \frac{P_2}{P_1} \quad (kJ/kmol \cdot K)$$

EXAMPLE 7–9 Entropy Change of an Ideal Gas

Air is compressed from an initial state of 100 kPa and 17°C to a final state of 600 kPa and 57°C. Determine the entropy change of air during this compression process by using (*a*) property values from the air table and (*b*) average specific heats.

SOLUTION

(a) The properties of air are given in the air table (Table A–17). Reading s° values at given temperatures and substituting, we find

$$s_2 - s_1 = s_2^\circ - s_1^\circ - R \ln \frac{P_2}{P_1}$$

= [(1.79783 - 1.66802) kJ/kg·K] - (0.287 kJ/kg·K) ln $\frac{600 \text{ kPa}}{100 \text{ kPa}}$
= -0.3844 kJ/kg·K

(b) The entropy change of air during this process can also be determined approximately from Eq. 7–34 by using a c_p value at the average temperature of 37°C (Table A–2*b*) and treating it as a constant:





Example 1: A quantity of air undergoes a thermodynamic cycle consisting of three processes in series:

Process 1-2 : constant volume heating from p1 =1 bar, T1 = 288 K, V1 = 0.02 m3, to p2 = 4.2 bar. Process 2-3 : constant pressure cooling Process 3-1 : isothermal heating to the initial state. Evaluate the change in entropy for each process. Sketch the cycle on p-v and T-s diagram. Take cp = 1 KJ/kg.K, R = 0.287 KJ/kg.k

 $P_1V_1 = mrT_1$

1*100*0.02=m*0.287*288

M=0.024 kg

For gas $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Also, since $V_1 = V_2$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
$$T_2 = \frac{P_2}{T_2}$$

$$T_2 = \frac{T_2}{P_1} T_1$$

 $R = C_P - C_V$

 $C_{V=} C_{P}-R=1-0.287=0.713 \text{ KJ.K/Kg}$

Process 3-1 : constant volume $V_1 = V_2$

$$S_1 - S_2 = mC_v \ln \frac{T_2}{T_1} = 0.024 \times 0.713 \ln \frac{1210}{288} = 0.02456 \frac{KJ}{K}$$

Process 2-3 : constant pressure $P_1 = P_2$

$$S_1 - S_2 = mC_p \ln \frac{T_2}{T_1} = 0.024 \times 1 \times \ln \frac{288}{1210} = -0.0344 \frac{KJ}{K}$$

Process 3-1 : constant temperature $T_1 = T_2$ isothermal

$$S_1 - S_2 = mR \ln \frac{p_2}{p_1} = 0.024 \times 0.287 \ln \frac{4.2}{1} = 0.0099 \frac{KJ}{K}$$

Example -2

0.4 kg of air at 6 bar receives an addition of heat at constant volume so that its temperature rises from 383 K to 923 K. It then expands in a cylinder polytropically to its original temperature and the index of expansion (polytropic index n=1.32). Finally, it is compressed isothermally to its original volume. Calculate, (a) the change in entropy during each of three processes ; (b) the pressure at the end of constant volume heat addition and at the end of expansion. Show the process on p-v diagram. Assume Cv = 0.718KJ/kg.K, and R=0.287 KJ/kg.K.

Solution :

 $P_1V_1 = mRT_1$

M=0.4 kg , P₁= 6 bar
$$*\frac{10^5}{10^3} = 600 N/m^2$$
 , T₁=383 K , R=0.287 KJ/Kg.K

600* V₁=0.4*0.287*383
V₁= 0.0732 m³
V₁= V₂= 0.0732 m³
For gas
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Since V₁= V₂= 0.0732 m³
 $\frac{P_1}{T_1} = \frac{P_2}{T_2}$
 $p_2 = \frac{T_2}{T_1}P_1 = 6 \times \frac{923}{383} = 14.45 \ bar$
 $\frac{V_3}{V_2} = (\frac{T_2}{T_3})^{\frac{1}{n-1}}$
 $V_3 = V_2(\frac{T_2}{T_3})^{\frac{1}{n-1}} = 0.0732(\frac{923}{383})^{\frac{1}{1.32-1}} = 1.1435 \ m^3$
P₃V₃=mRT 3
1.1435* P₃=0.4*0.287*383
P₃=38.45 KN/m²=0.3845 \ bar
 $S_1 - S_2 = mC_v \ln \frac{T_2}{T_1} = 0.4 \times 0.718 \ \ln \frac{923}{383} = 0.25266 \ \frac{K}{K}$
 $S_1 - S_2 = mR \ln \frac{P_2}{P_1} + mC_p \ln \frac{T_3}{T_2}$
R=C_P-C_V
0.287₋ C_P-0.718 C_P=1.005 KJ.K/Kg

$$S_{1} - S_{2} = 0.4 \times 0.287 \ln \frac{14.5}{0.384} + 0.4 \times 0.287 \ln \frac{383}{923} = 0.0623 \, KJ/K$$
$$S_{3} - S_{1} = mR \ln \frac{p_{1}}{p_{3}}$$
$$S_{3} - S_{1} = 0.4 \times 0.287 \ln \frac{6}{0.384} = 0.3155 \, KJ/Kg$$

Example-3 : Calculate the change in entropy when 5 kg of water at 100 °C is converted into steam at the same temperature. (Given ; latent heat of steam = 540 cal/gram. Solution :

1 cal = 4.1868 joule 1 kcal = 4.1868 KJ 1 kg= 1000 gram Q=5*1000*540=270000 cal 1 cal = 4.1868 J

$$Q = \frac{270000 \times 4.1868}{1}$$
Q=1130.44 * 10³ Joule

 $\Delta S = \frac{Q}{T} \frac{1130.44}{100+273} = \frac{1130.44}{373} = 3.03 \text{ KJ/K}$ Change in entropy

H.W :

Problem 1 :

Calculate the change in entropy when 10 grams of ice at 0 °C is converted into water at the same temperature (Given : Latent heat of ice = 80 cal/gram)

GASPOWERCYCLES

OTTO CYCLE: THE IDEAL CYCLE FOR SPARK-IGNITION ENGINES



FIGURE 9–12 Actual and ideal cycles in spark-ignition engines and their *P*-*v* diagrams.

Four-stroke cycle

1 cycle = 4 stroke = 2 revolution **Two-stroke cycle** 1 cycle = 2 stroke = 1 revolution

The two-stroke engines are generally less efficient than their four-stroke counterparts but they are relatively simple and inexpensive, and they have high power-to-weight and power-to-volume ratios.



FIGURE 9–15T-s diagram of the ideal Otto cycle



FIGURE 9–13 Schematic of a twostroke reciprocating engine.

- 1-2 Isentropic compression
- 2-3 Constant-volume heat addition
- 3-4 Isentropic expansion
- 4-1 Constant-volume heat rejection



FIGURE 9–16 *P*-*v* diagram of the ideal Otto cycle that includes intake and exhaust strokes.



$$(q_{\rm in} - q_{\rm out}) + (w_{\rm in} - w_{\rm out}) = \Delta u \quad (kJ/kg)$$

$$q_{\rm in} = u_3 - u_2 = c_v(T_3 - T_2)$$

$$q_{\rm out} = u_4 - u_1 = c_v(T_4 - T_1)$$

$$\eta_{\rm th,Oto} = \frac{w_{\rm net}}{q_{\rm in}} = 1 - \frac{q_{\rm out}}{q_{\rm in}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{T_1(T_4/T_1 - 1)}{T_2(T_3/T_2 - 1)}$$

Processes 1-2 and 3-4 are isentropic, and $v_2 = v_3$ and $v_4 = v_1$. Thus

$$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1}\right)^{k-1} = \left(\frac{v_3}{v_4}\right)^{k-1} = \frac{T_4}{T_3}$$

Substituting these equations into the thermal efficiency relation and simplifying give

$$\eta_{\rm th,Otto} = 1 - \frac{1}{r^{k-1}}$$

$$r = \frac{V_{\text{max}}}{V_{\text{min}}} = \frac{V_1}{V_2} = \frac{V_1}{V_2}$$

R is the **compression ratio** and *k* is the specific heat ratio cp/cv.

In SI engines, the compression ratio is limited by autoignition or engine knock

FIGURE 9–18 The thermal efficiency of the Otto cycle increases with the specific heat ratio k of the working fluid.

9–6 .DIESEL CYCLE: THE IDEAL CYCLE FOR COMPRESSION-IGNITION ENGINES

In diesel engines, only air is compressed during the compression stroke, eliminating the possibility of autoignition (engine knock). Therefore, diesel engines can be designed to operate at much higher compression ratios than SI engines, typically between 12 and 24.



FIGURE 9–20 In diesel engines, the spark plug is replaced by a fuel injector, and only air is compressed during the compression process

FIGURE 9–21 *T-s* and *P-v* diagrams for the ideal Diesel cycle.

In diesel engines, the spark plug is replaced by a fuel injector, and only air is compressed during the compression process.

$$q_{in} - w_{b,out} = u_3 - u_2 \rightarrow q_{in} = P_2(v_3 - v_2) + (u_3 - u_2)$$
$$= h_3 - h_2 = c_p(T_3 - T_2)$$
$$-q_{out} = u_1 - u_4 \rightarrow q_{out} = u_4 - u_1 = c_v(T_4 - T_1)$$

Then the thermal efficiency of the ideal Diesel cycle under the cold-air standard assumptions becomes

$$\eta_{\text{th,Diesel}} = \frac{w_{\text{net}}}{q_{\text{in}}} = 1 - \frac{q_{\text{out}}}{q_{\text{in}}} = 1 - \frac{T_4 - T_1}{k(T_3 - T_2)} = 1 - \frac{T_1(T_4/T_1 - 1)}{kT_2(T_3/T_2 - 1)}$$

We now define a new quantity, the **cutoff ratio** *r_c*, as the ratio of the cylinder volumes after and before the combustion process:

$$r_c = \frac{V_3}{V_2} = \frac{V_3}{V_2}$$

we see that the thermal efficiency relation reduces to

$$\eta_{\text{th,Diesel}} = 1 - \frac{1}{r^{k-1}} \left[\frac{r_c^k - 1}{k(r_c - 1)} \right]$$

for the same compression ratio

 $\eta_{\rm th,Otto} > \eta_{\rm th,Diesel}$



FIGURE 9–22 Thermal efficiency of the ideal Diesel

cycle as a function of compression and cutoff ratios (k 5 1.4).

Dual cycle: A more realistic ideal cycle model for modern, high-speed compression ignition engine.



FIGURE 9–23 *P-v* diagram of an ideal dual cycle

QUESTIONS

Diesel engines operate at higher air-fuel ratios than gasoline engines. Why?

Despite higher power to weight ratios, twostroke engines are not used in automobiles. Why?

The stationary diesel engines are among the most efficient power producing devices (about 50%). Why?

What is a turbocharger? Why are they mostly used in diesel engines compared to gasoline engines.

Home work

Q1: An ideal Otto cycle has a compression ratio of 8. At the beginning of the compression process, air is at 95 kPa and 278C, and 750 kJ/kg of heat is transferred to air during the constant-volume heat addition process. Taking into account the variation of specific heats with temperature, determine (*a*) the pressure and temperature at the end of the heat-addition process, (*b*) the net work output, (*c*) the thermal efficiency, and (*d*) the mean effective pressure for the cycle. *Answers:* (*a*) 3898 kPa, 1539 K, (*b*) 392.4 kJ/kg, (*c*) 52.3 percent, (*d*) 495 kPa.

Q2: An air-standard Diesel cycle has a compression ratio of 16 and a cutoff ratio of 2. At the beginning of the compression process, air is at 95 kPa and 278C. Accounting for the variation of specific heats with temperature, determine (*a*) the temperature after the heat-addition process, (*b*) the thermal efficiency, and (*c*) the mean effective pressure. *Answers:* (*a*) 1725 K, (*b*) 56.3 percent, (*c*) 675.9 kPa

Q3: An ideal Diesel cycle has a compression ratio of 17 and a cutoff ratio of 1.3. Determine the maximum temperature of the air and the rate of heat addition to this cycle when it produces 140 kW of power and the state of the air at the beginning of the compression is 90 kPa and 578C. Use constant specific heats at room temperature.

9-7 .STIRLING AND ERICSSON CYCLES

The ideal Otto and Diesel cycles discussed in the preceding sections are composed entirely of internally reversible processes and thus are internally reversible cycles. These cycles are not totally reversible, however, since they involve heat transfer through a finite temperature difference during the nonisothermal heat-addition and heat-rejection processes, which are irreversible. Therefore, the thermal efficiency of an Otto or Diesel engine will be less than that of a Carnot engine operating between the same temperature limits.

There are two other cycles that involve an isothermal heat-addition process at TH and an isothermal heat-rejection process at TL: the *Stirling cycle* and the *Ericsson cycle*. They differ from the Carnot cycle in that the two isentropic processes are replaced by two constant-volume regeneration processes in the Stirling cycle and by two constant-pressure regeneration processes in the Ericsson cycle. Both cycles utilize **regeneration**, a process during which heat is transferred to a thermal energy storage device (called a *regenerator*) during one part of the cycle and is transferred back to the working fluid during another part of the cycle (Fig. 9–25)





FIGURE 9–26 *T-s* and *P-v* diagrams of Carnot, Stirling, and Ericsson cycles.

Notice that the second constant-volume process takes place at a smaller volume than the first one, and the net heat transfer to the regenerator during a cycle is zero. That is, the amount of energy stored in the regenerator during process 2-3 is equal to the amount picked up by the gas during process 4-1. The *T-s* and *P-v* diagrams of the **Ericsson cycle** are shown in Fig. 9-26c. The Ericsson cycle is very much like the Stirling cycle, except that the two constant-volume processes are replaced by two constant-pressure processes. A steady-flow system operating on an Ericsson cycle is shown in Fig. 9–28. Here the isothermal expansion and compression processes are executed in a compressor and a turbine, respectively, and a counter-flow heat exchanger serves as a regenerator. Hot and cold fluid streams enter the heat exchanger from opposite ends, and heat transfer takes place between the two streams. In the ideal case, the temperature difference between the two fluid streams does not exceed a differential amount at any point, and the cold fluid stream leaves the heat exchanger at the inlet temperature of the hot stream. Both the Stirling and Ericsson cycles are totally reversible, as is the Carnot cycle, and thus according to the Carnot principle, all threse cycles must have the same thermal efficiency when operating between the same temperature limits: $T_I = \text{const}$

(9–14)

$$\eta_{ ext{th,Stirling}} = \eta_{ ext{th,Ericsson}} = \eta_{ ext{th,Carnot}} = 1 - rac{T_L}{T_H}$$

This is proved for the Carnot cycle in Example 9–1 and can be proved in a similar manner for both the Stirling and Ericsson cycles.



EXAMPLE 9–4 Thermal Efficiency of the Ericsson Cycle

Using an ideal gas as the working fluid, show that the thermal efficiency of
 an Ericsson cycle is identical to the efficiency of a Carnot cycle operating
 between the same temperature limits.

SOLUTION It is to be shown that the thermal efficiencies of Carnot and Ericsson cycles are identical.

Analysis Heat is transferred to the working fluid isothermally from an external source at temperature T_H during process 1-2, and it is rejected again isothermally to an external sink at temperature T_L during process 3-4. For a reversible isothermal process, heat transfer is related to the entropy change by

$$q = T \Delta s$$

The entropy change of an ideal gas during an isothermal process is

$$\Delta s = c_p \ln \frac{T_e}{T_i} - R \ln \frac{P_e}{P_i} = -R \ln \frac{P_e}{P_i}$$

The heat input and heat output can be expressed as

$$q_{\rm in} = T_H(s_2 - s_1) = T_H\left(-R \ln \frac{P_2}{P_1}\right) = RT_H \ln \frac{P_1}{P_2}$$

and

$$q_{\text{out}} = T_L(s_4 - s_3) = -T_L\left(-R \ln \frac{P_4}{P_3}\right) = RT_L \ln \frac{P_4}{P_3}$$

Then the thermal efficiency of the Ericsson cycle becomes

$$\eta_{\text{th,Ericsson}} = 1 - \frac{q_{\text{out}}}{q_{\text{in}}} = 1 - \frac{RT_L \ln(P_4/P_3)}{RT_H \ln(P_1/P_2)} = 1 - \frac{T_L}{T_H}$$

since $P_1 = P_4$ and $P_3 = P_2$. Notice that this result is independent of whether the cycle is executed in a closed or steady-flow system.

9–8 BRAYTON CYCLE: THE IDEAL CYCLE FOR GAS-TURBINE ENGINES

The Brayton cycle was first proposed by George Brayton for use in the reciprocating oil-burning engine that he developed around 1870. Today, it is used for gas turbines only where both the compression and expansion processes take place in rotating machinery. Gas turbines usually operate on an *open cycle*, as shown in Fig. 9–29. Fresh air at ambient conditions is drawn into the compressor, where its temperature and pressure are raised. The high-pressure air proceeds into the combustion chamber, where the fuel is burned at constant pressure. The resulting high-temperature gases then

enter the turbine, where they expand to the atmospheric pressure while producing power. The exhaust gases leaving the turbine are thrown out (not recirculated), causing the cycle to be classified as an open cycle.

The open gas-turbine cycle described above can be modeled as a *closed cycle*, as shown in Fig. 9–30, by utilizing the air-standard assumptions. Here the compression and expansion processes remain the same, but the combustion process is replaced by a constant-pressure heat-addition process from an external source, and the exhaust process is replaced by a constant-pressure





Development of Gas Turbines

The gas turbine has experienced phenomenal progress and growth since its first successful development in the 1930s. The early gas turbines built in the 1940s and even 1950s had simple-cycle efficiencies of about 17 percent because of the low compressor and turbine efficiencies and low turbine inlet temperatures due to metallurgical limitations of those times. Therefore, gas turbines found only limited use despite their versatility and their ability to burn a variety of fuels. The efforts to improve the cycle efficiency concentrated in three areas:

1. Increasing the turbine inlet (or firing) temperatures This has been the primary approach taken to improve gas-turbine efficiency. The turbine inlet temperatures have increased steadily from about 5408C (10008F) in the 1940s to 14258C (26008F) and even higher today. These increases were made possible by the development of new materials and the innovative cooling techniques for the critical components such as coating the turbine blades with ceramic layers and cooling the blades with the discharge air from the compressor. Maintaining high turbine inlet temperatures with an air-cooling technique requires the combustion temperature to be higher to compensate for the cooling effect of the cooling air. However, higher combustion temperatures increase the amount of nitrogen oxides (NO*x*), which are responsible for the formation of ozone at ground level and smog. Using steam as

the coolant allowed an increase in the turbine inlet temperatures by 2008F without an increase in the combustion temperature. Steam is also a much more effective heat transfer medium than air.

2. Increasing the efficiencies of turbomachinery components The performance of early turbines suffered greatly from the inefficiencies of turbines and compressors. However, the advent of computers and advanced techniques for computer-aided design made it possible to design these components aerodynamically with minimal losses. The increased efficiencies of the turbines and compressors resulted in a significant increase in the cycle efficiency.

3. Adding modifications to the basic cycle The simple-cycle efficiencies of early gas turbines were practically doubled by incorporating intercooling, regeneration (or recuperation), and reheating, discussed in the next two sections. These improvements, of course, come at the expense of increased initial and operation costs, and they cannot be justified unless the decrease in fuel costs offsets the increase in other costs.



FIGURE 9–35 *T-s* diagram for the Brayton cycle discussed in Example 9–5.

EXAMPLE 9–5 The Simple Ideal Brayton Cycle

A gas-turbine power plant operating on an ideal Brayton cycle has a pressure ratio of 8. The gas temperature is 300 K at the compressor inlet and 1300 K at the turbine inlet. Utilizing the air-standard assumptions, determine (*a*) the gas temperature at the exits of the compressor and the turbine, (*b*) the back work ratio, and (*c*) the thermal efficiency.

SOLUTION A power plant operating on the ideal Brayton cycle is considered. The compressor and turbine exit temperatures, back work ratio, and the thermal efficiency are to be determined.

Assumptions 1 Steady operating conditions exist. 2 The air-standard assumptions are applicable. 3 Kinetic and potential energy changes are negligible.
4 The variation of specific heats with temperature is to be considered.

Analysis The *T-s* diagram of the ideal Brayton cycle described is shown in Fig. 9–35. We note that the components involved in the Brayton cycle are steady-flow devices.

(*a*) The air temperatures at the compressor and turbine exits are determined from isentropic relations:

Process 1–2 (isentropic compression of an ideal gas):

$$T_1 = 300 \text{ K} \rightarrow h_1 = 300.19 \text{ kJ/kg}$$

$$P_{r1} = 1.386$$

 $P_{r2} = \frac{P_2}{P_1} P_{r1} = (8)(1.386) = 11.09 \rightarrow T_2 = 540 \text{ K}$ (at compressor exit)

 $h_2 = 544.35 \text{ kJ/kg}$

Process 3-4 (isentropic expansion of an ideal gas):

$$T_{3} = 1300 \text{ K} \rightarrow h_{3} = 1395.97 \text{ kJ/kg}$$

$$P_{r3} = 330.9$$

$$P_{r4} = \frac{P_{4}}{P_{3}} P_{r3} = \left(\frac{1}{8}\right)(330.9) = 41.36 \rightarrow T_{4} = 770 \text{ K} \quad \text{(at turbine exit)}$$

$$h_{4} = 789.37 \text{ kJ/kg}$$

(*b*) To find the back work ratio, we need to find the work input to the compressor and the work output of the turbine:

$$v_{\text{comp,in}} = h_2 - h_1 = 544.35 - 300.19 = 244.16 \text{ kJ/kg}$$

$$w_{\text{turb,out}} = h_3 - h_4 = 1395.97 - 789.37 = 606.60 \text{ kJ/kg}$$

Thus,

v

$$r_{\rm bw} = \frac{w_{\rm comp,in}}{w_{\rm turb,out}} = \frac{244.16 \text{ kJ/kg}}{606.60 \text{ kJ/kg}} = 0.403$$

That is, 40.3 percent of the turbine work output is used just to drive the compressor.

(c) The thermal efficiency of the cycle is the ratio of the net power output to the total heat input:

$$q_{\text{in}} = h_3 - h_2 = 1395.97 - 544.35 = 851.62 \text{ kJ/kg}$$

 $w_{\text{net}} = w_{\text{out}} - w_{\text{in}} = 606.60 - 244.16 = 362.4 \text{ kJ/kg}$

Thus,

$$\eta_{\rm th} = \frac{w_{\rm net}}{q_{\rm in}} = \frac{362.4 \text{ kJ/kg}}{851.62 \text{ kJ/kg}} = 0.426 \text{ or } 42.6\%$$

The thermal efficiency could also be determined from

$$\eta_{\rm th} = 1 - \frac{q_{\rm out}}{q_{\rm in}}$$

where

$$q_{\text{out}} = h_4 - h_1 = 789.37 - 300.19 = 489.2 \text{ kJ/kg}$$

Discussion Under the cold-air-standard assumptions (constant specific heat values at room temperature), the thermal efficiency would be, from Eq. 9–17,

$$\eta_{\text{th,Brayton}} = 1 - \frac{1}{r_p^{(k-1)/k}} = 1 - \frac{1}{8^{(1.4-1)/1.4}} = 0.448 \text{ or } 44.8\%$$

which is sufficiently close to the value obtained by accounting for the variation of specific heats with temperature.

Deviation of Actual Gas-Turbine Cycles from Idealized Ones

The actual gas-turbine cycle differs from the ideal Brayton cycle on several accounts. For one thing, some pressure drop during the heat-addition and heat-rejection processes is inevitable. More importantly, the actual work input to the compressor is more, and the actual work output from the turbine is less because of irreversibilities. The deviation of actual compressor and turbine behavior from the idealized isentropic behavior can be accurately accounted for by utilizing the isentropic efficiencies of the turbine and compressor as



9–9 THE BRAYTON CYCLE WITH REGENERATION

In gas-turbine engines, the temperature of the exhaust gas leaving the turbine is often considerably higher than the temperature of the air leaving the compressor. Therefore, the high-pressure air leaving the compressor can be heated by transferring heat to it from the hot exhaust gases in a counter-flow



EXAMPLE 9–6 An Actual Gas-Turbine Cycle

Assuming a compressor efficiency of 80 percent and a turbine efficiency of 85 percent, determine (a) the back work ratio, (b) the thermal efficiency, and (c) the turbine exit temperature of the gas-turbine cycle discussed in Example 9-5.

SOLUTION The Brayton cycle discussed in Example 9–5 is reconsidered. For specified turbine and compressor efficiencies, the back work ratio, the thermal efficiency, and the turbine exit temperature are to be determined. *Analysis* (*a*) The *T-s* diagram of the cycle is shown in Fig. 9–37. The actual compressor work and turbine work are determined by using the definitions of compressor and turbine efficiencies, Eqs. 9–19 and 9–20:

Compressor:	$w_{\text{comp,in}} = \frac{w_s}{\eta_C} = \frac{244.16 \text{ kJ/kg}}{0.80} = 305.20 \text{ kJ/kg}$
Turbine:	$w_{\text{turb,out}} = \eta_T w_s = (0.85)(606.60 \text{ kJ/kg}) = 515.61 \text{ kJ/kg}$

Thus,

$$r_{\rm bw} = \frac{w_{\rm comp,in}}{w_{\rm turb,out}} = \frac{305.20 \text{ kJ/kg}}{515.61 \text{ kJ/kg}} = 0.592$$

That is, the compressor is now consuming 59.2 percent of the work produced by the turbine (up from 40.3 percent). This increase is due to the irreversibilities that occur within the compressor and the turbine.

(*b*) In this case, air leaves the compressor at a higher temperature and enthalpy, which are determined to be

$$w_{\text{comp,in}} = h_{2a} - h_1 \rightarrow h_{2a} = h_1 + w_{\text{comp,in}}$$

= 300.19 + 305.20
= 605.39 kJ/kg (and T_{2a} = 598 K)

Thus,

 $q_{\text{in}} = h_3 - h_{2a} = 1395.97 - 605.39 = 790.58 \text{ kJ/kg}$ $w_{\text{net}} = w_{\text{out}} - w_{\text{in}} = 515.61 - 305.20 = 210.41 \text{ kJ/kg}$

and

$$\eta_{\rm th} = \frac{w_{\rm net}}{q_{\rm in}} = \frac{210.41 \text{ kJ/kg}}{790.58 \text{ kJ/kg}} = 0.266 \text{ or } 26.6\%$$

That is, the irreversibilities occurring within the turbine and compressor caused the thermal efficiency of the gas turbine cycle to drop from 42.6 to 26.6 percent. This example shows how sensitive the performance of a gasturbine power plant is to the efficiencies of the compressor and the turbine. In fact, gas-turbine efficiencies did not reach competitive values until significant improvements were made in the design of gas turbines and compressors. (*c*) The air temperature at the turbine exit is determined from an energy balance on the turbine:

$$w_{\text{turb,out}} = h_3 - h_{4a} \rightarrow h_{4a} = h_3 - w_{\text{turb,out}}$$

= 1395.97 - 515.61
= 880.36 kJ/kg

Then, from Table A-17,

$$T_{4a} = 853 \text{ K}$$

Discussion The temperature at turbine exit is considerably higher than that at the compressor exit ($T_{2a} = 598$ K), which suggests the use of regeneration to reduce fuel cost.

However, achieving a higher effectiveness requires the use of a larger regenerator, which carries a higher price tag and causes a larger pressure drop. Therefore, the use of a regenerator with a very high effectiveness cannot be justified economically unless the savings from the fuel costs exceed the additional expenses involved. The effectiveness of most regenerators used in practice is below 0.85.

Under the cold-air-standard assumptions, the thermal efficiency of an ideal Brayton cycle with regeneration is

$$\eta_{\text{th,regen}} = 1 - \left(\frac{T_1}{T_3}\right) (r_p)^{(k-1)/k}$$
 (9–25)

Therefore, the thermal efficiency of an ideal Brayton cycle with regeneration depends on the ratio of the minimum to maximum temperatures as well as the pressure ratio. The thermal efficiency is plotted in Fig. 9–40 for various pressure ratios and minimum-to-maximum temperature ratios. This figure shows that regeneration is most effective at lower pressure ratios and low minimum-to-maximum temperature ratios.

EXAMPLE 9–7 Actual Gas-Turbine Cycle with Regeneration

Determine the thermal efficiency of the gas-turbine described in Example 9–6
 if a regenerator having an effectiveness of 80 percent is installed.

SOLUTION The gas-turbine discussed in Example 9–6 is equipped with a regenerator. For a specified effectiveness, the thermal efficiency is to be determined.

Analysis The *T*-s diagram of the cycle is shown in Fig. 9–41. We first determine the enthalpy of the air at the exit of the regenerator, using the definition of effectiveness:

$$\epsilon = \frac{h_5 - h_{2a}}{h_{4a} - h_{2a}}$$

$$0.80 = \frac{(h_5 - 605.39) \text{ kJ/kg}}{(880.36 - 605.39) \text{ kJ/kg}} \rightarrow h_5 = 825.37 \text{ kJ/kg}$$

Thus,

$$q_{\rm in} = h_3 - h_5 = (1395.97 - 825.37) \,\text{kJ/kg} = 570.60 \,\text{kJ/kg}$$

This represents a savings of 220.0 kJ/kg from the heat input requirements. The addition of a regenerator (assumed to be frictionless) does not affect the net work output. Thus,

$$\eta_{\rm th} = \frac{w_{\rm net}}{q_{\rm in}} = \frac{210.41 \text{ kJ/kg}}{570.60 \text{ kJ/kg}} = 0.369 \text{ or } 36.9\%$$

Discussion Note that the thermal efficiency of the gas turbine has gone up from 26.6 to 36.9 percent as a result of installing a regenerator that helps to recuperate some of the thermal energy of the exhaust gases.



FIGURE 9-40

Thermal efficiency of the ideal Brayton cycle with and without regeneration.



FIGURE 9–41 *T-s* diagram of the regenerative Brayton cycle described in Example 9–7.

9–10 .THE BRAYTON CYCLE WITH INTERCOOLING, REHEATING, AND REGENERATION

The net work of a gas-turbine cycle is the difference between the turbine work output and the compressor work input, and it can be increased by either decreasing the compressor work or increasing the turbine work, or both. It was shown in Chap. 7 that the work required to compress a gas between two specified pressures can be decreased by carrying out the compression process in stages and cooling the gas in between (Fig. 9–42)—that is, using *multistage compression with intercooling*. As the number of stages is increased, the compression process becomes nearly isothermal at the compressor inlet temperature, and the compression work decreases.

Likewise, the work output of a turbine operating between two pressure levels can be increased by expanding the gas in stages and reheating it in between—that is, utilizing *multistage expansion with reheating*. This is accomplished without raising the maximum temperature in the cycle. As the number of stages is increased, the expansion process becomes nearly isothermal. The foregoing argument is based on a simple principle: *The steady-flow compression or expansion work is proportional to the specific volume of the fluid. Therefore, the specific volume of the working fluid should be as low as possible during a compression process and as high as possible during an expansion process.* This is precisely what intercooling and reheating accomplish.

Combustion in gas turbines typically occurs at four times the amount of air needed for complete combustion to avoid excessive temperatures. Therefore, the exhaust gases are rich in oxygen, and reheating can be accomplished by simply spraying additional fuel into the exhaust gases between two expansion states.

The working fluid leaves the compressor at a lower temperature, and the turbine at a higher temperature, when intercooling and reheating are utilized. This makes regeneration more attractive since a greater potential for regeneration exists. Also, the gases leaving the compressor can be heated to a higher temperature before they enter the combustion chamber because of the higher temperature of the turbine exhaust.

A schematic of the physical arrangement and the *T-s* diagram of an ideal two-stage gas-turbine cycle with intercooling, reheating, and regeneration are shown in Figs. 9–43 and 9–44. The gas enters the first stage of the compressor at state 1, is compressed isentropically to an intermediate pressure *P* 2, is cooled at constant pressure to state 3 (*T*3 5 *T*1), and is compressed in the second stage isentropically to the final pressure *P*4. At state 4 the gas enters the regenerator, where it is heated to *T*5 at constant pressure. In an ideal regenerator, the gas leaves the regenerator at the temperature of the turbine exhaust, that is, *T*5 5 *T*9. The primary heat addition (or combustion) process takes place between states 5 and 6. The gas enters the first stage of the turbine at state 6 and expands isentropically to state 7, where it enters the reheater. It is reheated at constant pressure to state 8 (*T*8 5 *T*6), where it enters the second stage of the turbine. The gas exits the turbine at state 9 and enters the regenerator, where it is cooled to state 10 at constant pressure. The cycle is completed by cooling the gas to the initial state (or purging the exhaust gases).




EXAMPLE 9–8 A Gas Turbine with Reheating and Intercooling

An ideal gas-turbine cycle with two stages of compression and two stages of expansion has an overall pressure ratio of 8. Air enters each stage of the compressor at 300 K and each stage of the turbine at 1300 K. Determine the back work ratio and the thermal efficiency of this gas-turbine cycle, assuming (*a*) no regenerators and (*b*) an ideal regenerator with 100 percent effectiveness. Compare the results with those obtained in Example 9–5.

SOLUTION An ideal gas-turbine cycle with two stages of compression and two stages of expansion is considered. The back work ratio and the thermal efficiency of the cycle are to be determined for the cases of no regeneration and maximum regeneration.

Assumptions 1 Steady operating conditions exist. **2** The air-standard assumptions are applicable. **3** Kinetic and potential energy changes are negligible. **Analysis** The *T-s* diagram of the ideal gas-turbine cycle described is shown in Fig. 9–46. We note that the cycle involves two stages of expansion, two stages of compression, and regeneration.

For two-stage compression and expansion, the work input is minimized and the work output is maximized when both stages of the compressor and the turbine have the same pressure ratio. Thus,

$$\frac{P_2}{P_1} = \frac{P_4}{P_3} = \sqrt{8} = 2.83$$
 and $\frac{P_6}{P_7} = \frac{P_8}{P_9} = \sqrt{8} = 2.83$

Air enters each stage of the compressor at the same temperature, and each stage has the same isentropic efficiency (100 percent in this case). Therefore, the temperature (and enthalpy) of the air at the exit of each compression stage will be the same. A similar argument can be given for the turbine. Thus,

At inlets: $T_1 = T_3$, $h_1 = h_3$ and $T_6 = T_8$, $h_6 = h_8$ At exits: $T_2 = T_4$, $h_2 = h_4$ and $T_7 = T_9$, $h_7 = h_9$

Under these conditions, the work input to each stage of the compressor will be the same, and so will the work output from each stage of the turbine. (*a*) In the absence of any regeneration, the back work ratio and the thermal efficiency are determined by using data from Table A–17 as follows:

$$T_1 = 300 \text{ K} \rightarrow h_1 = 300.19 \text{ kJ/kg}$$

 $P_{r1} = 1.386$

$$P_{r2} = \frac{P_2}{P_1} P_{r1} = \sqrt{8}(1.386) = 3.92 \rightarrow T_2 = 403.3 \text{ K}$$

 $h_2 = 404.31 \text{ kJ/kg}$

$$T_6 = 1300 \text{ K} \rightarrow h_6 = 1395.97 \text{ kJ/kg}$$

 $P_{r6} = 330.9$
 $P_7 = \frac{1}{1000} (320.0) = 117.0 \Rightarrow T_7 = 1006.000$

 $P_{r7} =$

$$\frac{1}{P_6}P_{r6} = \frac{1}{\sqrt{8}}(330.9) = 117.0 \rightarrow T_7 = 1006.4 \text{ K}$$

 $h_7 = 1053.33 \text{ kJ/kg}$

Then

$$\begin{split} w_{\text{comp,in}} &= 2(w_{\text{comp,in,I}}) = 2(h_2 - h_1) = 2(404.31 - 300.19) = 208.24 \text{ kJ/kg} \\ w_{\text{turb,out}} &= 2(w_{\text{turb,out,I}}) = 2(h_6 - h_7) = 2(1395.97 - 1053.33) = 685.28 \text{ kJ/kg} \\ w_{\text{net}} &= w_{\text{turb,out}} - w_{\text{comp,in}} = 685.28 - 208.24 = 477.04 \text{ kJ/kg} \\ q_{\text{in}} &= q_{\text{primary}} + q_{\text{reheat}} = (h_6 - h_4) + (h_8 - h_7) \\ &= (1395.97 - 404.31) + (1395.97 - 1053.33) = 1334.30 \text{ kJ/kg} \end{split}$$

Thus,

$$r_{\rm bw} = \frac{w_{\rm comp,in}}{w_{\rm turb out}} = \frac{208.24 \text{ kJ/kg}}{685.28 \text{ kJ/kg}} = 0.304$$

and

$$\eta_{\rm th} = \frac{w_{\rm net}}{q_{\rm in}} = \frac{477.04 \text{ kJ/kg}}{1334.30 \text{ kJ/kg}} = 0.358 \text{ or } 35.8\%$$

A comparison of these results with those obtained in Example 9–5 (singlestage compression and expansion) reveals that multistage compression with intercooling and multistage expansion with reheating improve the back work ratio (it drops from 0.403 to 0.304) but hurt the thermal efficiency (it drops from 42.6 to 35.8 percent). Therefore, intercooling and reheating are not recommended in gas-turbine power plants unless they are accompanied by regeneration.

(b) The addition of an ideal regenerator (no pressure drops, 100 percent effectiveness) does not affect the compressor work and the turbine work. Therefore, the net work output and the back work ratio of an ideal gas-turbine cycle are identical whether there is a regenerator or not. A regenerator, however, reduces the heat input requirements by preheating the air leaving the compressor, using the hot exhaust gases. In an ideal regenerator, the compressed air is heated to the turbine exit temperature T_9 before it enters the combustion chamber. Thus, under the air-standard assumptions, $h_5 = h_7 = h_9$.

The heat input and the thermal efficiency in this case are

$$q_{\rm in} = q_{\rm primary} + q_{\rm reheat} = (h_6 - h_5) + (h_8 - h_7)$$
$$= (1395.97 - 1053.33) + (1395.97 - 1053.33) = 685.28 \text{ kJ/kg}$$

and

$$\eta_{\rm th} = \frac{w_{\rm net}}{q_{\rm in}} = \frac{477.04 \text{ kJ/kg}}{685.28 \text{ kJ/kg}} = 0.696 \text{ or } 69.6\%$$

Discussion Note that the thermal efficiency almost doubles as a result of regeneration compared to the no-regeneration case. The overall effect of two-stage compression and expansion with intercooling, reheating, and regeneration on the thermal efficiency is an increase of 63 percent. As the number of compression and expansion stages is increased, the cycle will approach the Ericsson cycle, and the thermal efficiency will approach

$$\eta_{\text{th,Ericsson}} = \eta_{\text{th,Carnot}} = 1 - \frac{T_L}{T_H} = 1 - \frac{300 \text{ K}}{1300 \text{ K}} = 0.769$$

11–1 .REFRIGERATORS AND HEAT PUMPS

We all know from experience that heat flows in the direction of decreasing temperature, that is, from high-temperature regions to low-temperature ones. This heat-transfer process occurs in nature without requiring any devices. The reverse process, however, cannot occur by itself. The transfer of heat from a low-temperature region to a high-temperature one requires special devices called **refrigerators**.

Refrigerators are cyclic devices, and the working fluids used in the refrigeration cycles are called **refrigerants**. A refrigerator is shown schematically in Fig. 11–1*a*. Here Q_L is the magnitude of the heat removed from the refrigerated space at temperature T_L , Q_H is the magnitude of the heat rejected to the warm space at temperature T_H , and $W_{\text{net,in}}$ is the net work input to the refrigerator. As discussed in Chap. 6, Q_L and Q_H represent magnitudes and thus are positive quantities.

Another device that transfers heat from a low-temperature medium to a high-temperature one is the **heat pump**. Refrigerators and heat pumps are essentially the same devices; they differ in their objectives only. The objective of a refrigerator is to maintain the refrigerated space at a low temperature by removing heat from it. Discharging this heat to a higher-temperature medium is merely a necessary part of the operation, not the purpose. The objective of a heat pump, however, is to maintain a heated space at a high temperature. This is accomplished by absorbing heat from a low-temperature source, such as well water or cold outside air in winter, and supplying this heat to a warmer medium such as a house (Fig. 11-1b).

The performance of refrigerators and heat pumps is expressed in terms of the **coefficient of performance** (COP), defined as



These relations can also be expressed in the rate form by replacing the quantities Q_L , Q_{H^p} and $W_{\text{net,in}}$ by \dot{Q}_L , \dot{Q}_{H^p} and $\dot{W}_{\text{net,in}}$, respectively. Notice that both COP_{R} and COP_{HP} can be greater than 1. A comparison of Eqs. 11–1 and 11–2 reveals that

$$COP_{HP} = COP_{R} + 1$$
 (11-3)

for fixed values of QL and QH. This relation implies that COPHP . 1 since COP R is a positive quantity. That is, a heat pump functions, at worst, as a resistance heater, supplying as much energy to the house as it consumes. In reality, however, part of QH is lost to the outside air through piping and other devices, and COPHP may drop below unity when the outside air temperature is too low. When this happens, the system normally switches to the fuel (natural gas, propane, oil, etc.) or resistance-heating mode.

The *cooling capacity* of a refrigeration system—that is, the rate of heat removal from the refrigerated space—is often expressed in terms of **tons of refrigeration**. The capacity of a refrigeration system that can freeze 1 ton (2000 lbm) of liquid water at 08C (328F) into ice at 08C in 24 h is said to be 1 ton. One ton of refrigeration is equivalent to 211 kJ/min or 200 Btu/min. The cooling load of a typical 200-m2 residence is in the 3-ton (10-kW) range.



pump is to supply heat (QH) to a

warm medium.

11–2 THE REVERSED CARNOT CYCLE

Recall from Chap. 6 that the Carnot cycle is a totally reversible cycle that consists of two reversible isothermal and two isentropic processes. It has the maximum thermal efficiency for given temperature limits, and it serves as a standard against which actual power cycles can be compared.

Since it is a reversible cycle, all four processes that comprise the Carnot cycle can be reversed. Reversing the cycle does also reverse the directions of any heat and work interactions. The result is a cycle that operates in the counterclockwise direction on a *T*-*s* diagram, which is called the **reversed Carnot cycle**. A refrigerator or heat pump that operates on the reversed Carnot cycle is called a **Carnot refrigerator** or a **Carnot heat pump**.

Consider a reversed Carnot cycle executed within the saturation dome of a refrigerant, as shown in Fig. 11–2. The refrigerant absorbs heat isothermally from a low-temperature source at TL in the amount of QL (process 1-2), is compressed isentropically to state 3 (temperature rises to TH), rejects heat isothermally to a high-temperature sink at TH in the amount of QH (process 3-4), and expands isentropically to state 1 (temperature drops to TL). The refrigerant changes from a saturated vapor state to a saturated liquid state in the condenser during process 3-4.

The coefficients of performance of Carnot refrigerators and heat pumps are expressed in terms of temperatures as

and

$$\text{COP}_{\text{HP,Carnot}} = \frac{1}{1 - T_I / T_H}$$

 $\text{COP}_{\text{R,Carnot}} = \frac{1}{T_H/T_L - 1}$

(11–5)

(11-4)

Notice that both COPs increase as the difference between the two temperatures decreases, that is, as *TL* rises or *TH* falls.

The reversed Carnot cycle is the *most efficient* refrigeration cycle operating between two specified temperature levels. Therefore, it is natural to look at it first as a prospective ideal cycle for refrigerators and heat pumps. If we could, we certainly would adapt it as the ideal cycle. As explained below, however, the reversed Carnot cycle is not a suitable model for refrigeration cycles.

11–3 ■ THE IDEAL VAPOR-COMPRESSION REFRIGERATION CYCLE

Many of the impracticalities associated with the reversed Carnot cycle can be eliminated by vaporizing the refrigerant completely before it is compressed and by replacing the turbine with a throttling device, such as an expansion valve or capillary tube. The cycle that results is called the **ideal vapor-compression refrigeration cycle**, and it is shown schematically and on a *T-s* diagram in Fig. 11–3. The vapor-compression refrigerators, air-conditioning systems, and heat pumps. It consists of four processes:

1-2 Isentropic compression in a compressor

- 2-3 Constant-pressure heat rejection in a
- condenserThrottling in an expansion
- 3-4
 4-1
 deviceConstant-pressure heat absorption in an evaporator

In an ideal vapor-compression refrigeration cycle, the refrigerant enters the compressor at state 1 as saturated vapor and is compressed isentropically to the condenser pressure. The temperature of the refrigerant increases during this isentropic compression process to well above the temperature of the surrounding medium. The refrigerant then enters the condenser as superheated vapor at state 2



and leaves as saturated liquid at state 3 as a result of heat rejection to the surroundings. The temperature of the refrigerant at this state is still above the temperature of the surroundings.

All four components associated with the vaporcompression refrigeration cycle are steady-flow devices, and thus all four processes that make up the cycle can be analyzed as steady-flow processes. The kinetic and potential energy changes of the refrigerant are usually small relative to the work and heat transfer terms, and therefore they can be neglected. Then the steady flow energy equation on a unit–mass basis reduces to

$$(q_{\rm in} - q_{\rm out}) + (w_{\rm in} - w_{\rm out}) = h_e - h_i$$
 (11-6)

The condenser and the evaporator do not involve any work, and the compressor can be approximated as adiabatic. Then the COPs of refrigerators and heat pumps operating on the vapor-compression refrigeration cycle can be expressed as

 $\text{COP}_{\text{R}} = \frac{q_L}{w_{\text{net,in}}} = \frac{h_1 - h_4}{h_2 - h_1}$

(11–7)

(11-8)

and

$$\text{COP}_{\text{HP}} = \frac{q_H}{w_{\text{net in}}} = \frac{h_2 - h_3}{h_2 - h_1}$$

where $h_1 = h_{g @ P_1}$ and $h_3 = h_{f @ P_3}$ for the ideal case.



FIGURE 11–4

An ordinary household refrigerator





FIGURE 11-6

T-s diagram of the ideal vaporcompression refrigeration cycle described in Example 11–1.

EXAMPLE 11–1 The Ideal Vapor-Compression Refrigeration Cycle

A refrigerator uses refrigerant-134a as the working fluid and operates on an ideal vapor-compression refrigeration cycle between 0.14 and 0.8 MPa. If the mass flow rate of the refrigerant is 0.05 kg/s, determine (*a*) the rate of heat removal from the refrigerated space and the power input to the compressor, (*b*) the rate of heat rejection to the environment, and (*c*) the COP of the refrigerator.

SOLUTION A refrigerator operates on an ideal vapor-compression refrigeration cycle between two specified pressure limits. The rate of refrigeration, the power input, the rate of heat rejection, and the COP are to be determined.

Assumptions 1 Steady operating conditions exist. **2** Kinetic and potential energy changes are negligible.

Analysis The *T*-s diagram of the refrigeration cycle is shown in Fig. 11–6. We note that this is an ideal vapor-compression refrigeration cycle, and thus the compressor is isentropic and the refrigerant leaves the condenser as a saturated liquid and enters the compressor as saturated vapor. From the refrigerant-134a tables, the enthalpies of the refrigerant at all four states are determined as follows:

$$P_{1} = 0.14 \text{ MPa} \longrightarrow h_{1} = h_{g@0.14 \text{ MPa}} = 239.19 \text{ kJ/kg}$$

$$s_{1} = s_{g@0.14 \text{ MPa}} = 0.94467 \text{ kJ/kg.K}$$

$$P_{2} = 0.8 \text{ MPa}$$

$$s_{2} = s_{1}$$

$$h_{2} = 275.40 \text{ kJ/kg}$$

$$P_{3} = 0.8 \text{ MPa} \longrightarrow h_{3} = h_{f@0.8 \text{ MPa}} = 95.48 \text{ kJ/kg}$$

$$h \approx h \text{ (throttling)} \longrightarrow h = 95.48 \text{ kJ/kg}$$

(a) The rate of heat removal from the refrigerated space and the power input to the compressor are determined from their definitions:

 $\dot{Q}_L = \dot{m}(h_1 - h_4) = (0.05 \text{ kg/s})[(239.19 - 95.48) \text{ kJ/kg}] = 7.19 \text{ kW}$ and

 $\dot{W}_{in} = \dot{m}(h_2 - h_1) = (0.05 \text{ kg/s})[(275.40 - 239.19) \text{ kJ/kg}] = 1.81 \text{ kW}$

(b) The rate of heat rejection from the refrigerant to the environment is

$$\dot{Q}_{H} = \dot{m}(h_2 - h_3) = (0.05 \text{ kg/s})[(275.40 - 95.48) \text{ kJ/kg}] = 9.00 \text{ kW}$$

It could also be determined from

$$\dot{Q}_H = \dot{Q}_L + \dot{W}_{in} = 7.19 + 1.81 = 9.00 \,\text{kW}$$

(c) The coefficient of performance of the refrigerator is

$$\text{COP}_{\text{R}} = \frac{\dot{Q}_L}{\dot{W}_{\text{in}}} = \frac{7.19 \text{ kW}}{1.81 \text{ kW}} = 3.97$$

That is, this refrigerator removes about 4 units of thermal energy from the refrigerated space for each unit of electric energy it consumes.

11-4 ACTUAL VAPOR-COMPRESSION REFRIGERATION CYCLE

An actual vapor-compression refrigeration cycle differs from the ideal one in several ways, owing mostly to the irreversibilities that occur in various components. Two common sources of irreversibilities are fluid friction (causes pressure drops) and heat transfer to or from the surroundings. The *T*-*s* diagram of an actual vapor-compression refrigeration cycle is shown in Fig. 11-7



EXAMPLE 11-2

The Actual Vapor-Compression Refrigeration Cycle

Refrigerant-134a enters the compressor of a refrigerator as superheated vapor at 0.14 MPa and -10° C at a rate of 0.05 kg/s and leaves at 0.8 MPa and 50°C. The refrigerant is cooled in the condenser to 26°C and 0.72 MPa and is throttled to 0.15 MPa. Disregarding any heat transfer and pressure drops in the connecting lines between the components, determine (*a*) the rate of heat removal from the refrigerated space and the power input to the compressor, (*b*) the isentropic efficiency of the compressor, and (*c*) the coefficient of performance of the refrigerator.

SOLUTION A refrigerator operating on a vapor-compression cycle is considered. The rate of refrigeration, the power input, the compressor efficiency, and the COP are to be determined.

Assumptions 1 Steady operating conditions exist. 2 Kinetic and potential energy changes are negligible.

Analysis The *T*-s diagram of the refrigeration cycle is shown in Fig. 11–8. We note that the refrigerant leaves the condenser as a compressed liquid and enters the compressor as superheated vapor. The enthalpies of the refrigerant at various states are determined from the refrigerant tables to be

$$\begin{array}{l} P_{1} = 0.14 \text{ MPa} \\ T_{1} = -10^{\circ}\text{C} \end{array} \hspace{0.2cm} h_{1} = 246.37 \text{ kJ/kg} \\ \end{array} \\ \begin{array}{l} P_{2} = 0.8 \text{ MPa} \\ T_{2} = 50^{\circ}\text{C} \end{array} \end{array} \hspace{0.2cm} h_{2} = 286.71 \text{ kJ/kg} \\ \end{array} \\ \begin{array}{l} P_{3} = 0.72 \text{ MPa} \\ T_{3} = 26^{\circ}\text{C} \end{array} \end{array} \hspace{0.2cm} h_{3} \cong h_{f@\ 26^{\circ}\text{C}} = 87.83 \text{ kJ/kg} \\ \end{array} \\ \begin{array}{l} h_{4} \cong h_{3} \text{ (throttling)} \longrightarrow h_{4} = 87.83 \text{ kJ/kg} \end{array}$$

(a) The rate of heat removal from the refrigerated space and the power input to the compressor are determined from their definitions:

$$\dot{Q}_L = \dot{m}(h_1 - h_4) = (0.05 \text{ kg/s})[(246.37 - 87.83) \text{ kJ/kg}] = 7.93 \text{ kW}$$

and

$$\dot{W}_{in} = \dot{m}(h_2 - h_1) = (0.05 \text{ kg/s})[(286.71 - 246.37) \text{ kJ/kg}] = 2.02 \text{ kW}$$



FIGURE 11–8 *T-s* diagram for Example 11–2.

(b) The isentropic efficiency of the compressor is determined from

$$\eta_C \cong \frac{h_{2s} - h_1}{h_2 - h_1}$$

where the enthalpy at state 2s (P_{2s} = 0.8 MPa and s_{2s} = s_1 = 0.9724 kJ/ kg·K) is 284.20 kJ/kg. Thus,

$$\eta_C = \frac{284.20 - 246.37}{286.71 - 246.37} = 0.938 \text{ or } 93.8\%$$

(c) The coefficient of performance of the refrigerator is

$$\text{COP}_{\text{R}} = \frac{Q_L}{\dot{W}_{\text{in}}} = \frac{7.93 \text{ kW}}{2.02 \text{ kW}} = 3.93$$

Discussion This problem is identical to the one worked out in Example 11–1, except that the refrigerant is slightly superheated at the compressor inlet and subcooled at the condenser exit. Also, the compressor is not isentropic. As a result, the heat removal rate from the refrigerated space increases (by 10.3 percent), but the power input to the compressor increases even more (by 11.6 percent). Consequently, the COP of the refrigerator decreases from 3.97 to 3.93.

GASMIXTURES

13–1 . COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

To determine the properties of a mixture, we need to know the *composition* of the mixture as well as the properties of the individual components. There are two ways to describe the composition of a mixture: either by specifying the number of moles of each component, called **molar analysis**, or by specifying the mass of each component, called **gravimetric analysis**.

Consider a gas mixture composed of k components. The mass of the mixture m m is the sum of the masses of the individual components, and the mole number of the mixture N m is the sum of the mole numbers of the individual components* (Figs. 13–1 and 13–2). That is,

$$m_m = \sum_{i=1}^k m_i$$
 and $N_m = \sum_{i=1}^k N_i$ (13–1a, b)

The ratio of the mass of a component to the mass of the mixture is called the **mass fraction** mf, and the ratio of the mole number of a component to the mole number of the mixture is called the **mole fraction** *y*:

$$\mathrm{mf}_i = \frac{m_i}{m_m}$$
 and $y_i = \frac{N_i}{N_m}$ (13–2*a*, *b*)

Dividing Eq. 13-1a by *mm* or Eq. 13-1b by *Nm*, we can easily show that the sum of the mass fractions or mole fractions for a mixture is equal to 1 (Fig. 13-3):

$$\sum_{i=1}^{k} mf_i = 1$$
 and $\sum_{i=1}^{k} y_i = 1$

The mass of a substance can be expressed in terms of the mole number N and molar mass M of the substance as m 5 NM. Then the **apparent** (or **average**) **molar mass** and the **gas constant** of a mixture can be expressed as

$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_{i=1}^k y_i M_i \text{ and } R_m = \frac{R_u}{M_m} \quad (13-3a, b)$$

The molar mass of a mixture can also be expressed as

$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i / M_i} = \frac{1}{\sum m_i / (m_m M_i)} = \frac{1}{\sum_{i=1}^k \frac{\mathrm{mf}_i}{M_i}}$$
(13-4)

Mass and mole fractions of a mixture are related by



EXAMPLE 13-1 Mass and Mole Fractions of a Gas Mixture

Consider a gas mixture that consists of 3 kg of O_2 , 5 kg of N_2 , and 12 kg of CH₄, as shown in Fig. 13–4. Determine (*a*) the mass fraction of each component, (*b*) the mole fraction of each component, and (*c*) the average molar mass and gas constant of the mixture.

SOLUTION The masses of components of a gas mixture are given. The mass fractions, the mole fractions, the molar mass, and the gas constant of the mixture are to be determined.

Analysis (a) The total mass of the mixture is

$$m_m = m_{O_2} + m_{N_2} + m_{CH_4} = 3 + 5 + 12 = 20 \text{ kg}$$

Then, the mass fraction of each component becomes

$$mf_{O_2} = \frac{m_{O_2}}{m_m} = \frac{3 \text{ kg}}{20 \text{ kg}} = 0.15$$
$$mf_{N_2} = \frac{m_{N_2}}{m_m} = \frac{5 \text{ kg}}{20 \text{ kg}} = 0.25$$
$$mf_{CH_4} = \frac{m_{CH_4}}{m_m} = \frac{12 \text{ kg}}{20 \text{ kg}} = 0.60$$

(*b*) To find the mole fractions, we need to determine the mole numbers of each component first:

$$N_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{3 \text{ kg}}{32 \text{ kg/kmol}} = 0.094 \text{ kmol}$$
$$N_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{5 \text{ kg}}{28 \text{ kg/kmol}} = 0.179 \text{ kmol}$$
$$N_{CH_4} = \frac{m_{CH_4}}{M_{CH_4}} = \frac{12 \text{ kg}}{16 \text{ kg/kmol}} = 0.750 \text{ kmol}$$

Thus,

$$N_m = N_{O_2} + N_{N_2} + N_{CH_4} = 0.094 + 0.179 + 0.750 = 1.023 \text{ kmol}$$

and

$$y_{O_2} = \frac{N_{O_2}}{N_m} = \frac{0.094 \text{ kmol}}{1.023 \text{ kmol}} = 0.092$$
$$y_{N_2} = \frac{N_{N_2}}{N_m} = \frac{0.179 \text{ kmol}}{1.023 \text{ kmol}} = 0.175$$
$$y_{CH_4} = \frac{N_{CH_4}}{N_m} = \frac{0.750 \text{ kmol}}{1.023 \text{ kmol}} = 0.733$$

(c) The average molar mass and gas constant of the mixture are determined from their definitions,

$$M_m = \frac{m_m}{N_m} = \frac{20 \text{ kg}}{1.023 \text{ kmol}} = 19.6 \text{ kg/kmol}$$

or

$$M_m = \sum y_i M_i = y_{O_2} M_{O_2} + y_{N_2} M_{N_2} + y_{CH_4} M_{CH_4}$$

= (0.092)(32) + (0.175)(28) + (0.733)(16)
= 19.6 kg/kmol

Also,

$$R_m = \frac{R_u}{M_m} = \frac{8.314 \text{ kJ/kmol} \cdot \text{K}}{19.6 \text{ kg/kmol}} = 0.424 \text{ kJ/kg} \cdot \text{K}$$

Discussion When mass fractions are available, the molar mass and mole fractions could also be determined directly from Eqs. 13–4 and 13–5.

13–2 . *P-v-T* BEHAVIOR OF GAS MIXTURES: IDEAL AND REAL GASES

An ideal gas is defined as a gas whose molecules are spaced far apart so that the behavior of a molecule is not influenced by the presence of other molecules—a situation encountered at low densities. We also mentioned that real gases approximate this behavior closely when they are at a low pressure or high temperature relative to their critical-point values. The *P-v-T* behavior of an ideal gas is expressed by the simple relation Pv 5 RT, which is called the *ideal-gas equation of state*. The *P-v-T* behavior of real gases is expressed by more complex equations of state or by Pv 5 ZRT, where *Z* is the compressibility factor. When two or more ideal gases are mixed, the behavior of a molecule normally is not influenced by the presence of other similar or dissimilar molecules, and therefore a nonreacting mixture of ideal gases also behaves as an ideal gas. Air, for example, is conveniently treated as an ideal gas in the range where nitrogen and oxygen behave as ideal gases. When a gas mixture consists of real (nonideal) gases, however, the prediction of the *P-v-T* behavior of the mixture becomes rather involved. The prediction of the *P-v-T* behavior of gas mixtures is usually based on two models: *Dalton's law of additive pressures* and *Amagat's law of additive volumes*. Both models are described and discussed below.

Dalton's law of additive pressures: The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at the mixture temperature and volume (Fig. 13–5). **Amagat's law of additive volumes:** The volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure (Fig. 13–6).



Dalton's and Amagat's laws hold exactly for ideal-gas mixtures, but only approximately for real-gas mixtures. This is due to intermolecular forces that may be significant for real gases at high densities. For ideal gases, these two laws are identical and give identical results. Dalton's and Amagat's laws can be expressed as follows:

Dalton's law:

$$P_{m} = \sum_{i=1}^{k} P_{i}(T_{m}, V_{m}) \begin{cases} \text{exact for ideal gases,} & (13-6) \\ \text{approximate} \\ \text{for real gases} & (13-7) \end{cases}$$

In these relations, Pi is called the **component pressure** and Vi is called the **component volume** (Fig. 13–7). Note that Vi is the volume a component *would* occupy if it existed alone at Tm and Pm, not the actual volume occupied by the component in the mixture. (In a vessel that holds a gas mixture, each component fills the entire volume of the vessel.) Therefore, the volume of each component is equal to the volume of the vessel.) Also, the ratio P i/Pm is called the **pressure fraction** and the ratio Vi/Vm is called the **volume fraction** of component *i*.



IGURE 13–7

The volume a component would occupy if it existed alone at the mixture T and P is called the *component volume* (for ideal gases, it is equal to the partial volume yiVm).

Ideal-Gas Mixtures

For ideal gases, Pi and Vi can be related to yi by using the ideal-gas relation for both the components and the gas mixture:

$$\frac{P_i(T_m, V_m)}{P_m} = \frac{N_i R_u T_m / V_m}{N_m R_u T_m / V_m} = \frac{N_i}{N_m} = y_i$$
$$\frac{V_i(T_m, P_m)}{V_m} = \frac{N_i R_u T_m / P_m}{N_m R_u T_m / P_m} = \frac{N_i}{N_m} = y_i$$

Therefore,

$$\frac{P_i}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$
(13-8)

Equation 13–8 is strictly valid for ideal-gas mixtures since it is derived by assuming ideal-gas behavior for the gas mixture and each of its components. The quantity *yiPm* is called the **partial pressure** (identical to the *component pressure* for ideal gases), and the quantity *yiVm* is called the **partial volume** (identical to the *component volume* for ideal gases). *Note that for an idealgas mixture, the mole fraction, the pressure fraction, and the volume fraction of a component are identical.*

Real-Gas Mixtures

Dalton's law of additive pressures and Amagat's law of additive volumes can also be used for real gases, often with reasonable accuracy. This time, however, the component pressures or component volumes should be evaluated from relations that take into account the deviation of each component from ideal-gas behavior. One way of doing that is to use more exact equations of state (van der Waals, Beattie–Bridgeman, Benedict–Webb–Rubin, etc.) instead of the ideal-gas equation of state. Another way is to use the compressibility factor (Fig. 13–8) as

(13 - 9)

$PV = ZNR_{u}T$

The compressibility factor of the mixture Z_m can be expressed in terms of the compressibility factors of the individual gases Z_i by applying Eq. 13–9 to both sides of Dalton's law or Amagat's law expression and simplifying. We obtain

$$Z_m = \sum_{i=1}^k y_i Z_i$$
 (13-10)

where Z_i is determined either at T_m and V_m (Dalton's law) or at T_m and P_m (Amagat's law) for each individual gas. It may seem that using either law gives the same result, but it does not.

Another approach for predicting the P-v-T behavior of a gas mixture is to treat the gas mixture as a pseudopure substance (Fig. 13–9). One such method, proposed by W. B. Kay in 1936 and called **Kay's rule**, involves the use of a *pseudocritical pressure* Pcr 9,m and *pseudocritical temperature* T9 cr,m for the mixture, defined in terms of the critical pressures and temperatures of the mixture components as .

$$P'_{cr,m} = \sum_{i=1}^{k} y_i P_{cr,i}$$
 and $T'_{cr,m} = \sum_{i=1}^{k} y_i T_{cr,i}$ (13-11*a*, *b*)



FIGURE 13-8

One way of predicting the *P-v-T* behavior of a real-gas mixture is to use compressibility factor.



The compressibility factor of the mixture Zm is then easily determined by using these pseudocritical properties. The result obtained by using Kay's rule is accurate to within about 10 percent over a wide range of temperatures and pressures, which is acceptable for most engineering purposes.

Another way of treating a gas mixture as a pseudopure substance is to use a more accurate equation of state such as the van der Waals, Beattie– Bridgeman, or Benedict–Webb–Rubin equation for the mixture, and to determine the constant coefficients in terms of the coefficients of the components. In the van der Waals equation, for example, the two constants for the mixture are determined from

$$a_m = \left(\sum_{i=1}^k y_i a_i^{1/2}\right)^2$$
 and $b_m = \sum_{i=1}^k y_i b_i$ (13–12*a*, *b*)

where expressions for *ai* and *bi* are given in Chapter 3

EXAMPLE 13–2 P-v-T Behavior of Nonideal Gas Mixtures

A rigid tank contains 2 kmol of N_2 and 6 kmol of CO_2 gases at 300 K and 15 MPa (Fig. 13–10). Estimate the volume of the tank on the basis of (*a*) the ideal-gas equation of state, (*b*) Kay's rule, (*c*) compressibility factors and Amagat's law, and (*d*) compressibility factors and Dalton's law.

SOLUTION The composition of a mixture in a rigid tank is given. The volume of the tank is to be determined using four different approaches. *Assumptions* Stated in each section.

Analysis (a) When the mixture is assumed to behave as an ideal gas, the volume of the mixture is easily determined from the ideal-gas relation for the mixture:

$$V_m = \frac{N_m R_u T_m}{P_m} = \frac{(8 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(300 \text{ K})}{15,000 \text{ kPa}} = 1.330 \text{ m}^3$$

since

$$N_m = N_{N_0} + N_{CO_0} = 2 + 6 = 8$$
 kmol

(b) To use Kay's rule, we need to determine the pseudocritical temperature and pseudocritical pressure of the mixture by using the critical-point properties of N₂ and CO₂ from Table A–1. However, first we need to determine the mole fraction of each component:

$$y_{N_2} = \frac{N_{N_2}}{N_m} = \frac{2 \text{ kmol}}{8 \text{ kmol}} = 0.25 \text{ and } y_{CO_2} = \frac{N_{CO_2}}{N_m} = \frac{6 \text{ kmol}}{8 \text{ kmol}} = 0.75$$
$$T'_{cr,m} = \sum y_i T_{cr,i} = y_{N_2} T_{cr,N_2} + y_{CO_2} T_{cr,CO_2}$$
$$= (0.25)(126.2 \text{ K}) + (0.75)(304.2 \text{ K}) = 259.7 \text{ K}$$

$$P_{\text{cr},m} = \sum y_i P_{\text{cr},i} = y_{N_2} P_{\text{cr},N_2} + y_{\text{CO}_2} P_{\text{cr},\text{CO}_2}$$

= (0.25)(3.39 MPa) + (0.75)(7.39 MPa) = 6.39 MPa



FIGURE 13–10 Schematic for Example 13–2.

Then,

$$T_{R} = \frac{T_{m}}{T'_{cr,m}} = \frac{300 \text{ K}}{259.7 \text{ K}} = 1.16$$

$$P_{R} = \frac{P_{m}}{P'_{cr,m}} = \frac{15 \text{ MPa}}{6.39 \text{ MPa}} = 2.35$$

$$Z_{m} = 0.49 \quad \text{(Fig. A-15b)}$$

Thus,

$$V_m = \frac{Z_m N_m R_u T_m}{P_m} = Z_m V_{\text{ideal}} = (0.49)(1.330 \text{ m}^3) = 0.652 \text{ m}^3$$

(c) When Amagat's law is used in conjunction with compressibility factors, Z_m is determined from Eq. 13–10. But first we need to determine the Z of each component on the basis of Amagat's law:

$$N_{2}: \quad T_{R,N_{2}} = \frac{T_{m}}{T_{cr,N_{2}}} = \frac{300 \text{ K}}{126.2 \text{ K}} = 2.38$$

$$P_{R,N_{2}} = \frac{P_{m}}{P_{cr,N_{2}}} = \frac{15 \text{ MPa}}{3.39 \text{ MPa}} = 4.42$$

$$Z_{N_{2}} = 1.02 \quad (\text{Fig. A-15}b)$$

$$CO_{2}: \quad T_{R,CO_{2}} = \frac{T_{m}}{T_{cr,CO_{2}}} = \frac{300 \text{ K}}{304.2 \text{ K}} = 0.99$$

$$P_{R,CO_{2}} = \frac{P_{m}}{P_{cr,CO_{2}}} = \frac{15 \text{ MPa}}{7.39 \text{ MPa}} = 2.03$$

$$Z_{CO_{2}} = 0.30 \quad (\text{Fig. A-15}b)$$

Mixture:

$$Z_m = \sum y_i Z_i = y_{N_2} Z_{N_2} + y_{CO_2} Z_{CO_2}$$

= (0.25)(1.02) + (0.75)(0.30) = 0.48

Thus,

$$V_m = \frac{Z_m N_m R_u T_m}{P_m} = Z_m V_{\text{ideal}} = (0.48)(1.330 \text{ m}^3) = 0.638 \text{ m}^3$$

The compressibility factor in this case turned out to be almost the same as the one determined by using Kay's rule.

(d) When Dalton's law is used in conjunction with compressibility factors, Z_m is again determined from Eq. 13–10. However, this time the Z of each component is to be determined at the mixture temperature and volume, which is not known. Therefore, an iterative solution is required. We start the calculations by assuming that the volume of the gas mixture is 1.330 m³, the value determined by assuming ideal-gas behavior.

The T_R values in this case are identical to those obtained in part (*c*) and remain constant. The pseudoreduced volume is determined from its definition in Chap. 3:

$$v_{R,N_2} = \frac{\overline{v}_{N_2}}{R_u T_{cr,N_2} / P_{cr,N_2}} = \frac{V_m / N_{N_2}}{R_u T_{cr,N_2} / P_{cr,N_2}}$$
$$= \frac{(1.33 \text{ m}^3) / (2 \text{ kmol})}{(8.314 \text{ kPa} \cdot \text{m}^3 / \text{kmol} \cdot \text{K})(126.2 \text{ K}) / (3390 \text{ kPa})} = 2.15$$

Similarly,

$$v_{R,CO_2} = \frac{(1.33 \text{ m}^3)/(6 \text{ kmol})}{(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(304.2 \text{ K})/(7390 \text{ kPa})} = 0.648$$

From Fig. A–15, we read $Z_{N_2} = 0.99$ and $Z_{CO_2} = 0.56$. Thus,

$$Z_m = y_{N_2} Z_{N_2} + y_{CO_2} Z_{CO_2} = (0.25)(0.99) + (0.75)(0.56) = 0.67$$

and

$$V_m = \frac{Z_m N_m R T_m}{P_m} = Z_m V_{\text{ideal}} = (0.67)(1.330 \text{ m}^3) = 0.891 \text{ m}^3$$

This is 33 percent lower than the assumed value. Therefore, we should repeat the calculations, using the new value of V_m . When the calculations are repeated we obtain 0.738 m³ after the second iteration, 0.678 m³ after the third iteration, and 0.648 m³ after the fourth iteration. This value does not change with more iterations. Therefore,

$$V_m = 0.648 \text{ m}^3$$

Discussion Notice that the results obtained in parts (*b*), (*c*), and (*d*) are very close. But they are very different from the ideal-gas values. Therefore, treating a mixture of gases as an ideal gas may yield unacceptable errors at high pressures.

13-3 .PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

Consider a gas mixture that consists of 2 kg of N₂ and 3 kg of CO₂. The total mass (an *extensive property*) of this mixture is 5 kg. How did we do it? Well, we simply added the mass of each component. This example suggests a simple way of evaluating the **extensive properties** of a nonreacting idealor real-gas mixture: *Just add the contributions of each component of the mixture* (Fig. 13–11). Then the total internal energy, enthalpy, and entropy of a gas mixture can be expressed, respectively, as

$U_{m} = \sum_{i=1}^{k} U_{i} = \sum_{i=1}^{k} m_{i} u_{i} = \sum_{i=1}^{k} N_{i} \bar{u}_{i} (kJ)$	(13–13)	0
$H_m = \sum_{i=1}^{k} H_i = \sum_{i=1}^{k} m_i h_i = \sum_{i=1}^{k} N_i \overline{h}_i$ (kJ)	(13–14)	$\begin{array}{c} \bullet \\ & 2 \text{ kmol } A \\ & 6 \text{ kmol } B \\ \hline \\ & U_A = 1000 \text{ kJ} \end{array}$
$S_m = \sum_{i=1}^k S_i = \sum_{i=1}^k m_i s_i = \sum_{i=1}^k N_i \overline{s}_i (kJ/K)$	(13–15)	$U_B = 1800 \text{ kJ}$ $U_m = 2800 \text{ kJ}$
enthalpy, and entropy of a gas mixture during a pr expressed, respectively, as	rocess can be	·
$\Delta U_m = \sum_{i=1}^{n} \Delta U_i = \sum_{i=1}^{n} m_i \Delta u_i = \sum_{i=1}^{n} N_i \Delta \bar{u}_i \text{(kJ)}$	(13–16)	FIGURE 13–11 The extensive properties of a mixture are determined by simply adding the properties of the components.

$$\Delta H_m = \sum_{i=1}^k \Delta H_i = \sum_{i=1}^k m_i \,\Delta h_i = \sum_{i=1}^k N_i \,\Delta \bar{h}_i \quad \text{(kJ)} \quad (13-17)$$
$$\Delta S_m = \sum_{i=1}^k \Delta S_i = \sum_{i=1}^k m_i \,\Delta s_i = \sum_{i=1}^k N_i \,\Delta \bar{s}_i \quad \text{(kJ/K)} \quad (13-18)$$

Now reconsider the same mixture, and assume that both N2 and CO2 are at 258C. The temperature (an *intensive* property) of the mixture is, as you would expect, also 258C. Notice that we did not add the component temperatures to determine the mixture temperature. Instead, we used some kind of averaging scheme, a characteristic approach for determining the **intensive properties** of a mixture. The internal energy, enthalpy, and entropy of a mixture *per unit mass* or *per unit mole* of the mixture can be determined by dividing the equations above by the mass or the mole number of the mixture (*mm* or *Nm*). We obtain (Fig. 13–12)

$$u_m = \sum_{i=1}^{k} \mathrm{mf}_i u_i \quad (\mathrm{kJ/kg}) \quad \mathrm{and} \quad \bar{u}_m = \sum_{i=1}^{k} y_i \bar{u}_i \, (\mathrm{kJ/kmol}) \tag{13-19}$$

$$h_m = \sum_{i=1}^{k} \mathrm{mf}_i h_i \quad (\mathrm{kJ/kg}) \quad \mathrm{and} \quad \bar{h}_m = \sum_{i=1}^{k} y_i \bar{h}_i \quad (\mathrm{kJ/kmol}) \tag{13-20}$$

$$s_m = \sum_{i=1}^{k} \mathrm{mf}_i s_i \quad (\mathrm{kJ/kg} \cdot \mathrm{K}) \quad \mathrm{and} \quad \bar{s}_m = \sum_{i=1}^{k} y_i \bar{s}_i \quad (\mathrm{kJ/kmol} \cdot \mathrm{K}) \tag{13-21}$$

Similarly, the specific heats of a gas mixture can be expressed as

$$c_{v,m} = \sum_{i=1}^{k} \text{mf}_{i} c_{v,i} \quad (kJ/kg\cdot K) \text{ and } \bar{c}_{v,m} = \sum_{i=1}^{k} y_{i} \bar{c}_{v,i} \quad (kJ/kmol\cdot K) \quad (13-22)$$
$$c_{p,m} = \sum_{i=1}^{k} \text{mf}_{i} c_{p,i} \quad (kJ/kg\cdot K) \text{ and } \bar{c}_{p,m} = \sum_{i=1}^{k} y_{i} \bar{c}_{p,i} \quad (kJ/kmol\cdot K) \quad (13-23)$$





Notice that *properties per unit mass involve* mass fractions (mfi) and properties per unit *mole involve mole fractions* (*y^{<i>i*}). The relations given above are exact for ideal-gas mixtures, and approximate for real-gas mixtures. (In fact, they are also applicable to nonreacting liquid and solid solutions especially when they form an "ideal solution.") The only major difficulty associated with these relations is the determination of properties for each individual gas in the mixture. The analysis can be simplified greatly, however, by treating the individual gases as ideal gases, if doing so does not introduce a significant error.

Ideal-Gas Mixtures

The gases that comprise a mixture are often at a high temperature and low pressure relative to the critical-point values of individual gases. In such cases, the gas mixture and its components can be treated as ideal gases with negligible error. Under the ideal-gas approximation, the properties of a gas are not influenced by the presence of other gases, and each gas component in the mixture behaves as if it exists alone at the mixture temperature Tm and mixture volume Vm. This principle is known as the **Gibbs–Dalton law**, which is an extension of Dalton's law of additive pressures. Also, the *h*, *u*, *cv*, and *cp* of

an ideal gas depend on temperature only and are independent of the pressure or the volume of the ideal-gas mixture. The partial pressure of a component in an ideal-gas mixture is simply Pi 5 yi Pm, where Pm is the mixture pressure.

Evaluation of Du or Dh of the components of an ideal-gas mixture during a process is relatively easy since it requires only a knowledge of the initial and final temperatures. Care should be exercised, however, in evaluating the Ds of the components since the entropy of an ideal gas depends on the pressure or volume of the component as well as on its temperature. The entropy change of individual gases in an ideal-gas mixture during a process can be determined from

$$\Delta s_i = s_{i,2}^{\circ} - s_{i,1}^{\circ} - R_i \ln \frac{P_{i,2}}{P_{i,1}} \cong c_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_i \ln \frac{P_{i,2}}{P_{i,1}}$$
(13-24)

$$\Delta \bar{s}_{i} = \bar{s}_{i,2}^{\circ} - \bar{s}_{i,1}^{\circ} - R_{u} \ln \frac{P_{i,2}}{P_{i,1}} \cong \bar{c}_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_{u} \ln \frac{P_{i,2}}{P_{i,1}}$$
(13-25)

where *P i*,2 5 *yi*,2*Pm*,2 and *Pi*,1 5 *yi*,1*Pm*,1. Notice that the partial pressure *Pi* of each component is used in the evaluation of the entropy change, not the mixture pressure *Pm* (Fig. 13–13).



EXAMPLE 13-3 Expansion of an Ideal Gas Mixture in a Turbine

A mixture of oxygen (O_2), carbon dioxide (CO_2), and helium (He) gases with mass fractions of 0.0625, 0.625, and 0.3125, respectively, enter an adiabatic turbine at 1000 kPa and 600 K steadily and expand to 100 kPa pressure (Fig. 13–14). The isentropic efficiency of the turbine is 90 percent. For gas components assuming constant specific heats at room temperature, determine (*a*) the work output her unit mass of mixture and (*b*) the exergy destruction and the second-law efficiency of the turbine. Take the environment temperature to be $T_0 = 25^{\circ}$ C.

SOLUTION The mass fractions of the components of a gas mixture that expands in an adiabatic turbine are given. The work output, the exergy destruction, and the second-law efficiency are to be determined.

Assumptions All gases will be modeled as ideal gases with constant specific heats.

Analysis (a) The mass fractions of mixture components are given to be $mf_{O_2} = 0.0625$, $mf_{CO_2} = 0.625$, and $mf_{He} = 0.3125$. The specific heats of these gases at room temperature are (Table A–2a):

	<i>c</i> _v , kJ/kg⋅K	<i>c_p,</i> kJ/kg⋅K
0 ₂ :	0.658	0.918
CO ₂ :	0.657	0.846
He:	3.1156	5.1926

Then, the constant-pressure and constant-volume specific heats of the mixture become $% \left({{{\left[{{{c_{\rm{m}}}} \right]}_{\rm{max}}}} \right)$



FIGURE 13–14 Schematic for Example 13–3.

or

$$\begin{split} c_p &= \mathrm{mf}_{\mathrm{O}_2} c_{p,\mathrm{O}_2} + \mathrm{mf}_{\mathrm{CO}_2} c_{p,\mathrm{CO}_2} + \mathrm{mf}_{\mathrm{He}} c_{p,\mathrm{He}} \\ &= 0.0625 \times 0.918 + 0.625 \times 0.846 + 0.3125 \times 5.1926 \\ &= 2.209 \,\mathrm{kJ/kg\cdot K} \\ c_v &= \mathrm{mf}_{\mathrm{O}_2} c_{v,\mathrm{O}_2} + \mathrm{mf}_{\mathrm{CO}_2} c_{v,\mathrm{CO}_2} + \mathrm{mf}_{\mathrm{He}} c_{v,\mathrm{He}} \\ &= 0.0625 \times 0.658 + 0.625 \times 0.657 + 0.3125 \times 3.1156 \\ &= 1.425 \,\mathrm{kJ/kg\cdot K} \end{split}$$

The apparent gas constant of the mixture and the specific heat ratio are

$$R = c_p - c_v = 2.209 - 1.425 = 0.7836 \text{ kJ/kg} \cdot \text{K}$$
$$k = \frac{c_p}{c_v} = \frac{2.209 \text{ kJ/kg} \cdot \text{K}}{1.425 \text{ kJ/kg} \cdot \text{K}} = 1.550$$

The temperature at the end of the expansion for the isentropic process is

$$T_{2s} = T_1 \left(\frac{P_2}{P_1}\right)^{(k-1)/k} = (600 \text{ K}) \left(\frac{100 \text{ kPa}}{1000 \text{ kPa}}\right)^{0.55/1.55} = 265.0 \text{ K}$$

Using the definition of turbine isentropic efficiency, the actual outlet temperature is

$$T_2 = T_1 - \eta_{\text{turb}}(T_1 - T_{2s}) = (600 \text{ K}) - (0.90)(600 - 265) \text{ K} = 298.5 \text{ K}$$

Noting that the turbine is adiabatic and thus there is no heat transfer, the actual work output is determined to be

$$w_{\text{out}} = h_1 - h_2 = c_p (T_1 - T_2) = (2.209 \text{ kJ/kg} \cdot \text{K})(600 - 298.5)$$

= 666.0 kJ/kg

(*b*) The entropy change of the gas mixture and the exergy destruction in the turbine are

$$s_{2} - s_{1} = c_{p} \ln \frac{T_{2}}{T_{1}} - R \ln \frac{P_{2}}{P_{1}} = (2.209 \text{ kJ/kg} \cdot \text{K}) \ln \frac{298.5 \text{ K}}{600 \text{ K}}$$
$$- (0.7836 \text{ kJ/kg} \cdot \text{K}) \ln \frac{100 \text{ kPa}}{1000 \text{ kPa}} = 0.2658 \text{ kJ/kg} \cdot \text{K}$$
$$x_{\text{dest}} = T_{0} s_{\text{gen}} = T_{0} (s_{2} - s_{1}) = (298 \text{ K})(0.2658 \text{ kJ/kg} \cdot \text{K}) = 79.2 \text{ kJ/kg}$$

The expended exergy is the sum of the work output of turbine (exergy recovered) and the exergy destruction (exergy wasted),

$$x_{\text{expended}} = x_{\text{recovered}} + x_{\text{dest}} = w_{\text{out}} + x_{\text{dest}} = 666.0 + 79.2 = 745.2 \text{ kJ/kg}$$

The second-law efficiency is the ratio of the recovered to expended exergy,

$$\eta_{\rm II} = \frac{x_{\rm recovered}}{x_{\rm expended}} = \frac{w_{\rm out}}{x_{\rm expended}} = \frac{666.0 \text{ kJ/kg}}{745.2 \text{ kJ/kg}} = 0.894 \text{ or } 89.4 \text{ percent}$$

Discussion The second-law efficiency is a measure of thermodynamic perfection. A process that generates no entropy and thus destroys no exergy always has a second-law efficiency of 100 percent.

EXAMPLE 13-4 Exergy Destruction during Mixing of Ideal Gases

An insulated rigid tank is divided into two compartments by a partition, as shown in Fig. 13–15. One compartment contains 3 kmol of O_2 , and the other compartment contains 5 kmol of CO_2 . Both gases are initially at 25°C and 200 kPa. Now the partition is removed, and the two gases are allowed to mix. Assuming the surroundings are at 25°C and both gases behave as ideal gases, determine the entropy change and exergy destruction associated with this process.

SOLUTION A rigid tank contains two gases separated by a partition. The entropy change and exergy destroyed after the partition is removed are to be determined.

Assumptions Both gases and their mixture are ideal gases.

Analysis We take the entire contents of the tank (both compartments) as the system. This is a *closed system* since no mass crosses the boundary during the process. We note that the volume of a rigid tank is constant, and there is no energy transfer as heat or work. Also, both gases are initially at the same temperature and pressure.

When two ideal gases initially at the same temperature and pressure are mixed by removing a partition between them, the mixture will also be at the same temperature and pressure. (Can you prove it? Will this be true for nonideal gases?) Therefore, the temperature and pressure in the tank will still be 25° C and 200 kPa, respectively, after the mixing. The entropy change of each component gas can be determined from Eqs. 13–18 and 13–25:

$$\Delta S_{m} = \sum \Delta S_{i} = \sum N_{i} \Delta \bar{s}_{i} = \sum N_{i} \left(\bar{c}_{p,i} \ln \frac{T_{i,2}}{T_{i,1}} - R_{u} \ln \frac{P_{i,2}}{P_{i,1}} \right)$$
$$= -R_{u} \sum N_{i} \ln \frac{y_{i,2}P_{m,2}}{P_{i,1}} = -R_{u} \sum N_{i} \ln y_{i,2}$$

since $P_{m,2} = P_{i,1} = 200$ kPa. It is obvious that the entropy change is independent of the composition of the mixture in this case and depends on only the mole fraction of the gases in the mixture. What is not so obvious is that if the same gas in two different chambers is mixed at constant temperature and pressure, the entropy change is zero.

Substituting the known values, the entropy change becomes

$$N_{m} = N_{O_{2}} + N_{CO_{2}} = (3 + 5) \text{ kmol} = 8 \text{ kmol}$$

$$y_{O_{2}} = \frac{N_{O_{2}}}{N_{m}} = \frac{3 \text{ kmol}}{8 \text{ kmol}} = 0.375$$

$$y_{CO_{2}} = \frac{N_{CO_{2}}}{N_{m}} = \frac{5 \text{ kmol}}{8 \text{ kmol}} = 0.625$$

$$\Delta S_{m} = -R_{u}(N_{O_{2}} \ln y_{O_{2}} + N_{CO_{2}} \ln y_{CO_{2}})$$

$$= -(8.314 \text{ kJ/kmol·K})[(3 \text{ kmol})(\ln 0.375) + (5 \text{ kmol})(\ln 0.625)]$$

$$= 44.0 \text{ kJ/K}$$



FIGURE 13–15 Schematic for Example 13–4.

The exergy destruction associated with this mixing process is determined from

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} = T_0 \Delta S_{\text{sys}}$$

= (298 K)(44.0 kJ/K)
= **13.1 MJ**

Discussion This large value of exergy destruction shows that mixing processes are highly irreversible.

Real-Gas Mixtures

When the components of a gas mixture do not behave as ideal gases, the analysis becomes more complex because the properties of real (nonideal) gases such as *u*, *h*, *cv*, and *cp* depend on the pressure (or specific volume) as well as on the temperature. In such cases, the effects of deviation from ideal-gas behavior on the mixture properties should be accounted for.

Consider two nonideal gases contained in two separate compartments of an adiabatic rigid tank at 100 kPa and 258C. The partition separating the two gases is removed, and the two gases are allowed to mix. What do you think the final pressure in the tank will be? You are probably tempted to say 100 kPa, which would be true for ideal gases. However, this is not true for nonideal gases because of the influence of the molecules of different gases on each other (deviation from Dalton's law, Fig. 13–16).

When real-gas mixtures are involved, it may be necessary to account for the effect of nonideal behavior on the mixture properties such as enthalpy and entropy. One way of doing that is to use compressibility factors in conjunction with generalized equations and charts developed in Chapter 12 for real gases.

Consider the following T ds relation for a gas mixture:

It can also be expressed as

or

or

$$\sum \mathrm{mf}_i(dh_i - T_m \, ds_i - v_i \, dP_m) = 0$$

 $dh_m = T_m ds_m + v_m dP_m$

 $d\left(\sum \mathrm{mf}_{i}h_{i}\right) = T_{m} d\left(\sum \mathrm{mf}_{i}s_{i}\right) + \left(\sum \mathrm{mf}_{i}\vee_{i}\right)dP_{m}$

which yields

$$dh_i = T_m \, ds_i + v_i \, dP_m$$

(13–26)

This is an important result because Eq. 13–26 is the starting equation in the development of the generalized relations and charts for enthalpy and entropy. It suggests that the generalized property relations and charts for real gases developed in Chapter 12 can also be used for the components of real-gas mixtures. But the reduced temperature TR and reduced pressure PR for each component should be evaluated by using the mixture temperature Tm and mixture pressure Pm. This is because Eq. 13–26 involves the mixture pressure Pm, not the component pressure Pi.



FIGURE 13–16

It is difficult to predict the behavior of nonideal-gas mixtures because of the influence of dissimilar molecules on each other The approach described above is somewhat analogous to Amagat's law of additive volumes (evaluating mixture properties at the mixture pressure and temperature), which holds exactly for ideal-gas mixtures and approximately for real-gas mixtures. Therefore, the mixture properties determined with this approach are not exact, but they are sufficiently accurate.

What if the mixture volume and temperature are specified instead of the mixture pressure and temperature? Well, there is no need to panic. Just evaluate the mixture pressure, using Dalton's law of additive pressures, and then use this value (which is only approximate) as the mixture pressure.

Another way of evaluating the properties of a real-gas mixture is to treat the mixture as a pseudopure substance having pseudocritical properties, determined in terms of the critical properties of the component gases by using Kay's rule. The approach is quite simple, and the accuracy is usually acceptable.

EXAMPLE 13-5 Cooling of a Nonideal Gas Mixture

Air is a mixture of N₂, O₂, and small amounts of other gases, and it can be approximated as 79 percent N₂ and 21 percent O₂ on mole basis. During a steady-flow process, air is cooled from 220 to 160 K at a constant pressure of 10 MPa (Fig. 13–17). Determine the heat transfer during this process per kmol of air, using (*a*) the ideal-gas approximation, (*b*) Kay's rule, and (*c*) Amagat's law.

 ${\rm SOLUTION}~$ Air at a low temperature and high pressure is cooled at constant pressure. The heat transfer is to be determined using three different approaches.

Assumptions 1 This is a steady-flow process since there is no change with time at any point and thus $\Delta m_{\rm CV} = 0$ and $\Delta E_{\rm CV} = 0$. 2 The kinetic and potential energy changes are negligible.

Analysis We take the *cooling section* as the system. This is a *control volume* since mass crosses the system boundary during the process. We note that heat is transferred out of the system.

The critical properties are $T_{\rm cr} = 126.2$ K and $P_{\rm cr} = 3.39$ MPa for N₂ and $T_{\rm cr} = 154.8$ K and $P_{\rm cr} = 5.08$ MPa for O₂. Both gases remain above their critical temperatures, but they are also above their critical pressures. Therefore, air will probably deviate from ideal-gas behavior, and thus it should be treated as a real-gas mixture.

The energy balance for this steady-flow system can be expressed on a unit mole basis as $\label{eq:steady-flow}$

$$e_{\rm in} - e_{\rm out} = \Delta e_{\rm system}^{\circ} = 0 \rightarrow e_{\rm in} = e_{\rm out} \rightarrow \bar{h}_1 = \bar{h}_2 + \bar{q}_{\rm out}$$
$$\bar{q}_{\rm out} = \bar{h}_1 - \bar{h}_2 = y_{\rm N_2}(\bar{h}_1 - \bar{h}_2)_{\rm N_2} + y_{\rm O_2}(\bar{h}_1 - \bar{h}_2)_{O_2}$$

where the enthalpy change for either component can be determined from the generalized enthalpy departure chart (Fig. A–29) and Eq. 12–58:

$$\overline{h}_1 - \overline{h}_2 = \overline{h}_{1,\text{ideal}} - \overline{h}_{2,\text{ideal}} - R_u T_{\text{cr}}(Z_{h_1} - Z_{h_2})$$



FIGURE 13–17 Schematic for Example 13–5.

The first two terms on the right-hand side of this equation represent the ideal-gas enthalpy change of the component. The terms in parentheses represent the deviation from the ideal-gas behavior, and their evaluation requires a knowledge of reduced pressure P_R and reduced temperature T_R , which are calculated at the mixture temperature T_m and mixture pressure P_m .

(a) If the N₂ and O₂ mixture is assumed to behave as an ideal gas, the enthalpy of the mixture will depend on temperature only, and the enthalpy values at the initial and the final temperatures can be determined from the ideal-gas tables of N₂ and O₂ (Tables A–18 and A–19):

$$T_{1} = 220 \text{ K} \rightarrow \overline{h}_{1,\text{ideal},N_{2}} = 6391 \text{ kJ/kmol}$$
$$\overline{h}_{1,\text{ideal},O_{2}} = 6404 \text{ kJ/kmol}$$
$$T_{2} = 160 \text{ K} \rightarrow \overline{h}_{2,\text{ideal},N_{2}} = 4648 \text{ kJ/kmol}$$
$$\overline{h}_{2,\text{ideal},O_{2}} = 4657 \text{ kJ/kmol}$$
$$\overline{q}_{\text{out}} = y_{N_{2}}(\overline{h}_{1} - \overline{h}_{2})_{N_{2}} + y_{O_{2}}(\overline{h}_{1} - \overline{h}_{2})_{O_{2}}$$

= (0.79)(6391 - 4648) kJ/kmol + (0.21)(6404 - 4657) kJ/kmol

(*b*) Kay's rule is based on treating a gas mixture as a pseudopure substance whose critical temperature and pressure are

$$T'_{cr,m} = \sum y_i T_{cr,i} = y_{N_2} T_{cr,N_2} + y_{O_2} T_{cr,O_2}$$

= (0.79)(126.2 K) + (0.21)(154.8 K) = 132.2 K

and

$$P'_{cr,m} = \sum y_i P_{cr,i} = y_{N_2} P_{cr,N_2} + y_{O_2} P_{cr,O_2}$$

= (0.79)(3.39 MPa) + (0.21)(5.08 MPa) = 3.74 MPa

Then,

$$T_{R,1} = \frac{T_{m,1}}{T_{cr,m}} = \frac{220 \text{ K}}{132.2 \text{ K}} = 1.66 \\P_R = \frac{P_m}{P_{cr,m}} = \frac{10 \text{ MPa}}{3.74 \text{ MPa}} = 2.67 \\T_{R,2} = \frac{T_{m,2}}{T_{cr,m}} = \frac{160 \text{ K}}{132.2 \text{ K}} = 1.21 \end{cases} Z_{h_2,m} = 2.6$$

Also,

$$\begin{aligned} \overline{h}_{m_{1},\text{ideal}} &= y_{N_{2}}\overline{h}_{1,\text{ideal},N_{2}} + y_{O_{2}}\overline{h}_{1,\text{ideal},O_{2}} \\ &= (0.79)(6391 \text{ kJ/kmol}) + (0.21)(6404 \text{ kJ/kmol}) \\ &= 6394 \text{ kJ/kmol} \\ \overline{h}_{m_{2},\text{ideal}} &= y_{N_{2}}\overline{h}_{2,\text{ideal},N_{2}} + y_{O_{2}}\overline{h}_{2,\text{ideal},O_{2}} \\ &= (0.79)(4648 \text{ kJ/kmol}) + (0.21)(4657 \text{ kJ/kmol}) \\ &= 4650 \text{ kJ/kmol} \end{aligned}$$

Therefore,

$$\bar{q}_{out} = (\bar{h}_{m_1,ideal} - \bar{h}_{m_2,ideal}) - R_u T_{cr} (Z_{h_1} - Z_{h_2})_m$$

= [(6394 - 4650) kJ/kmol] - (8.314 kJ/kmol·K)(132.2 K)(1.0 - 2.6)
= **3503 kJ/kmol**

(c) The reduced temperatures and pressures for both $\rm N_2$ and $\rm O_2$ at the initial and final states and the corresponding enthalpy departure factors are, from Fig. A–29,

N₂:

$$T_{R_{1},N_{2}} = \frac{T_{m,1}}{T_{cr,N_{2}}} = \frac{220 \text{ K}}{126.2 \text{ K}} = 1.74$$

$$P_{R,N_{2}} = \frac{P_{m}}{P_{cr,N_{2}}} = \frac{10 \text{ MPa}}{3.39 \text{ MPa}} = 2.95$$

$$T_{R_{2},N_{2}} = \frac{T_{m,2}}{T_{cr,N_{2}}} = \frac{160 \text{ K}}{126.2 \text{ K}} = 1.27$$

$$Z_{h_{1},N_{2}} = 0.9$$

O₂:

$$T_{R_{1},O_{2}} = \frac{T_{m,1}}{T_{cr,O_{2}}} = \frac{220 \text{ K}}{154.8 \text{ K}} = 1.42$$

$$P_{R,O_{2}} = \frac{P_{m}}{P_{cr,O_{2}}} = \frac{10 \text{ MPa}}{5.08 \text{ MPa}} = 1.97$$

$$T_{R_{1},O_{2}} = \frac{T_{m,2}}{T_{cr,O_{2}}} = \frac{160 \text{ K}}{154.8 \text{ K}} = 1.03$$

$$Z_{h_{2},O_{2}} = 4.0$$

From Eq. 12-58,

$$(\bar{h}_1 - \bar{h}_2)_{N_2} = (\bar{h}_{1,\text{ideal}} - \bar{h}_{2,\text{ideal}})_{N_2} - R_u T_{\text{cr}} (Z_{h_1} - Z_{h_2})_{N_2}$$

= [(6391 - 4648) kJ/kmol] - (8.314 kJ/kmol·K) (126.2 K) (0.9 - 2.4)
= 3317 kJ/kmol

$$(\overline{h}_1 - \overline{h}_2)_{O_2} = (\overline{h}_{1,\text{ideal}} - \overline{h}_{2,\text{ideal}})_{O_2} - R_u T_{\text{cr}} (Z_{h_1} - Z_{h_2})_{O_2}$$

= [(6404 - 4657) kJ/kmol] - (8.314 kJ/kmol·K) (154.8 K) (1.3 - 4.0)
= 5222 kJ/kmol

Therefore,

$$\bar{q}_{out} = y_{N_2}(\bar{h}_1 - \bar{h}_2)_{N_2} + y_{O_2}(\bar{h}_1 - \bar{h}_2)_{O_2}$$

= (0.79)(3317 kJ/kmol) + (0.21)(5222 kJ/kmol)
= **3717 kJ/kmol**

Discussion This result is about 6 percent greater than the result obtained in part (*b*) by using Kay's rule. But it is more than twice the result obtained by assuming the mixture to be an ideal gas.

CHEMICALREACTIONS

In this chapter we focus on a particular type of chemical reaction, known as *combustion*, because of its importance in engineering. But the reader should keep in mind, however, that the principles developed are equally applicable to other chemical reactions.

We start this chapter with a general discussion of fuels and combustion. Then we apply the mass and energy balances to reacting systems. In this regard we discuss the adiabatic flame temperature, which is the highest temperature a reacting mixture can attain. Finally, we examine the second-law aspects of chemical reactions

5–1 **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 CnHm. Hydrocarbon fuels exist in all phases, some examples being coal, gasoline, and natural gas.

The main constituent of coal is carbon. Coal also contains varying amounts of oxygen, hydrogen, nitrogen, sulfur, moisture, and ash. It is difficult to give an exact mass analysis for coal since its composition varies considerably from one geographical area to the next and even within the same geographical location. Most liquid hydrocarbon fuels are a mixture of numerous hydrocarbons and are obtained from crude oil by distillation (Fig. 15–1). The most volatile hydrocarbons vaporize first, forming what we know as gasoline. The less volatile fuels obtained during distillation are kerosene, diesel fuel, and fuel oil. The composition of a particular fuel depends on the source of the crude oil as well as on the refinery.

Although liquid hydrocarbon fuels are mixtures of many different hydrocarbons, they are usually considered to be a single hydrocarbon for convenience. For example, gasoline is treated as **octane**, C8H18, and the diesel fuel as **dodecane**, C12H26. Another common liquid hydrocarbon fuel is **methyl alcohol**, CH3OH, which is also called *methanol* and is used in some gasoline blends. The gaseous hydrocarbon fuel natural gas, which is a mixture of methane and smaller amounts of other gases, is often treated as **methane**, CH 4, for simplicity.

Natural gas is produced from gas wells or oil wells rich in natural gas. It is composed mainly of methane, but it also contains small amounts of ethane, propane, hydrogen, helium, carbon dioxide, nitrogen, hydrogen sulfate, and water vapor. On vehicles, it is stored either in the gas phase at pressures of 150 to 250 atm as CNG (compressed natural gas), or in the liquid phase at 21628C as LNG (liquefied natural gas). Over a million vehicles in the world, mostly buses, run on natural gas. Liquefied petroleum gas (LPG) is a byproduct of natural gas processing or the crude oil refining. It consists mainly of propane and thus LPG is usually referred to as propane. However, it also contains varying amounts of butane, propylene, and butylenes. Propane is commonly used in fleet vehicles, taxis, school buses, and private cars. Ethanol is obtained from corn, grains, and organic waste. Methonal is produced mostly from natural gas, but it can also be obtained from coal and biomass. Both alcohols are commonly used as additives in oxygenated gasoline and reformulated fuels to reduce air pollution.

Vehicles are a major source of air pollutants such as nitric oxides, carbon monoxide, and hydrocarbons, as well as the greenhouse gas carbon dioxide, and thus there is a growing shift in the transportation industry from the traditional petroleum-based fuels such as gaoline and diesel fuel to the cleaner burning *alternative fuels* friendlier to the environment such as natural gas, alcohols (ethanol and methanol), liquefied petroleum gas (LPG), and hydrogen. The use of electric and hybrid cars is also on the rise. A comparison of some alternative fuels for transportation to gasoline is given in Table 15–1. Note that the energy contents of alternative fuels per unit volume are lower than that of gasoline or diesel fuel, and thus

the driving range of a vehicle on a full tank is lower when running on an alternative fuel. Also, when comparing cost, a realistic measure is the cost per unit energy rather than cost per unit volume. For example, methanol at a unit cost of \$1.20/L may appear cheaper than gasoline at \$1.80/L, but this is not the case since the cost of 10,000 kJ of energy is \$0.57 for gasoline and \$0.66 for methanol. A chemical reaction during which a fuel is oxidized and a large quantity of energy is released is called **combustion**. The oxidizer most often used in combustion processes is air, for obvious reasons—it is free and readily available. Pure oxygen O2 is used as an oxidizer only in some specialized applications, such as cutting and welding, where air cannot be used. Therefore, a few words about the composition of air are in order.

On a mole or a volume basis, dry air is composed of 20.9 percent oxygen, 78.1 percent nitrogen, 0.9 percent 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 percent oxygen and 79 percent nitrogen by mole numbers.



TABLE 15-1

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

*Amount of fuel whose energy content is equal to the energy content of 1-L gasoline.

Therefore, each mole of oxygen entering a combustion chamber is accompanied by 0.79/0.21 5 3.76 mol of nitrogen (Fig. 15–2). That is,

 $1 \text{ kmol } O_2 + 3.76 \text{ kmol } N_2 = 4.76 \text{ kmol air}$ (15–1)

During combustion, nitrogen behaves as an inert gas and does not react with other elements, other than forming a very small amount of nitric oxides. However, even then the presence of nitrogen greatly affects the outcome of a combustion process since nitrogen usually enters a combustion chamber in large quantities at low temperatures and exits at considerably higher temperatures, absorbing a large proportion of the chemical energy released during combustion. Throughout this chapter, nitrogen is assumed to remain perfectly inert. Keep in mind, however, that at very high temperatures, such as those encountered in internal combustion engines, a small fraction of nitrogen reacts with oxygen, forming hazardous gases such as nitric oxide.

During a combustion process, the components that exist before the reaction are called **reactants** and the components that exist after the reaction are called **products** (Fig. 15–3). Consider, for example, the combustion of 1 kmol of carbon with 1 kmol of pure oxygen, forming carbon dioxide,

$$C + O_2 \rightarrow CO_2 \tag{15-2}$$

Here C and O 2 are the reactants since they exist before combustion, and CO 2 is the product since it exists after combustion. Note that a reactant does not have to react chemically in the combustion chamber. For example, if carbon is burned with air instead of pure oxygen, both sides of the combustion equation will include N2. That is, the N2 will appear both as a reactant and as a product. We should also mention that bringing a fuel into intimate contact with oxygen is not sufficient to start a combustion process. (Thank goodness it is not. Otherwise, the whole world would be on fire now.) 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 2608C for gasoline, 4008C for carbon, 5808C for hydrogen, 6108C for carbon monoxide, and 6308C for methane. Moreover, the proportions of the fuel and air must be in the proper range for combustion to begin. For example, natural gas does not burn in air in concentrations less than 5 percent or greater than about 15 percent.

As you may recall from your chemistry courses, chemical equations are balanced on the basis of the **conservation of mass principle** (or the **mass balance**), which can be stated as follows: *The total mass of each element is conserved during a chemical reaction* (Fig. 15–4). That is, the total mass of each element on the right-hand side of the reaction equation (the products) must be equal to the total mass of that element on the left-hand side (the reactants) even though the elements exist in different chemical compounds in the reactants and products. Also, the total number of atoms of each element is conserved during a chemical reaction since the total number of atoms is equal to the total mass of the element divided by its atomic mass.

For example, both sides of Eq. 15–2 contain 12 kg of carbon and 32 kg of oxygen, even though the carbon and the oxygen exist as elements in the reactants and as a compound in the product. Also, the total mass of



reactants is equal to the total mass of products, each being 44 kg. (It is common practice to round the molar masses to the nearest integer if great accuracy is not required.) However, notice that the total

mole number of the reactants (2 kmol) is not equal to the total mole number of the products (1 kmol). That is, *the total number of moles is not 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 (Fig. 15–5). That is,

$$AF = \frac{m_{air}}{m_{fuel}}$$

(15 - 3)

The mass m of a substance is related to the number of moles N through the relation m 5 NM, where M is the molar mass.

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 Balancing the Combustion Equation

One kmol of octane (C_8H_{18}) is burned with air that contains 20 kmol of O_2 , as shown in Fig. 15–6. 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.

SOLUTION The amount of fuel and the amount of oxygen in the air are given. The amount of the products and the AF are to be determined. *Assumptions* The combustion products contain CO₂, H₂O, O₂, and N₂ only. *Properties* The molar mass of air is $M_{\text{air}} = 28.97 \text{ kg/kmol} \cong 29.0 \text{ kg/kmol}$ (Table A-1).

Analysis The chemical equation for this combustion process can be written as

 $C_8H_{18} + 20(O_2 + 3.76N_2) \rightarrow xCO_2 + yH_2O + zO_2 + wN_2$

where the terms in the parentheses represent the composition of dry air that contains 1 kmol of O_2 and x, y, z, and w represent the unknown mole numbers of the gases in the products. These unknowns are determined by applying the mass balance to each of the elements—that is, by requiring that the total mass or mole number of each element in the reactants be equal to that in the products:

C: $8 = x \rightarrow x = 8$ H: $18 = 2y \rightarrow y = 9$ O: $20 \times 2 = 2x + y + 2z \rightarrow z = 7.5$ N₂: $(20)(3.76) = w \rightarrow w = 75.2$

Substituting yields

 $C_8H_{18} + 20(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 7.5O_2 + 75.2N_2$

Note that the coefficient 20 in the balanced equation above represents the number of moles of *oxygen*, not the number of moles of air. The latter is obtained by adding $20 \times 3.76 = 75.2$ moles of nitrogen to the 20 moles of oxygen, giving a total of 95.2 moles of air. The air-fuel ratio (AF) is determined from Eq. 15–3 by taking the ratio of the mass of the air and the mass of the fuel,

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{(NM)_{air}}{(NM)_{C} + (NM)_{H_2}}$$
$$= \frac{(20 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(8 \text{ kmol})(12 \text{ kg/kmol}) + (9 \text{ kmol})(2 \text{ kg/kmol})}$$
$$= 24.2 \text{ kg air/kg fuel}$$

That is, 24.2 kg of air is used to burn each kilogram of fuel during this combustion process.







FIGURE 15–6 Schematic for Example 15–1.

15-2 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 H2O, and all the sulfur (if any) burns to SO2. That is, all the combustible components of a fuel are burned to completion during a complete combustion process (Fig. 15–7). 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.

Oxygen has a much greater tendency to combine with hydrogen than it does with carbon. Therefore, the hydrogen in the fuel normally burns to completion, forming H2O, even when there is less oxygen than needed for complete combustion. Some of the carbon, however, ends up as CO or just as plain C particles (soot) in the products.

The minimum amount of air needed for the complete combustion of a fuel is called the stoichiometric or theoretical air. Thus, when a fuel is completely burned with theoretical air, no uncombined oxygen is present in the product gases. The theoretical air is also referred to as the *chemically correct* amount of air, or 100 percent theoretical air. A combustion



the products is called theoretical combustion.

components of the fuel are burned to completion.

process with less than the theoretical air is bound to be incomplete. The ideal combustion process during which a fuel is burned completely with theoretical air is called the **stoichiometric** or **theoretical combustion** of that fuel (Fig. 15-8). For example, the theoretical combustion of methane is

$$\rm CH_4 \, + \, 2(O_2 \, + \, 3.76N_2) \, {\rightarrow} \, \rm CO_2 \, + \, 2H_2O \, + \, 7.52N_2$$

Notice that the products of the theoretical combustion contain no unburned methane and no C, H2, CO, OH, or free O2.

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. The amount of excess air is usually expressed in terms of the stoichiometric air as percent excess air or percent theoretical air. For example, 50 percent excess air is equivalent to 150 percent theoretical air, and 200 percent excess air is equivalent to 300 percent theoretical air. Of course, the stoichiometric air can be expressed as 0 percent excess air or 100 percent theoretical air. Amounts of air less than the stoichiometric amount are called **deficiency of air** and are often expressed as **percent deficiency of** air. For example, 90 percent theoretical air is equivalent to 10 percent deficiency of air. The 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.

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. Things are not so simple, 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.

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



. In this device, a sample of the combustion gases is collected and cooled to room temperature and pressure, at which point its volume is measured. The sample is then brought into contact with a chemical that absorbs the CO 2. The remaining gases are returned to the room temperature and pressure, and the new volume they occupy is measured. The ratio of the reduction in volume to the original volume is the volume fraction of the CO 2, which is equivalent to the mole fraction if ideal-gas behavior is assumed (Fig. 15–9). The volume fractions of the other gases are determined by repeating this procedure. In Orsat analysis the gas sample is collected over water and is maintained saturated at all times. Therefore, the vapor pressure of water remains constant during the entire test. For this reason the presence of water vapor in the test chamber is ignored and data are reported on a dry basis. However, the amount of H2O formed during combustion is easily determined by balancing the combustion equation.



FIGURE 15–10 Schematic for Example 15–2.

EXAMPLE 15–2 Combustion of Coal with Theoretical Air

analyzer

Coal from Pennsylvania which has an ultimate analysis (by mass) as 84.36 percent C, 1.89 percent H₂, 4.40 percent O₂, 0.63 percent N₂, 0.89 percent S, and 7.83 percent ash (non-combustibles) is burned with theoretical amount of air (Fig. 15-10). Disregarding the ash content, determine the mole fractions of the products and the apparent molar mass of the product gases. Also determine the air-fuel ratio required for this combustion process.

SOLUTION Coal with known mass analysis is burned with theoretical amount of air. The mole fractions of the product gases, their apparent molar mass, and the air-fuel ratio are to be determined.

Assumptions 1 Combustion is stoichiometric and thus complete. 2 Combustion products contain CO_2 , H_2O , SO_2 , and N_2 only (ash disregarded). 3 Combustion gases are ideal gases.

Analysis The molar masses of C, H_2 , O_2 , S, and air are 12, 2, 32, 32, and 29 kg/kmol, respectively (Table A-1). We now consider 100 kg of coal for simplicity. Noting that the mass percentages in this case correspond to the masses of the constituents, the mole numbers of the constituent of the coal are determined to be

$$N_{\rm C} = \frac{m_{\rm C}}{M_{\rm C}} = \frac{84.36 \text{ kg}}{12 \text{ kg/kmol}} = 7.030 \text{ kmol}$$

$$N_{\rm H_2} = \frac{m_{\rm H_2}}{M_{\rm H_2}} = \frac{1.89 \text{ kg}}{2 \text{ kg/kmol}} = 0.9450 \text{ kmol}$$

$$N_{\rm O_2} = \frac{m_{\rm O_2}}{M_{\rm O_2}} = \frac{4.40 \text{ kg}}{32 \text{ kg/kmol}} = 0.1375 \text{ kmol}$$

$$N_{\rm N_2} = \frac{m_{\rm N_2}}{M_{\rm N_2}} = \frac{0.63 \text{ kg}}{28 \text{ kg/kmol}} = 0.0225 \text{ kmol}$$

$$N_{\rm S} = \frac{m_{\rm S}}{M_{\rm S}} = \frac{0.89 \text{ kg}}{32 \text{ kg/kmol}} = 0.0278 \text{ kmol}$$

Ash consists of the non-combustible matter in coal. Therefore, the mass of ash content that enters the combustion chamber is equal to the mass content that leaves. Disregarding this non-reacting component for simplicity, the combustion equation may be written as

 $7.03C + 0.945H_2 + 0.1375O_2 + 0.0225N_2 + 0.0278S + a_{th}(O_2 + 3.76N_2)$ $\rightarrow xCO_2 + yH_2O + zSO_2 + wN_2$

Performing mass balances for the constituents gives

C balance: x = 7.03H₂ balance: y = 0.945S balance: z = 0.0278O₂ balance: $0.1375 + a_{th} = x + 0.5y + z \rightarrow a_{th} = 7.393$ N₂ balance: $w = 0.0225 + 3.76a_{th} = 0.0225 + 3.76 \times 7.393 = 27.82$ Substituting, the balanced combustion equation without the ash becomes $7.03C + 0.945H_2 + 0.1375O_2 + 0.0225N_2 + 0.0278S + 7.393(O_2 + 3.76N_2)$ $\rightarrow 7.03CO_2 + 0.945H_2O + 0.0278SO_2 + 27.82N_2$

The mole fractions of the product gases are determined as follows:

$$N_{\text{prod}} = 7.03 + 0.945 + 0.0278 + 27.82 = 35.82 \text{ kmol}$$

$$y_{\text{CO}_2} = \frac{N_{\text{CO}_2}}{N_{\text{prod}}} = \frac{7.03 \text{ kmol}}{35.82 \text{ kmol}} = 0.1963$$

$$y_{\text{H}_2\text{O}} = \frac{N_{\text{H}_2\text{O}}}{N_{\text{prod}}} = \frac{0.945 \text{ kmol}}{35.82 \text{ kmol}} = 0.02638$$

$$y_{\text{SO}_2} = \frac{N_{\text{SO}_2}}{N_{\text{prod}}} = \frac{0.0278 \text{ kmol}}{35.82 \text{ kmol}} = 0.000776$$

$$y_{\text{N}_2} = \frac{N_{\text{N}_2}}{N_{\text{prod}}} = \frac{27.82 \text{ kmol}}{35.82 \text{ kmol}} = 0.7767$$

Then, the apparent molar mass of product gases becomes

$$M_{\text{prod}} = \frac{m_{\text{prod}}}{N_{\text{prod}}} = \frac{(7.03 \times 44 + 0.945 \times 18 + 0.0278 \times 64 + 27.82 \times 28)\text{kg}}{35.82 \text{ kmol}}$$
$$= 30.9 \text{ kg/kmol}$$

Finally, the air-fuel mass ratio is determined from its definition to be

AF =
$$\frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{(7.393 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{100 \text{ kg}} = 10.2 \text{ kg air/kg fuel}$$

That is, 10.2 kg of air is supplied for each kg of coal in the furnace. **Discussion** We could also solve this problem by considering just 1 kg of coal, and still obtain the same results. But we would have to deal with very small fractions in calculations in this case.

EXAMPLE 15–3 Combustion of a Gaseous Fuel with Moist Air

A certain natural gas has the following volumetric analysis: 72 percent CH₄, 9 percent H₂, 14 percent N₂, 2 percent O₂, and 3 percent CO₂. This gas is now burned with the stoichiometric amount of air that enters the combustion chamber at 20°C, 1 atm, and 80 percent relative humidity, as shown in Fig. 15–11. Assuming complete combustion and a total pressure of 1 atm, determine the dew-point temperature of the products.



FIGURE 15–11 Schematic for Example 15–3.

SOLUTION A gaseous fuel is burned with the stoichiometric amount of moist air. The dew point temperature of the products is to be determined.

Assumptions 1 The fuel is burned completely and thus all the carbon in the fuel burns to CO_2 and all the hydrogen to H_2O . 2 The fuel is burned with the stoichiometric amount of air and thus there is no free O_2 in the product gases. 3 Combustion gases are ideal gases.

Properties The saturation pressure of water at 20°C is 2.3392 kPa (Table A–4).

Analysis We note that the moisture in the air does not react with anything; it simply shows up as additional H_2O in the products. Therefore, for simplicity,

we balance the combustion equation by using dry air and then add the moisture later to both sides of the equation. Considering 1 kmol of fuel,

$$\overbrace{(0.72\text{CH}_4 + 0.09\text{H}_2 + 0.14\text{N}_2 + 0.02\text{O}_2 + 0.03\text{CO}_2)}^{\text{fuel}} + \overbrace{a_{\text{th}}(\text{O}_2 + 3.76\text{N}_2)}^{\text{dry air}} \rightarrow x\text{CO}_2 + y\text{H}_2\text{O} + z\text{N}_2}^{\text{dry air}}$$

The unknown coefficients in the above equation are determined from mass balances on various elements,

C:	0.72 + 0.03 = x	\rightarrow	x = 0.75
H:	$0.72 \times 4 + 0.09 \times 2 = 2y$	\rightarrow	y = 1.53
O ₂ :	$0.02 + 0.03 + a_{\rm th} = x + \frac{y}{2}$	\rightarrow	$a_{\rm th} = 1.465$
N ₂ :	$0.14 + 3.76a_{\rm th} = z$	\rightarrow	z = 5.648

Next we determine the amount of moisture that accompanies $4.76a_{\rm th} = (4.76)(1.465) = 6.97$ kmol of dry air. The partial pressure of the moisture in the air is

$$P_{v,\text{air}} = \phi_{\text{air}} P_{\text{sat @ 20^{\circ}C}} = (0.80)(2.3392 \text{ kPa}) = 1.871 \text{ kPa}$$

Assuming ideal-gas behavior, the number of moles of the moisture in the air is

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

which yields

$$N_{\rm vair} = 0.131 \,\rm kmol$$

The balanced combustion equation is obtained by substituting the coefficients determined earlier and adding 0.131 kmol of H_2O to both sides of the equation:

$$\overbrace{(0.72\text{CH}_4 + 0.09\text{H}_2 + 0.14\text{N}_2 + 0.02\text{O}_2 + 0.03\text{CO}_2)}^{\text{moisture}} + \overbrace{0.131\text{H}_2\text{O}}^{\text{moisture}} \rightarrow 0.75\text{CO}_2 + \overbrace{1.661\text{H}_2\text{O}}^{\text{includes moisture}} + 5.648\text{N}_2$$

The dew-point temperature of the products is the temperature at which the water vapor in the products starts to condense as the products are cooled. Again, assuming ideal-gas behavior, the partial pressure of the water vapor in the combustion gases is

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

Thus,

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

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 Reverse Combustion Analysis

Octane (C_8H_{18}) is burned with dry air. The volumetric analysis of the products on a dry basis is (Fig. 15–12)

CO ₂ :	10.02 percent
O ₂ :	5.62 percent
CO:	0.88 percent
N ₂ :	83.48 percent

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.

SOLUTION Combustion products whose composition is given are cooled to 25° C. The AF, the percent theoretical air used, and the fraction of water vapor that condenses are to be determined.

Assumptions Combustion gases are ideal gases.

Properties The saturation pressure of water at 25°C is 3.1698 kPa (Table A-4).

Analysis Note that we know the relative composition of the products, but we do not know how much fuel or air is used during the combustion process. However, they can be determined from mass balances. The H_2O in the combustion gases will start condensing when the temperature drops to the dewpoint temperature.

For ideal gases, the volume fractions are equivalent to the mole fractions. Considering 100 kmol of dry products for convenience, the combustion equation can be written as

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

The unknown coefficients x, a, and b are determined from mass balances,

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

The $\rm O_2$ balance is not necessary, but it can be used to check the values obtained from the other mass balances, as we did previously. Substituting, we get

 $\begin{array}{l} 1.36 \mathrm{C_8H_{18}}\,+\,22.2 (\mathrm{O_2}\,+\,3.76 \mathrm{N_2}) \rightarrow \\ \\ 10.02 \mathrm{CO_2}\,+\,0.88 \mathrm{CO}\,+\,5.62 \mathrm{O_2}\,+\,83.48 \mathrm{N_2}\,+\,12.24 \mathrm{H_2O} \end{array}$

The combustion equation for 1 kmol of fuel is obtained by dividing the above equation by 1.36, $% \int_{\mathbb{R}^{n}} \left(\int_{\mathbb{R}^{n}} \int_{\mathbb{R}$

 $\begin{array}{l} C_8H_{18}\,+\,16.32(O_2\,+\,3.76N_2)\rightarrow\\ \\ 7.37CO_2\,+\,0.65CO\,+\,4.13O_2\,+\,61.38N_2\,+\,9H_2O \end{array}$



Schematic for Example 15-4.

(a) The air-fuel ratio is determined by taking the ratio of the mass of the air to the mass of the fuel (Eq. 15-3),

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

= **19.76 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,

$$C_8 H_{18} + a_{th} (O_2 + 3.76 N_2) \rightarrow 8 CO_2 + 9 H_2 O + 3.76 a_{th} N_2$$

$$D_2: \qquad a_{th} = 8 + 4.5 \rightarrow a_{th} = 12.5$$

Then,

(

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. If N_w kmol of H₂O condenses, there will be $(9 - N_w)$ kmol of water vapor left in the products. The mole number of the products in the gas phase will also decrease to $82.53 - N_w$ as a result. By treating the product gases (including the remaining water vapor) as ideal gases, N_w is determined by equating the mole fraction of the water vapor to its pressure fraction,

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

Therefore, the majority of the water vapor in the products (73 percent of it) condenses as the product gases are cooled to 25°C.

15–3 ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

We mentioned in Chap. 2 that the molecules of a system possess energy in various forms such as *sensible* and *latent energy* (associated with a change of state), *chemical energy* (associated with the molecular structure), and *nuclear energy* (associated with the atomic structure), as illustrated in Fig. 15–13. In this text we do not intend to deal with nuclear energy. We also ignored chemical energy until now since the systems considered in previous chapters involved no changes in their chemical structure, and thus no changes in chemical energy. Consequently, all we needed to deal with were the sensible and latent energies.

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 involves changes in chemical energies, which must be accounted for in an energy balance (Fig. 15–14). Assuming the atoms of each reactant remain intact (no nuclear reactions) and disregarding any changes in kinetic and potential energies, the energy change of a system during a chemical reaction is due to a change in state and a change in chemical composition. That is,



Therefore, when the products formed during a chemical reaction exit the reaction chamber at the inlet state of the reactants, we have DEstate 5 0 and the energy change of the system in this case is due to the changes in its chemical composition only.

In thermodynamics we are concerned with the *changes* in the energy of a system during a process, and not the energy values at the particular states. Therefore, we can choose any state as the reference state and assign a value of zero to the internal energy or enthalpy of a substance at that state. When a process involves no changes in chemical composition, the reference state chosen has no effect on the results. When the process involves chemical reactions, however, the composition of the system at the end of a process is no longer the same as that at the beginning of the process. In this case it becomes necessary to have a common reference state for all substances. The chosen reference state is 258C (778F) and 1 atm, which is known as the **standard reference state**. Property values at the standard reference state are indicated by a superscript (8) (such as *h*8 and *u*8).

When analyzing reacting systems, we must use property values relative to the standard reference state. However, it is not necessary to prepare a new set of property tables for this purpose. We can use the existing tables by subtracting the property values at the standard reference state from the values at the specified state. The ideal-gas enthalpy of N2 at 500 K relative to the standard reference state, for example, is h# 500 K 2 h#8 5 14,581 2 8669 5 5912 kJ/kmol.

Consider the formation of CO 2 from its elements, carbon and oxygen, during a steady-flow combustion process (Fig. 15–15). Both the carbon and the oxygen enter the combustion chamber at 258C and 1 atm. The CO2 formed during this process also leaves the combustion chamber at 258C and 1 atm. The combustion of carbon is an *exothermic reaction* (a reaction during
which chemical energy is released in the form of heat). Therefore, some heat is transferred from the combustion chamber to the surroundings during this process, which is 393,520 kJ/kmol CO2 formed. (When one is dealing with chemical reactions, it is more convenient to work with quantities per unit mole than per unit time, even for steady-flow processes.)

The process described above involves no work interactions. Therefore, from the steady-flow energy balance relation, the heat transfer during this process must be equal to the difference between the enthalpy of the products and the enthalpy of the reactants. That is,

$$Q = H_{\text{prod}} - H_{\text{react}} = -393,520 \text{ kJ/kmol}$$
 (15–5)

Since both the reactants and the products are at the same state, the enthalpy change during this process is solely due to the changes in the chemical composition of the system. This enthalpy change is different for different reactions, and it is very desirable to have a property to represent the changes in chemical energy during a reaction. This property is the **enthalpy of reaction** *h R*, which is defined as 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.

For combustion processes, the enthalpy of reaction is usually referred to as the **enthalpy of combustion** hC, which represents 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 (Fig. 15–16). It is expressed as

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

which is 2393,520 kJ/kmol for carbon at the standard reference state. The enthalpy of combustion of a particular fuel is different at different temperatures and pressures.

(15–6)

The enthalpy of combustion is obviously a very useful property for analyzing the combustion processes of fuels. However, there are so many different fuels and fuel mixtures that it is not practical to list hC values for all possible cases. Besides, the enthalpy of combustion is not of much use when the combustion is incomplete. Therefore a more practical approach would be to have a more fundamental property to represent the chemical energy of an element or a compound at some reference state. This property is the **enthalpy of formation** h#f, which can be viewed as *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 O2, N2, H2, and C) a value of zero at the standard reference state of 258C and 1 atm. That is, h#f50 for all stable elements. (This is no different from assigning the internal energy of saturated liquid water a value of zero at 0.018C.) Perhaps we should clarify what we mean by *stable*. The stable form of an element is simply the chemically stable form of that element at 258C and 1 atm. Nitrogen, for example, exists in diatomic form (N2) at 258C and 1 atm. Therefore, the stable form of nitrogen at the standard reference state is diatomic nitrogen N2, not monatomic nitrogen N. If an element exists in more than one



stable form at 258C and 1 atm, one of the forms should be specified as the stable form. For carbon, for example, the stable form is assumed to be graphite, not diamond.

Now reconsider the formation of CO 2 (a compound) from its elements C and O 2 at 258C and 1 atm during a steady-flow process. The enthalpy change during this process was determined to be 2393,520 kJ/kmol. However, *H*react 5 0 since both reactants are elements at the standard reference state, and the products consist of 1 kmol of CO2 at the same state. Therefore, the enthalpy of formation of CO2 at the standard reference state is 2393,520 kJ/kmol (Fig. 15–17). That is,

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

The negative sign is due to the fact that the enthalpy of 1 kmol of CO2 at 258C and 1 atm is 393,520 kJ less than the enthalpy of 1 kmol of C and 1 kmol of O 2 at the same state. In other words, 393,520 kJ of chemical energy is released (leaving the system as heat) when C and O2 combine to form 1 kmol of CO 2. Therefore, a negative enthalpy of formation for a compound indicates that heat is released during the formation of that compound from its stable elements. A positive value indicates heat is absorbed.

You will notice that two h#8 f values are given for H2O in Table A–26, one for liquid water and the other for water vapor. This is because both phases of H 2O are encountered at 258C, and the effect of pressure on the enthalpy of formation is small. (Note that under equilibrium conditions, water exists only as a liquid at 258C *and* 1 atm.) The difference between the two enthalpies of formation is equal to the *hfg* of water at 258C, which is 2441.7 kJ/kg or 44,000 kJ/kmol.

Another term commonly used in conjunction with the combustion of fuels is the **heating value** of the fuel, which is defined as 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. In other words, the heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel. That is,

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

The heating value depends on the *phase* of the H2O in the products. The heating value is called the **higher heating value** (HHV) when the H2O in the products is in the liquid form, and it is called the **lower heating value** (LHV) when the H2O in the products is in the vapor form (Fig. 15–18). The two heating values are related by

$HHV = LHV + (mh_{fg})_{H,O} \quad (kJ/kg \text{ fuel})$ (15–7)

where *m* is the mass of H 2O in the products per unit mass of fuel and hfg is the enthalpy of vaporization of water at the specified temperature. Higher and lower heating values of common fuels are given in Table A–27.

The heating value or enthalpy of combustion of a fuel can be determined from a knowledge of the enthalpy of formation for the compounds involved. This is illustrated with the following example.





FIGURE 15–19 Schematic for Example 15–5.

EXAMPLE 15–5 Evaluation of the Enthalpy of Combustion

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.

SOLUTION The enthalpy of combustion of a fuel is to be determined using enthalpy of formation data.

Properties The enthalpy of formation at 25°C and 1 atm is -393,520 kJ/ kmol for CO₂, -285,830 kJ/kmol for H₂O(ℓ), and -249,950 kJ/kmol for C₈H₁₈(ℓ) (Table A-26).

Analysis The combustion of C_8H_{18} is illustrated in Fig. 15–19. The stoichiometric equation for this reaction is

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

Both the reactants and the products are at the standard reference state of 25°C and 1 atm. Also, N₂ and O₂ are stable elements, and thus their enthalpy of formation is zero. Then the enthalpy of combustion of C₈H₁₈ becomes (Eq. 15–6)

$$\begin{split} \bar{h}_{C} &= H_{\text{prod}} - H_{\text{react}} \\ &= \sum N_{p} \bar{h}_{f,p}^{\circ} - \sum N_{r} \bar{h}_{f,r}^{\circ} = (N \bar{h}_{f}^{\circ})_{\text{CO}_{2}} + (N \bar{h}_{f}^{\circ})_{\text{H}_{2}\text{O}} - (N \bar{h}_{f}^{\circ})_{\text{C}_{8}\text{H}_{9}} \end{split}$$

Substituting,

$$\bar{h}_{c} = (8 \text{ kmol})(-393,520 \text{ kJ/kmol}) + (9 \text{ kmol})(-285,830 \text{ kJ/kmol})$$

-(1 kmol)(-249,950 kJ/kmol)

$$= -5,471,000 \text{ kJ/kmol } C_8 H_{18} = -47,891 \text{ kJ/kg } C_8 H_{18}$$

which is practially identical to the listed value of 47,890 kJ/kg in Table A–27. Since the water in the products is assumed to be in the liquid phase, this h_c value corresponds to the HHV of liquid C_8H_{18} . **Discussion** It can be shown that the result for gaseous octane is

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

15–4 .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

Before writing the energy balance relation, we need to express the enthalpy of a component in a form suitable for use for reacting systems. That is, we need to express the enthalpy such that it is relative to the standard reference state and the chemical energy term appears explicitly. When expressed properly, the enthalpy term should reduce to the enthalpy of formation h8f at the standard reference state. With this in mind, we express the enthalpy of a component on a unit mole basis as (Fig. 15–20) Enthalpy = $h_f^{\circ} + (h - h^{\circ})$ (kJ/kmol)

where the term in the parentheses represents the sensible enthalpy relative to the standard reference state, which is the difference between h# (the sensible enthalpy at the specified state) and h8 (the sensible enthalpy at the standard reference state of 258C and 1 atm). This definition enables us to use enthalpy values from tables regardless of the reference state used in their construction.

When the changes in kinetic and potential energies are negligible, the steadyflow energy balance relation *E*in = *E*out can be expressed for a *chemically reacting steady-flow system* more explicitly as

 $\dot{Q}_{in} + \dot{W}_{in} + \sum \dot{n}_r (\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ})_r = \dot{Q}_{out} + \dot{W}_{out} + \sum \dot{n}_p (\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ})_p$ (15–8)

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

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

where *np* and *nr*

r represent the molal flow rates of the product *p* and the reactant *r*, respectively.

In combustion analysis, it is more convenient to work with quantities expressed *per mole of fuel*. Such a relation is obtained by dividing each term of the equation above by the molal flow rate of the fuel, yielding

$$\underbrace{Q_{\text{in}} + W_{\text{in}} + \sum_{r} N_{r} (\bar{h}_{f}^{\circ} + \bar{h} - \bar{h}^{\circ})_{r}}_{\text{Energy transfer in per mole of fuel}} = \underbrace{Q_{\text{out}} + W_{\text{out}} + \sum_{r} N_{p} (\bar{h}_{f}^{\circ} + \bar{h} - \bar{h}^{\circ})_{p}}_{\text{Energy transfer out per mole of fuel}}$$
(15–9)
$$\underbrace{P_{\text{in}} + W_{\text{in}} + \sum_{r} N_{p} (\bar{h}_{f}^{\circ} + \bar{h} - \bar{h}^{\circ})_{p}}_{\text{by heat, work, and mass}}$$

where N r and Np represent the number of moles of the reactant r and the product p, respectively, per mole of fuel. Note that Nr 5 1 for the fuel, and the other N r and Np values can be picked directly from the balanced combustion equation. Taking heat transfer *to* the system and work done *by* the system to be *positive* quantities, the energy balance relation just discussed can be expressed more compactly as

(15 - 11)

$$Q - W = \sum N_p (\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ})_p - \sum N_r (\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ})_r$$
(15–10)

or as

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

where

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

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

If the enthalpy of combustion hC8 for a particular reaction is available, the steady-flow energy equation per mole of fuel can be expressed as

$$Q - W = \bar{h}_{c}^{\circ} + \sum N_{p}(\bar{h} - \bar{h}^{\circ})_{p} - \sum N_{r}(\bar{h} - \bar{h}^{\circ})_{r} \quad (kJ/kmol) \quad (15-12)$$

The energy balance relations above are sometimes written without the work term since most steadyflow combustion processes do not involve any work interactions. A combustion chamber normally involves heat output but no heat input. Then the energy balance for a *typical steady-flow combustion process* becomes

$$Q_{\text{out}} = \underbrace{\sum N_r (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r}_{\text{Energy in by mass}} - \underbrace{\sum N_p (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p}_{\text{Energy out by mass}}$$
(15–13)

It expresses that the heat output during a combustion process is simply the difference between the energy of the reactants entering and the energy of the products leaving the combustion chamber. **Closed Systems**

The general closed-system energy balance relation *E*in 2 *E*out 5 DEsystem can be expressed for a stationary *chemically reacting closed system* as



$$(Q_{\rm in} - Q_{\rm out}) + (W_{\rm in} - W_{\rm out}) = U_{\rm prod} - U_{\rm react}$$
 (kJ/kmol fuel) (15–14)

where *U* prod represents the internal energy of the products and *U*react represents the internal energy of the reactants. To avoid using another property— *the internal energy of formation u*#f8 —we utilize the definition of enthalpy (u# 5 h 2 Pv or u#f8 1 u# 2 u#8 5 hf8 1 h 2 h8 2 Pv#) and express the above equation as (Fig. 15–21)

$$Q - W = \sum N_{p}(\bar{h}_{f}^{\circ} + \bar{h} - \bar{h}^{\circ} - P\bar{\nu})_{p} - \sum N_{r}(\bar{h}_{f}^{\circ} + \bar{h} - \bar{h}^{\circ} - P\bar{\nu})_{r} \quad (15-15)$$

where we have taken heat transfer *to* the system and work done *by* the system to be *positive* quantities. The Pv terms are negligible for solids and liquids, and can be replaced by RuT for gases that behave as an ideal gas. Also, if desired, the $h \ 2 \ Pv$ terms in Eq. 15–15 can be replaced by u#. The work term in Eq. 15–15 represents all forms of work, including the boundary work. It was shown in Chap. 4 that $DU \ 1 \ Wb \ 5 \ DH$ for nonreacting closed systems undergoing a quasi-equilibrium $P \ 5$ constant expansion or compression process. This is also the case for chemically reacting systems. There are several important considerations in the analysis of reacting systems. For example, we need to know whether the fuel is a solid, a liquid, or a gas since the enthalpy of formation hf8 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. For entropy calculations it is especially important to know if the fuel and air enter the combustion chamber premixed or separately. When the combustion products are cooled to low temperatures, we need to consider the possibility of condensation of some of the water vapor in the product gases.

EXAMPLE 15–6 First-Law Analysis of Steady-Flow Combustion

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 percent excess air that enters the combustion chamber at 7°C, as shown in Fig. 15–22. An analysis of the combustion gases reveals that all the hydrogen in the fuel burns to H₂O but only 90 percent of the carbon burns to CO₂, 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.

SOLUTION Liquid propane is burned steadily with excess air. The mass flow rate of air and the rate of heat transfer are to be determined.

Assumptions 1 Steady operating conditions exist. **2** Air and the combustion gases are ideal gases. **3** Kinetic and potential energies are negligible.

Analysis We note that all the hydrogen in the fuel burns to H_2O but 10 percent of the carbon burns incompletely and forms CO. Also, the fuel is burned with excess air and thus there is some free O_2 in the product gases.

The theoretical amount of air is determined from the stoichiometric reaction to be

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

 $a_{\rm th} = 3 + 2 = 5$

O₂ balance:

Then the balanced equation for the actual combustion process with 50 percent excess air and some CO in the products becomes

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

(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 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**



FIGURE 15–22 Schematic for Example 15–6.

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

or

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

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

Assuming the air and the combustion products to be ideal gases, we have h = h(T), and we form the following minitable using data from the property tables:

	\overline{h}_{f}^{o}	<u></u> <i>h</i> _{280 к}	<u></u> <i>ћ</i> _{298К}	<u></u> <i>h</i> _{1500К}
Substance	kJ/kmol	kJ/kmol	kJ/kmol	kJ/kmol
C ₃ H ₈ (ℓ)	-118,910	_	_	_
02	0	8150	8682	49,292
N ₂	0	8141	8669	47,073
$H_2^{-}O(g)$	-241,820	_	9904	57,999
CO_2	-393,520	—	9364	71,078
CO	-110,530		8669	47,517

The \overline{h}_{f}° of liquid propane is obtained by subtracting the \overline{h}_{fg} of propane at 25°C from the \overline{h}_{f}° of gas propane. Substituting gives

$$Q_{\text{out}} = (1 \text{ kmol } C_3 H_8)[(-118,910 + \overline{h}_{298} - \overline{h}_{298}) \text{ kJ/kmol } C_3 H_8]$$

+
$$(7.5 \text{ kmol O}_2)[(0 + 8150 - 8682) \text{ kJ/kmol O}_2]$$

+ $(28.2 \text{ kmol } N_2)[(0 + 8141 - 8669) \text{ kJ/kmol } N_2]$

- $(2.7 \text{ kmol CO}_2)[(-393,520 + 71,078 9364) \text{ kJ/kmol CO}_2]$
- -(0.3 kmol CO)[(-110,530 + 47,517 8669) kJ/kmol CO]
- $(4 \text{ kmol H}_2\text{O})[(-241,820 + 57,999 9904) \text{ kJ/kmol H}_2\text{O}]$

$$- (2.65 \text{ kmol O}_2)[(0 + 49,292 - 8682) \text{ kJ/kmol O}_2]$$

$$- (28.2 \text{ kmol } \text{N}_2)[(0 + 47,073 - 8669) \text{ kJ/kmol } \text{N}_2]$$

 $= 363,880 \text{ kJ/kmol of } C_3 H_8$

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

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



FIGURE 15–23 Schematic for Example 15–7.

EXAMPLE 15–7 First-Law Analysis of Combustion in a Bomb

The constant-volume tank shown in Fig. 15–23 contains 1 lbmol of methane (CH₄) gas and 3 lbmol of O_2 at 77°F and 1 atm. The contents of the tank are ignited, and the methane gas burns completely. If the final temperature is 1800 R, determine (*a*) the final pressure in the tank and (*b*) the heat transfer during this process.

SOLUTION Methane is burned in a rigid tank. The final pressure in the tank and the heat transfer are to be determined.

Assumptions 1 The fuel is burned completely and thus all the carbon in the fuel burns to CO_2 and all the hydrogen to H_2O . 2 The fuel, the air, and the combustion gases are ideal gases. 3 Kinetic and potential energies are negligible. 4 There are no work interactions involved.

Analysis The balanced combustion equation is

$$CH_4(g) + 3O_2 \rightarrow CO_2 + 2H_2O + O_2$$

(a) At 1800 R, water exists in the gas phase. Using the ideal-gas relation for both the reactants and the products, the final pressure in the tank is determined to be

$$\begin{array}{l} P_{\text{react}} V = N_{\text{react}} R_u T_{\text{react}} \\ P_{\text{prod}} V = N_{\text{prod}} R_u T_{\text{prod}} \end{array} \right\} \quad P_{\text{prod}} = P_{\text{react}} \left(\frac{N_{\text{prod}}}{N_{\text{react}}} \right) \left(\frac{T_{\text{prod}}}{T_{\text{react}}} \right) \end{array}$$

Substituting, we get

$$P_{\text{prod}} = (1 \text{ atm}) \left(\frac{4 \text{ lbmol}}{4 \text{ lbmol}} \right) \left(\frac{1800 \text{ R}}{537 \text{ R}} \right) = 3.35 \text{ atm}$$

(b) Noting that the process involves no work interactions, the heat transfer during this constant-volume combustion process can be determined from the energy balance $E_{\rm in} - E_{\rm out} = \Delta E_{\rm system}$ applied to the tank,

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

Since both the reactants and the products are assumed to be ideal gases, all the internal energy and enthalpies depend on temperature only, and the $P\overline{v}$ terms in this equation can be replaced by $R_{u}T$. It yields

$$Q_{\text{out}} = \sum N_r (\bar{h}_f^{\circ} - R_u T)_r - \sum N_p (\bar{h}_f^{\circ} + \bar{h}_{1800 \text{ R}} - \bar{h}_{537 \text{ R}} - R_u T)_p$$

since the reactants are at the standard reference temperature of 537 R. From \overline{h}_{r}^{o} and ideal-gas tables in the Appendix,

	\overline{h}_{f}°	$\overline{h}_{537 \mathrm{R}}$	$\overline{h}_{1800 \text{ R}}$
Substance	Btu/Ibmol	Btu/Ibmol	Btu/Ibmol
CH ₄	-32,210	—	
02	0	3725.1	13,485.8
CO ₂	-169,300	4027.5	18,391.5
H ₂ O(<i>g</i>)	-104,040	4258.0	15,433.0

Substituting, we have

 $Q_{\text{out}} = (1 \text{ lbmol CH}_4)[(-32,210 - 1.986 \times 537) \text{ Btu/lbmol CH}_4]$

+ $(3 \text{ lbmol } O_2)[(0 - 1.986 \times 537) \text{ Btu/lbmol } O_2]$

 $-(1 \text{ lbmol CO}_2)[(-169,300 + 18,391.5 - 4027.5 - 1.986 \times 1800)]$ Btu/lbmol CO₂]

- $-(2 \text{ lbmol } \text{H}_2\text{O})[(-104,040 + 15,433.0 4258.0 1.986 \times 1800)]$ Btu/lbmol H₂O]
- $-(1 \text{ lbmol O}_2)[(0 + 13,485.8 3725.1 1.986 \times 1800) \text{ Btu/lbmol O}_2]$ = 308,730 Btu/lbmol CH₄

Discussion On a mass basis, the heat transfer from the tank would be 308,730/16 = 19,300 Btu/lbm of methane.



15–5 .ADIABATIC FLAME TEMPERATURE

(15 - 16)

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 ($Q \ 5 \ 0$), the temperature of the products reaches a maximum, which is called the **adiabatic flame** or **adiabatic combustion temperature** of the reaction (Fig. 15–24).

The adiabatic flame temperature of a steady-flow combustion process is determined from Eq. 15–11 by setting Q = 0 and W = 0. It yields

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

 $\sum N_{p}(\bar{h}_{f}^{o} + \bar{h} - \bar{h}^{o})_{p} = \sum N_{r}(\bar{h}_{f}^{o} + \bar{h} - \bar{h}^{o})_{r}$ (15–17)

Once the reactants and their states are specified, the enthalpy of the reactants *H* react can be easily determined. The calculation of the enthalpy of the products Hprod is not so straightforward, however, because the temperature of the products is not known prior to the calculations. Therefore, the determination of the adiabatic flame temperature requires the use of an iterative technique unless equations for the sensible enthalpy changes of the combustion products are available. A temperature is assumed for the product gases, and the Hprod is determined for this temperature. If it is not equal to H react, calculations are repeated with another temperature. The adiabatic flame temperature is then determined from these two results by interpolation. When the oxidant is air, the product gases mostly consist of N2, and a good first guess for the adiabatic flame temperature is obtained by treating the entire product gases as N2.



In combustion chambers, the highest temperature to which a material can be exposed is limited by metallurgical considerations. Therefore, the adiabatic flame temperature is an important consideration in the design of combustion chambers, gas turbines, and nozzles. The maximum temperatures that occur in these devices are considerably lower than the adiabatic flame temperature, however, since the combustion is usually incomplete, some heat loss takes place, and some combustion gases dissociate at high temperatures (Fig. 15–25). The maximum temperature in a combustion chamber can be controlled by adjusting the amount of excess air, which serves as a coolant.

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*.

EXAMPLE 15–8 Adiabatic Flame Temperature in Steady Combustion

Liquid octane (C_8H_{18}) enters the combustion chamber of a gas turbine steadily at 1 atm and 25°C, and it is burned with air that enters the combustion chamber at the same state, as shown in Fig. 15–26. Determine the adiabatic flame temperature for (*a*) complete combustion with 100 percent theoretical air, (*b*) complete combustion with 400 percent theoretical air, and (*c*) incomplete combustion (some CO in the products) with 90 percent theoretical air.

SOLUTION Liquid octane is burned steadily. The adiabatic flame temperature is to be determined for different cases.

Assumptions 1 This is a steady-flow combustion process. 2 The combustion chamber is adiabatic. 3 There are no work interactions. 4 Air and the combustion gases are ideal gases. 5 Changes in kinetic and potential energies are negligible.

Analysis (a) The balanced equation for the combustion process with the theoretical amount of air is

$$C_8H_{18}(\ell) + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 47N_2$$

The adiabatic flame temperature relation $H_{\text{prod}} = H_{\text{react}}$ in this case reduces to

$$\sum N_p (\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ)_p = \sum N_r \overline{h}_{f,r}^\circ = (N \overline{h}_f^\circ)_{C_8 H_{18}}$$

since all the reactants are at the standard reference state and $\bar{h}_{f}^{\circ} = 0$ for O₂ and N₂. The \bar{h}_{f}° and *h* values of various components at 298 K are

	\overline{h}_{f}°	$\overline{h}_{298\mathrm{K}}$
Substance	KJ/kmol	KJ/kmol
$C_8H_{18}(\ell)$	-249,950	
02	0	8682
N ₂	0	8669
$H_{2}O(g)$	-241,820	9904
CO ₂	-393,520	9364

Substituting, we have

$$(8 \text{ kmol CO}_2)[(-393,520 + h_{CO_2} - 9364) \text{ kJ/kmol CO}_2] + (9 \text{ kmol H}_2\text{O})[(-241,820 + \bar{h}_{H_2\text{O}} - 9904) \text{ kJ/kmol H}_2\text{O}] + (47 \text{ kmol N}_2)[(0 + \bar{h}_{N_2} - 8669) \text{ kJ/kmol N}_2] = (1 \text{ kmol C}_8\text{H}_{18})(-249,950 \text{ kJ/kmol C}_8\text{H}_{18})$$

which yields

$$8\bar{h}_{CO_{\gamma}} + 9\bar{h}_{H,O} + 47\bar{h}_{N_{\gamma}} = 5,646,081 \text{ kJ}$$

It appears that we have one equation with three unknowns. Actually we have only one unknown—the temperature of the products T_{prod} —since h = h(T) for



FIGURE 15–26 Schematic for Example 15–8.

ideal gases. Therefore, we have to use an equation solver such as EES or a trial-and-error approach to determine the temperature of the products.

A first guess is obtained by dividing the right-hand side of the equation by the total number of moles, which yields 5,646,081/(8 + 9 + 47) = 88,220 kJ/kmol. This enthalpy value corresponds to about 2650 K for N₂, 2100 K for H₂O, and 1800 K for CO₂. Noting that the majority of the moles are N₂, we see that T_{prod} should be close to 2650 K, but somewhat under it. Therefore, a good first guess is 2400 K. At this temperature,

$$8\overline{h}_{CO_2} + 9\overline{h}_{H_2O} + 47\overline{h}_{N_2} = 8 \times 125,152 + 9 \times 103,508 + 47 \times 79,320$$

= 5,660,828 kJ

This value is higher than 5,646,081 kJ. Therefore, the actual temperature is slightly under 2400 K. Next we choose 2350 K. It yields

$$8 \times 122,091 + 9 \times 100,846 + 47 \times 77,496 = 5,526,654$$

which is lower than 5,646,081 kJ. Therefore, the actual temperature of the products is between 2350 and 2400 K. By interpolation, it is found to be $T_{\rm prod} = 2395$ K.

(*b*) The balanced equation for the complete combustion process with 400 percent theoretical air is

$$C_8H_{18}(\ell) + 50(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 37.5O_2 + 188N_2$$

By following the procedure used in (a), the adiabatic flame temperature in this case is determined to be $T_{\text{prod}} = 962 \text{ K}.$

Notice that the temperature of the products decreases significantly as a result of using excess air.

(*c*) The balanced equation for the incomplete combustion process with 90 percent theoretical air is

$$C_8H_{18}(\ell) + 11.25(O_2 + 3.76N_2) \rightarrow 5.5CO_2 + 2.5CO + 9H_2O + 42.3N_2$$

Following the procedure used in (a), we find the adiabatic flame temperature in this case to be $T_{\text{prod}} = 2236 \text{ K}.$

Discussion Notice that the adiabatic flame temperature decreases as a result of incomplete combustion or using excess air. Also, the maximum adiabatic flame temperature is achieved when complete combustion occurs with the theoretical amount of air.

15–6 ENTROPY CHANGE OF REACTING SYSTEMS

So far we have analyzed combustion processes from the conservation of mass and the conservation of energy points of view. The thermodynamic analysis of a process is not complete, however, without

the examination of the second-law aspects. Of particular interest are the exergy and exergy destruction, both of which are related to entropy.

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

	÷ ;	
$S_{\rm in} - S_{\rm out} + S_{\rm gen} = \Delta S_{\rm system}$ (kJ/K)	(15–18)	Surroundings
Net entropy transfer Entropy Change by heat and mass generation in entropy	the positive	Reactants Reaction
direction of heat transfer to be <i>to</i> the system,	S_{react} ΔS_{sys} S_{prod}	
balance relation can be expressed more explicitly or <i>steady-flow</i> reacting system as (Fig. 15–27)	for a <i>closed</i>	FIGURE 15–27 The entropy change associated with a
$\sum \frac{Q_k}{T_k} + S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}} (\text{kJ/K})$	(15–19)	chemical relation.

where *T k* is temperature at the boundary where *Qk* crosses it. For an *adiabatic process* (Q 5 0), the entropy transfer term drops out and Eq. 15–19 reduces to

 $S_{\text{gen,adiabatic}} = S_{\text{prod}} - S_{\text{react}} \ge 0$ (15–20)

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*, as explained in Chap. 7.

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 in Chap. 7 as follows: *The entropy of a pure crystalline substance at absolute zero temperature is zero*.

Therefore, the third law of thermodynamics provides an absolute base for the entropy values for all substances. Entropy values relative to this base are called the **absolute entropy**. The *s*8 values listed in Tables A–18 through A–25 for various gases such as N2, O2, CO, CO2, H2, H2O, OH, and O are the *ideal-gas absolute entropy values* at the specified temperature and *at a pressure of 1 atm*. The absolute entropy values for various fuels are listed in Table A–26 together with the *h*8*f* values at the standard reference state of 258C and 1 atm.

Equation 15–20 is a general relation for the entropy change of a reacting system. It requires the determination of the entropy of each individual component of the reactants and the products, which in general is not very easy to do. The entropy calculations can be simplified somewhat if the gaseous components of the reactants and the products are approximated as ideal gases. However, entropy calculations are never as easy as enthalpy or internal energy calculations, since entropy is a function of both temperature and pressure even for ideal gases.

When evaluating the entropy of a component of an ideal-gas mixture, we should use the temperature and the partial pressure of the component.

Note that the temperature of a component is the same as the temperature of the mixture, and the partial pressure of a component is equal to the mixture pressure multiplied by the mole fraction of the component.

Absolute entropy values at pressures other than P051 atm for any temperature *T* can be obtained from the ideal-gas entropy change relation written for an imaginary isothermal process between states (*T*, *P*0) and (*T*, *P*), as illustrated in Fig. 15–28:

$$\bar{s}(T,P) = \bar{s}^{\circ}(T,P_0) - R_u \ln \frac{P}{P_0}$$
 (15–2)

For the component i of an ideal-gas mixture, this relation can be written as

$$\overline{s}_i(T,P_i) = \overline{s}_i^{\circ}(T,P_0) - R_u \ln \frac{y_i r_m}{P_o} \quad (kJ/kmol·K)$$
(15-

where P = 0 = 1 atm, Pi is the partial pressure, yi is the mole fraction of the component, and Pm is the total pressure of the mixture.

If a gas mixture is at a relatively high pressure or low temperature, the deviation from the ideal-gas behavior should be accounted for by incorporating more accurate equations of state or the generalized entropy charts.



FIGURE 15–28

At a specified temperature, the absolute entropy of an ideal gas at pressures other than $P_0 5 1$ atm can be determined by subtracting $R_{\rm u} \ln (P/P_0)$ from the tabulated value at 1 atm.

15–7 .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

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} \quad \text{(kJ)} \tag{15-23}$$

where T_{0} is the thermodynamic temperature of the surroundings.

When analyzing reacting systems, we are more concerned with the changes in the exergy of reacting systems than with the values of exergy at various states (Fig. 15–29). Recall from Chap. 8 that the **reversible work** W_{rev} represents the maximum work that can be done during a process. 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 with only the surroundings at T_0 can be obtained by replacing the enthalpy terms by $\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ$, yielding

$$W_{\rm rev} = \sum N_r (\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ} - T_0 \bar{s})_r - \sum N_p (\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ} - T_0 \bar{s})_p \quad (15-24)$$

An interesting situation arises when both the reactants and the products are at the temperature of the

$$\overline{h} - T_0 \overline{s} = (\overline{h} - T_0 \overline{s})_{T_0} = \overline{g}_0$$

surroundings T_0 . In that case , which is, by definition, the **Gibbs function** of a unit mole of a substance at temperature T_0 . The W_{rev} relation in this case can be written



where \bar{g}_{f}° is the Gibbs function of formation ($\bar{g}_{f}^{\circ} = 0$ for stable elements like N₂ and O₂ at the standard reference state of 25°C and 1 atm, just like the enthalpy of formation) and $\bar{g}_{T_0} - \bar{g}^{\circ}$ represents the value of the sensible Gibbs function of a substance at temperature T_0 relative to the standard reference state.

For the very special case of $T_{\text{react}} = T_{\text{prod}} = T_0 = 25^{\circ}\text{C}$ (i.e., the reactants, the products, and the surroundings are at 25°C) and the partial pressure $P_i = 1$ atm for each component of the reactants and the products, Eq. 15–26 reduces to

 $W_{\rm rev} = \sum N_r \bar{g}_{fr}^{\circ} - \sum n_r \bar{g}_{fp}^{\circ}$ (kJ) (15–27)

We can conclude from the above equation that the $-\bar{g}_f^{\circ}$ value (the negative of the Gibbs function of formation at 25°C and 1 atm) of a compound represents the *reversible work* associated with the formation of that compound from its stable elements at 25°C and 1 atm in an environment at 25°C and 1 atm (Fig. 15–30). The \bar{g}_f° values of several substances are listed in Table A–26.

EXAMPLE 15–9 Reversible Work Associated with a Combustion Process

One lbmol of carbon at 77°F and 1 atm is burned steadily with 1 lbmol of oxygen at the same state as shown in Fig. 15–31. The CO_2 formed during the process is then brought to 77°F and 1 atm, the conditions of the surroundings. Assuming the combustion is complete, determine the reversible work for this process.

SOLUTION Carbon is burned steadily with pure oxygen. The reversible work associated with this process is to be determined.

Assumptions 1 Combustion is complete. 2 Steady-flow conditions exist during combustion. 3 Oxygen and the combustion gases are ideal gases. 4 Changes in kinetic and potential energies are negligible.

Properties The Gibbs function of formation at 77°F and 1 atm is 0 for C and O_2 , and -169,680 Btu/lbmol for CO_2 . The enthalpy of formation is 0 for C and O_2 , and -169,300 Btu/lbmol for CO_2 . The absolute entropy is 1.36 Btu/lbmol·R for C, 49.00 Btu/lbmol·R for O_2 , and 51.07 Btu/lbmol·R for CO_2 (Table A–26E).

Analysis The combustion equation is

$$C + O_2 \rightarrow CO_2$$

The C, O_2 , and CO_2 are at 77°F and 1 atm, which is the standard reference state and also the state of the surroundings. Therefore, the reversible work in this case is simply the difference between the Gibbs function of formation of the reactants and that of the products (Eq. 15–27):

$$W_{\text{rev}} = \sum N_{r} \bar{g}_{f,r}^{\circ} - \sum N_{p} \bar{g}_{f,p}^{\circ}$$

= $N_{C} \bar{g}_{f,C}^{\circ,0} + N_{O_{2}} \bar{g}_{f,O_{2}}^{\circ,0} - N_{CO_{2}} \bar{g}_{f,CO_{2}}^{\circ} = -N_{CO_{2}} \bar{g}_{f,C}^{\circ}$
= $(-1 \text{ lbmol})(-169,680 \text{ Btu/lbmol})$
= **169,680 Btu**

since the \overline{g}_{f}° of stable elements at 77°F and 1 atm is zero. Therefore, 169,680 Btu of work could be done as 1 lbmol of C is burned with 1 lbmol of O₂ at 77°F and 1 atm in an environment at the same state. The reversible work in this case represents the exergy of the reactants since the product (the CO₂) is at the state of the surroundings.

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Discussion We could also determine the reversible work without involving the Gibbs function by using Eq. 15–24:

$$\begin{split} W_{\rm rev} &= \sum N_r (\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ} - T_0 \bar{s})_r - \sum N_p (\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ} - T_0 \bar{s})_p \\ &= \sum N_r (\bar{h}_f^{\circ} - T_0 \bar{s})_r - \sum N_p (\bar{h}_f^{\circ} - T_0 \bar{s})_p \\ &= N_C (\bar{h}_f^{\circ} - T_0 \bar{s}^{\circ})_C + N_{\rm O_2} (\bar{h}_f^{\circ} - T_0 \bar{s}^{\circ})_{\rm O_2} - N_{\rm CO_2} (\bar{h}_f^{\circ} - T_0 \bar{s}^{\circ})_{\rm CO_2} \end{split}$$



FIGURE 15–30

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



FIGURE 15–31 Schematic for Example 15–9.

Substituting the enthalpy of formation and absolute entropy values, we obtain

 $W_{\text{rev}} = (1 \text{ lbmol C})[0 - (537 \text{ R})(1.36 \text{ Btu/lbmol}\cdot\text{R})]$

+ $(1 \text{ lbmol } O_2)[0 - (537 \text{ R})(49.00 \text{ Btu/lbmol} \cdot \text{R})]$

- (1 lbmol CO₂)[-169,300 Btu/lbmol - (537 R)(51.07 Btu/lbmol·R)] = **169,680 Btu**

which is identical to the result obtained before.

EXAMPLE 15–10 Second-Law Analysis of Adiabatic Combustion

Methane (CH₄) gas enters a steady-flow adiabatic combustion chamber at 25°C and 1 atm. It is burned with 50 percent excess air that also enters at 25°C and 1 atm, as shown in Fig. 15–32. Assuming complete combustion, determine (*a*) the temperature of the products, (*b*) the entropy generation, and (*c*) the reversible work and exergy destruction. Assume that $T_0 = 298$ K and the products leave the combustion chamber at 1 atm pressure.

SOLUTION Methane is burned with excess air in a steady-flow combustion chamber. The product temperature, entropy generated, reversible work, and exergy destroyed are to be determined.

Assumptions 1 Steady-flow conditions exist during combustion. 2 Air and the combustion gases are ideal gases. 3 Changes in kinetic and potential energies are negligible. 4 The combustion chamber is adiabatic and thus there is no heat transfer. 5 Combustion is complete.

Analysis (a) The balanced equation for the complete combustion process with 50 percent excess air is

$$CH_4(g) + 3(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + O_2 + 11.28N_2$$

Under steady-flow conditions, the adiabatic flame temperature is determined from $H_{\rm prod}$ = $H_{\rm react}$, which reduces to

$$\sum N_p (\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ})_p = \sum N_r \overline{h}_{f,r}^{\circ} = (N \bar{h}_f^{\circ})_{CH_4}$$

since all the reactants are at the standard reference state and $\bar{h}_{f}^{o} = 0$ for O_{2} and N_{2} . Assuming ideal-gas behavior for air and for the products, the \bar{h}_{f}^{o} and h values of various components at 298 K can be listed as

	\overline{h}_{f}°	$\overline{h}_{298 \text{ K}}$	
Substance	kJ/kmol	kJ/kmol	
$CH_4(g)$	-74,850	—	
02	0	8682	
N ₂	0	8669	
$H_{2}O(g)$	-241,820	9904	
CO ₂	-393,520	9364	

Substituting, we have

$$(1 \text{ kmol CO}_2)[(-393.520 + \overline{h}_{CO} - 9364) \text{ kJ/kmol CO}_2]$$

+
$$(2 \text{ kmol H}_2\text{O})[(-241,820 + h_{HO} - 9904) \text{ kJ/kmol H}_2\text{O}]$$

+ (11.28 kmol N₂)[(0 + \bar{h}_{N_2} - 8669) kJ/kmol N₂]

+ $(1 \text{ kmol O}_2)[(0 + \overline{h}_{O_2} - 8682) \text{ kJ/kmol O}_2]$

$$= (1 \text{ kmol CH}_4)(-74,850 \text{ kJ/kmol CH}_4)$$

which yields

$$\bar{h}_{\rm CO_2} + 2\bar{h}_{\rm H,O} + \bar{h}_{\rm O_2} + 11.28\bar{h}_{\rm N_2} = 937,950 \,\text{kJ}$$

By trial and error, the temperature of the products is found to be

$$T_{\rm prod} = 1789 \, {\rm K}$$



FIGURE 15–32 Schematic for Example 15–10.

(*b*) Noting that combustion is adiabatic, the entropy generation during this process is determined from Eq. 15–20:

$$S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}} = \sum N_p \overline{s}_p - \sum N_r \overline{s}_r$$

The CH₄ is at 25°C and 1 atm, and thus its absolute entropy is \bar{s}_{CH_4} = 186.16 kJ/kmol·K (Table A–26). The entropy values listed in the ideal-gas tables are for 1 atm pressure. Both the air and the product gases are at a total pressure of 1 atm, but the entropies are to be calculated at the partial pressure of the components, which is equal to $P_i = y_i P_{total}$, where y_i is the mole fraction of component *i*. From Eq. 15–22:

$$S_i = N_i \bar{s}_i (T, P_i) = N_i [\bar{s}_i^{\circ} (T, P_0) - R_u \ln y_i P_m]$$

The entropy calculations can be represented in tabular form as follows:

	N_i	<i>Y</i> _i	<i>s</i> ₀́(<i>T</i> , 1 atm)	$-R_u \ln y_i P_m$	$N_i \overline{s}_i^{\circ}$
CH₄	1	1.00	186.16	_	186.16
0_2	3	0.21	205.04	12.98	654.06
N_2	11.28	0.79	191.61	1.96	2183.47
				$S_{ m react}$	= 3023.69
CO ₂	1	0.0654	302.517	22.674	325.19
H ₂ Ō	2	0.1309	258.957	16.905	551.72
02	1	0.0654	264.471	22.674	287.15
N ₂	11.28	0.7382	247.977	2.524	2825.65
	$S_{\rm prod} = 3989.71$				= 3989.71

Thus,

$$S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}} = (3989.71 - 3023.69)\text{kJ/kmol·K CH}_4$$

= 966.0 kJ/kmol·K

(c) The exergy destruction or irreversibility associated with this process is determined from Eq. 15–23,

 $X_{\text{destroyed}} = T_0 S_{\text{gen}} = (298 \text{ K})(966.0 \text{ kJ/kmol} \cdot \text{K})$ $= 288 \text{ MJ/kmol} \text{ CH}_4$

That is, 288 MJ of work potential is wasted during this combustion process for each kmol of methane burned. This example shows that even complete combustion processes are highly irreversible.

This process involves no actual work. Therefore, the reversible work and exergy destroyed are identical:

$$W_{\rm rev} = 288 \, {\rm MJ/kmol} \, {\rm CH}_4$$

That is, 288 MJ of work could be done during this process but is not. Instead, the entire work potential is wasted.



FIGURE 15–33 Schematic for Example 15–11.

EXAMPLE 15-11 Second-Law Analysis of Isothermal Combustion

Methane (CH₄) gas enters a steady-flow combustion chamber at 25°C and 1 atm and is burned with 50 percent excess air, which also enters at 25°C and 1 atm, as shown in Fig. 15–33. After combustion, the products are allowed to cool to 25°C. Assuming complete combustion, determine (*a*) the heat transfer per kmol of CH₄, (*b*) the entropy generation, and (*c*) the reversible work and exergy destruction. Assume that $T_0 = 298$ K and the products leave the combustion chamber at 1 atm pressure.

SOLUTION This is the same combustion process we discussed in Example 15–10, except that the combustion products are brought to the state of the surroundings by transferring heat from them. Thus the combustion equation remains the same:

$$CH_4(g) + 3(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + O_2 + 11.28N_2$$

At 25°C, part of the water will condense. The amount of water vapor that remains in the products is determined from (see Example 15–3)

$$\frac{N_{v}}{N_{\text{gas}}} = \frac{P_{v}}{P_{\text{total}}} = \frac{3.1698 \text{ kPa}}{101.325 \text{ kPa}} = 0.03128$$

and

$$N_v = \left(\frac{P_v}{P_{\text{total}}}\right) N_{\text{gas}} = (0.03128)(13.28 + N_v) \rightarrow N_v = 0.43 \text{ kmol}$$

Therefore, 1.57 kmol of the H_2O formed is in the liquid form, which is removed at 25°C and 1 atm. When one is evaluating the partial pressures of the components in the product gases, the only water molecules that need to be considered are those that are in the vapor phase. As before, all the gaseous reactants and products are treated as ideal gases.

(a) Heat transfer during this steady-flow combustion process is determined from the steady-flow energy balance $E_{out} = E_{in}$ on the combustion chamber,

$$Q_{\text{out}} + \sum N_p \overline{h}_{f,p}^\circ = \sum N_r \overline{h}_{f,r}^\circ$$

since all the reactants and products are at the standard reference of 25°C and the enthalpy of ideal gases depends on temperature only. Solving for Q_{out} and substituting the \overline{h}_{f}° values, we have

$$Q_{out} = (1 \text{ kmol CH}_4)(-74,850 \text{ kJ/kmol CH}_4)$$

-(1 kmol CO₂)(-393,520 kJ/kmol CO₂)
-[0.43 kmol H₂O(g)][-241,820 kJ/kmol H₂O(g)]
-[1.57 kmol H₂O(\ell)][-285.830 kJ/kmol H₂O(\ell)]
= 871,400 kJ/kmol CH₄

(b) The entropy of the reactants was evaluated in Example 15–10 and was determined to be $S_{\text{react}} = 3023.69 \text{ kJ/kmol} \cdot \text{K CH}_4$. By following a similar approach, the entropy of the products is determined to be

	N_i	У _i	$\overline{s}_{i}^{\circ}(T, 1 \text{ atm})$	$-R_u \ln y_i P_m$	$N_i \bar{s}_i$
H₂O(ℓ)	1.57	1.0000	69.92	_	109.77
$H_2^{-}O$	0.43	0.0314	188.83	28.77	93.57
CO_2	1	0.0729	213.80	21.77	235.57
02	1	0.0729	205.04	21.77	226.81
N_2	11.28	0.8228	191.61	1.62	2179.63
$S_{\rm prod} = 2845.35$					

Then the total entropy generation during this process is determined from an entropy balance applied on an *extended system* that includes the immediate surroundings of the combustion chamber

$$S_{gen} = S_{prod} - S_{react} + \frac{Q_{out}}{T_{surr}}$$

= (2845.35 - 3023.69) kJ/kmol + $\frac{871,400 \text{ kJ/kmol}}{298 \text{ K}}$
= 2746 kJ/kmol·K CH₄

(c) The exergy destruction and reversible work associated with this process are determined from

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} = (298 \text{ K})(2746 \text{ kJ/kmol}\cdot\text{K})$$
$$= 818 \text{ MJ/kmol} \text{ CH}_4$$

and

$$W_{\rm rev} = X_{\rm destroyed} = 818 \text{ MJ/kmol CH}_4$$

since this process involves no actual work. Therefore, 818 MJ of work could be done during this process but is not. Instead, the entire work potential is wasted. The reversible work in this case represents the exergy of the reactants before the reaction starts since the products are in equilibrium with the surroundings, that is, they are at the dead state.

Discussion Note that, for simplicity, we calculated the entropy of the product gases before they actually entered the atmosphere and mixed with the atmospheric gases. A more complete analysis would consider the composition of the atmosphere and the mixing of the product gases with the gases in the atmosphere, forming a homogeneous mixture. There is additional entropy generation during this mixing process, and thus additional wasted work potential.